SUSTAINABLE PLASTICS

Environmental Assessments of Biobased, Biodegradable, and Recycled Plastics

Joseph P. Greene

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Preface

Plastics are one of the greatest inventions of the twentieth century. Plastics enable products to be made that meet the needs of the public for plastic applications. Plastics make life easier for all of us. We can purchase food, drink, and consumables in safe, lightweight, and clean containers and packaging made from plastic. We can drive around or be transported in a vehicle that is comfortable, pleasing to the eye, and safe thanks in part to plastics. We can communicate with small electronic devices that keep us connected with one another and also help entertain us with real and fantasy worlds.

Plastics are lightweight and easily thrown away with other heavier debris. Plastics can be recycled and reused many times. However, the lightweight benefits of plastics can cause them to be airborne and difficult for waste management companies to collect and dispose them off in landfills or other disposal environments. The lightweight plastics can occupy large volumes of landfills and can be a litter problem for land and sea. Floating plastics debris might be the final legacy of our disposal-society generation. Through education and training we can help our younger people become the sustainable generation. We can educate them in the ways of producing products and services with reduced environmental impacts. Products and services can be created with minimal waste, greenhouse gases, and pollution. This book can help provide information on creating lightweight and sustainable plastic products for our sustainable world.

Bioplastics today can be made from corn, soy, sugarcane, potato, or other renewable material source. Petroleum plastics can also be sustainable if they are made from renewable or recycled material sources. The manufacturing process also can also be sustainable. Plastics have the opportunity to define sustainable materials that are made from renewable or recycled materials sources, made with lower energy, produce less pollution, and have a low carbon footprint. Sustainable plastic materials also are recycled or composted at the end of the product service life.

This book will define sustainability and sustainable materials and provide practical examples of sustainable plastics and provide examples of life cycle assessments (LCA) for these materials. This book can be used for education and training for plastics professionals and students who are interested in creating sustainable products.

Sustainable plastics can include biobased, biodegradable, and recycled plastics. LCAs will be used to provide a scientific explanation of sustainable plastics. The content of the book includes definitions of sustainability and sustainable materials, evaluations of the environmental concerns for industry, definitions of life cycle assessments, explanations of biobased and recycled plastics, and examples of sustainable plastics as defined by LCAs.

The author would like to thank Ms. Vanessa Vaquera for providing the artwork in the book.

Dedication

The author would like to dedicate this book to Dr. James O. Wilkes, Chemical Engineering Department, The University of Michigan, Ann Arbor, MI.

Glossary

ACC	American Chemistry Council
AHA	Alpha hydroxyl acid
AMS	Accelerator Mass Spectrometry (ASTM D6686)
ASTM	American Society for Testing Materials
BHET	(2-Hydroxyethyl)terephthalate
BOD	Biochemical oxygen demand (ISO 14851)
CFC	Chlorofluorocarbon
CO_2eq	Carbon dioxide equivalent
DIN	German Organization for Standardization
DOE	Department of Energy
EOL	End-of-life
EPA	Environmental Protection Agency
GHG	Greenhouse gas
GPPS	General purpose polystyrene
GSI	Greene sustainability index
GWP	Global warming potential
HDPE	High density ethylene
HIPS	High impact polystyrene
LCS	Liquid Scintillation Counting (ASTM D6686)
IRMS	Isotope Ratio Mass Spectrometry (ASTM D6686)
ISBM	Integrated stretch blow molding
LCA	Life cycle assessment
LCI	Life cycle inventory
LDPE	Low density polyethylene
MEG	Mono-ethylene glycol
MRF	Materials recovery facility
MSW	Municipal solid waste
OPS	Oriented polystyrene sheet
PET	Polyethylene terephthalate
PGA	Poly glycolic acid
PHA	Poly-hydroxy-alkanoate
PHB	Poly-hydroxy-butyrate

PHBV	Poly-hydroxy-valerate
PLA	Poly lactic acid
POCP	Photochemical Ozone Creation Potential
PP	Polypropylene
PS	Polystyrene
PVC	Poly vinyl chloride
RDF	Refused derived fuel
USDA	United States Department of Agriculture

CHAPTER 1

Introduction to Sustainability

1.1 SUSTAINABILITY DEFINITION

Sustainability has many definitions. The most common definition of sustainability has its roots in a 1987 United Nations conference, where sustainability was defined as “meeting the needs of the current generation without compromising the ability of future generations to meet their needs” (WCED 1987). Sustainable materials, processes, and systems must meet this definition and not compromise the ability of future generations to provide for their needs while providing for the needs of the current generation. Thus, for plastics manufacturing, materials and processes used today should not deplete resources for future generations to produce plastic materials.

Sustainability can be measured by the outcomes of using a material, process, or system on the environment, society, and economy. The three components of sustainability have economic, social, and environmental aspects and are related with each other as shown in Figure 1.1. Materials, processes, and systems can have environmental, economic, and societal impact. Sustainable materials, processes, and systems have all three impacts. For example, the development of materials will have environmental impacts of using raw materials, energy sources, and transportation that come from natural resources, which can create air, land,

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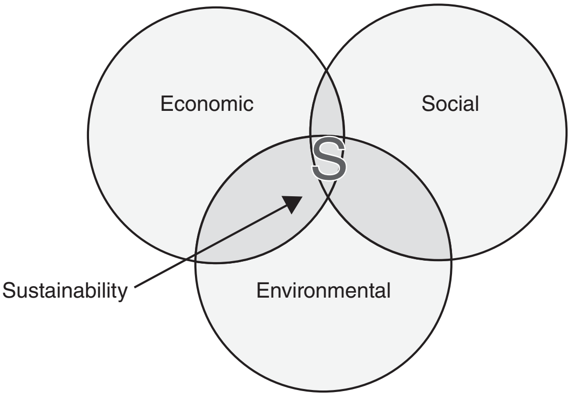

FIGURE 1.1 Sustainability definition.

and/or water pollution; economic impacts are creating commerce, jobs, and industries; societal impacts are creating roles for jobs and services. Organizations are often analyzed with a “Triple Bottom Line” approach to evaluate the social, economic, and environmental performances of a company (Esteves et al. 2012). This approach is the key to creating a sustainable organization.

Examples of sustainability measures were developed for using a holistic approach from sustainability measurements of technology use in the marine environment (Basurko and Mesbahi 2012). The environmental effects of ballast water were measured with an integrated quantitative approach of sustainable assessment. The systematic approach can provide environmental, economic, and social sustainability for marine technologies. The sustainable tool allows for the inclusion of sustainability principles to the design and operations of marine products. Sustainability can be effectively incorporated into the design phase of products and services and create reduced environmental, social, and economic impacts. The sustainable tool was created with LabView® software with SimPro® life cycle assessment (LCA) program to provide an integrated approach with a single indicator to reduce the environmental, social, and economic impacts of ballast water effects on the ocean quality.

1.1.1 Societal Impacts of Sustainability

The first aspect of sustainability can measure the impacts of products and processes on the society. The societal impact of using a material and manufacturing process can be measured by the effects on the population and the roles of the workers in the community. Sustainable manufacturing processes are defined as providing proper wages for the workers and a clean and safe work environment. The method and environment of producing a manufactured product can result in impacts on a person, group, and community.

The wages, benefits, hours per week, safety, and other human resources provided to an individual worker contribute to the quality of the product or process and the ability of that product or process to maintain its presence in the marketplace. A workplace that produces a product or process without wages and benefits that are appropriate to the workers in the region can lead to high turnover rates of workers, poor worker moral, and loss of personal buy-in for workers. The product or service will not be sustainable since it may not last if few workers are available or the environment may suffer tragic losses due to health or safety concerns. Poor working conditions and poor wage structures may benefit the economics of the current company but may lead to poor working environments for future workers and thus is not sustainable.

Sustainable workplaces feature the maintaining of welfare levels in the future (WCED 1987). Welfare can be defined as a subjective measure of the sum of all individual's utilities generated from the consumption of goods, products, and services (Perman et al. 2003).

1.1.2 Economic Impacts of Sustainability

The second aspect of sustainability can measure the economic impacts of using a material and manufacturing process to produce products. Sustainable manufacturing processes are defined as providing proper wages for the workers and clean and safe work environments.

Economic impacts of sustainability can be measured with a capital approach that can be defined as maintaining economic, environmental, human, and social capital over time for future generations (Kulig, Kolfoort, and Hoekstra 2010). The capital approach can be proposed as a theoretical basis for sustainable development indicators (Atkinson and Hamilton 2003; World Bank 2006; UNECE 2014). The capital approach provides a theoretical approach by measuring all capital stocks in their own units. The capital approach can provide consistent, theoretically sound, and policy-relevant comparisons between countries (Kulig et al. 2010).

The economic impact of using a material can be measured by the effects on the creation of jobs and industry for communities. The creation of jobs can lead to creation of taxable bases and tangible property. In addition, the use of sustainable materials and processes can lead to reduced energy, transportation, waste disposal, and utility costs for manufacturing operations. Sustainable enterprises can be defined as "Lean and Green," where manufacturing costs are minimized, and manufactured materials are made with reduced environmental impacts. Recycling of metals, plastics, glass, paper, wood, waste inks and concentrates, waste oils, and industrial fluids can reduce the amount of trash that is sent to landfills and hazardous disposal sites and reduce the waste disposal costs. Use of recycled or biobased plastics can reduce the manufacturing costs of some plastics. Use of lower energy pumps, motors, and lighting can reduce energy costs for plastics manufacturing.

The incorporation of sustainability into the business plan can lead to a design for sustainability paradigm where an eco-design approach can lead to integrating social, economic, environmental, and institutional aspects into the supply chain of an eco-friendly product line. This can lead to healthy organizations providing good jobs to healthy employees and contributing to the social network of the organization and community.

1.1.3 Environmental Impacts of Sustainability

The third aspect of sustainability can measure the environmental impacts of producing a product or system in terms of usage of natural resources for raw materials, energy, and real estate land. The production of plastic products can generate greenhouse gases (GHGs), solid and liquid waste, air pollution, water pollution, and toxic chemicals. Environmental aspects are measured with the life cycle process explained in Chapter 3.

Strategic environmental assessment can be used to provide a basis for establishing sustainability for products and services (White and Noble 2013). Strategic environmental assessment can help ensure that policies, plans, and programs are developed in a more environmentally sensitive way. Strategic environmental assessment can support sustainability by providing a framework for decision making, setting sustainability objectives, ensuring consideration of other sustainable alternatives, and promoting sustainability outcomes through institutional learning. Several common themes emerged from a review of using strategic environmental assessment of sustainability including:

- Providing a decision support framework for sustainability
- Being adaptive to the decision-making process
- Incorporating sustainability objectives and principles
- Considering relevant sustainability issues early on
- Adopting sustainability criteria
- Identifying and evaluating other sustainable alternatives
- Trickling-down sustainability
- Capturing large-scale and cumulative effects
- Enabling institutional change and transformational learning

Environmental aspects of sustainability can be measured by monitoring resource depletion and pollution generation during the production of products or services. Resource depletion can include land use, energy usage, water usage, fossil fuel usage, among others. The pollution emissions can include GHGs, water pollution, air pollution, climate change, toxic chemical released, human toxicity, carcinogens released, summer smog creation, acidification, eutrophication, among others.

An important environmental concern is the increased amount of GHGs in the atmosphere. Greenhouse gases are gases in the atmosphere that absorb and emit thermal radiation within the thermal infrared range causing the planet to increase in temperature. During plastic manufacturing, GHGs are produced by the energy sources needed to mine the raw materials, processing the raw materials into pellets, conversion of the pellet into finished products, and transportation. GHGs comprise of gases that contribute to global warming by creating a layer of insulating gases that insulate the planet. These gases absorb and emit radiation within the thermal infrared range. GHGs include methane, carbon dioxide, water vapor, fluorocarbons, nitrous oxide, and ozone. Carbon dioxide is the largest contributor to global warming due to its volume. Methane has a global warming rate of 22 times the rate for carbon dioxide. Typically, the production of these gases is listed in LCAs as CO_2 equivalent. Thus, the formation of GHGs is listed as CO_2eq. Reductions in GHGs can be done with lowering energy usage for products and services.

1.2 GREEN CHEMISTRY DEFINITIONS

The American Chemistry Institute established green chemistry principles. The green chemistry engineering principles provide a framework for scientists and engineers to design and build products, processes, materials, and systems with lower environmental impacts. Green chemistry principles can be used to develop chemical products and processes that reduce or eliminate the use and generation of hazardous or toxic chemicals. The 12 principles of green chemistry are as follows (Anastas and Warner 1998):

1. Prevention
2. Atom economy
3. Less hazardous chemical synthesis
4. Designing safer chemicals
5. Safer solvents and auxiliaries
6. Design for energy efficiency
7. Uses of renewable feedstock
8. Reduce derivatives
9. Use of catalytic reagents
10. Design for degradation
11. Real-time analysis for pollution prevention
12. Inherent safer chemistry

Prevention of waste generation during the manufacturing of the chemicals can help reduce environmental impacts of chemical production. Atom economy guides developers in incorporating all materials in the creation of chemicals. Synthetic chemicals should be created with little or no toxicity to the human health and the environment. Solvents, separation agents, and other auxiliary substances should be used sparingly or not at all. Energy usage should be minimized in the creation of chemical substances. Renewable feedstock should be the material source of the chemical substances rather than fossil fuel-based sources.

Creation of unnecessary intermediates or derivatives should be minimized or avoided if possible to reduce chemical waste. Catalytic reagents should be used rather than stoichiometric reagents. Chemical products should be designed to biodegrade in a disposal environment rather than be a persistent pollutant. Real-time, in-process monitoring and control of hazardous substances should use analytical methodologies. Chemical substances and processes should minimize the potentials for accidental chemical spills, explosions, and fires.

The 12 green chemistry definitions can be grouped into three areas for reduction in energy usage, reduction in waste, and reduction in pollution. The reduction in energy area includes design for energy efficiency, use of renewable feedstock, and reduces derivatives principles. The reduction in waste area includes prevention, atom recovery, and use of catalytic reagents principles. The reduction in pollution includes less hazardous chemical synthesis, reduce derivatives, designing safer chemicals, safer solvents and auxiliaries, design for degradation, pollution prevention, and inherent safer chemistry. These three areas are used to define sustainable manufacturing.

1.3 GREEN ENGINEERING DEFINITIONS

Green engineering can be defined as a process to develop products, processes, or systems with minimal environmental impacts. The full product life cycle is developed when evaluating the environmental sustainability of the product, process, or system. The 12 principles of green engineering are as follows (McDonough, Braungart, Anastas, and Zimmerman 2003):

1. Inherent rather than circumstantial
2. Prevention instead of treatment
3. Design for separation
4. Maximize efficiency
5. Output-pulled versus input-pushed
6. Conserve complexity
7. Durability rather than immortality
8. Meet need, minimize excess
9. Minimize material diversity
10. Integrate material and energy flows
11. Design for commercial “afterlife”
12. Renewable rather than depleting resources

Sustainable engineering is based on maximizing product throughput, quality, efficiency, productivity, space utilization, and reducing costs. Products are designed with inherently nonhazardous methods and nontoxic materials. Waste should be reduced at its source and not discarded after production. Production operations should be designed to minimize energy consumption and material use. Energy and materials should be utilized from a product requirement rather than a material input. Material and energy inputs should be based on renewable sources rather than from fossil fuel sources.

End-of-life options for the product should be designed at the beginning of a product life rather than at the end of it. The design goal should be product-targeted durability rather than product immortality. Universal functionality should not be a design goal.

Multicomponent products should be designed to promote disassembly and value retention. Integration and interconnectivity with available energy and material flows should be designed into products, processes, and systems.

1.4 SUSTAINABILITY DEFINITIONS FOR MANUFACTURING

Environmental aspects of product manufacturing include production of liquid and solids wastes, air pollution, water pollution, and GHG emissions. Discharges from manufacturing facilities can lead to pollution of the sewers, water treatment plants, and neighborhoods.

Pollution prevention in communities with manufacturing operations can be achieved with regional sustainability programs that provide small- and medium-sized manufacturing companies' pollution prevention technical assistance and financial incentives to reduce pollution at the manufacturing sources rather than at the waste water and sold waste disposal sites (Granek and Hassanali 2006). Pollution often includes heavy metals, particulates, sulfates, phosphates, petroleum-based oils, solid waste, oil-based inks and concentrates, and other contaminants. Sustainable practices can reduce the pollutants by installing filters, using water-based inks, biobased oils, and recovery units for waste water effluent.

Sustainability can be defined in many ways for manufactures to reduce GHGs and reduce pollution. Often missing from sustainability analysis, though, is waste generation. Products or services that are sustainable must also not produce significant amounts of solid or liquid waste. Sustainable products and practices should encourage the use of recycled materials during the production of products and processes and encourage the recycling of waste materials during the production of products and processes.

The essential components of sustainable products and services are ones with reduced GHG emission, reduced pollution, and reduced waste generation. Sustainable products, processes, and systems minimize the generation of GHGs, waste, and pollution.

Thus, sustainable manufacturing incorporates producing products and processes with

1. reduced GHGs emissions,
2. reduced solid waste, and
3. reduced pollution.

This definition will be used in subsequent chapters in the book.

The first component of sustainable manufacturing processes is the reduction in GHGs. Reductions in GHGs can be done with lowering energy usage, which has direct cost reduction implications. Sustainable materials and processes minimize the generation of CO_2eq gases.

The second component of sustainable manufacturing is the reduction in waste generation. This can be listed for plastics manufacturing as the solid waste that is generated during the extraction of raw materials, production of the plastic pellets, and conversion of the pellet into plastic products. The listing of waste generation is listed as *kilogram of solid waste*. California in the United States has a law that requires state agencies and schools to achieve greater than 50% diversion rate of solid waste (California Assembly Bill 939). Wherein, over 50% of the trash that could be sent to landfill is sent to recycling, composting, or reuse. Reductions in waste generation can reduce the cost for manufacturing operations. Sustainable materials and processes minimize the generation of solid waste.

The third component of sustainable manufacturing processes is the reduction in pollution of air, land, and water. The pollution component can be defined in LCAs as creation of chemicals that cause eutrophication, acidification, and human health concerns.

Eutrophication can be defined as the addition of nitrates and phosphates to the land through the use of fertilizers and soil conditioners. Eutrophication is a very common pollutant from fertilizers in farming or from natural causes. Eutrophication can deplete oxygen in ocean and freshwater lakes causing algae and phytoplankton blooms in the water.

Acidification can occur to ocean and freshwater, as well, as in soil when the pH is reduced due to the presence of sulfur and nitrous oxides. The presence of sulfur and nitrous oxides in the atmosphere can be released into the soil and water ways during rain storms. Sulfur and nitrous oxides are released during the combustion of fossil fuels at energy plants, burning of plastics as fuel, and during the combustion of fuels.

Toxic chemical pollution is caused by the presence of toxins that can cause human health problems, including cancer, blindness, sterility, and other health concerns. Combustion of fuels can lead to release of carcinogenic materials into the environment.

Sustainable materials and processes reduce the release of pollution in the land, air, and water.

1.5 LIFE CYCLE ASSESSMENT

LCAs are an essential component of sustainability and can be used to scientifically determine the environmental effects of products, processes, and systems. LCA can be used to calculate the energy and raw materials consumed and the resulting carbon footprint, waste, and pollution generated in the production of a product or process. LCA is needed to establish the sustainability of products and processes because it follows a worldwide thorough approach to establishing measureable environmental outcomes of products and processes. LCA will be more fully explained in later chapters.

1.6 LEAN AND GREEN MANUFACTURING

Sustainability is an essential component of manufacturing today. Plastics manufacturing can lead the way in producing products with lower carbon footprint, lower waste, and lower pollution through the use of recycled and biobased materials. Lean and Green are essential components of the manufacturing industry. Lean and Green manufacturing for plastics can be a unique feature of plastics manufacturers and can provide sustainable products for a promising marketplace.

1.7 SUMMARY

Sustainable materials, processes, and systems must not compromise the ability of future generations to provide for their needs while providing for the needs of the current generation. The three components of sustainability have economic, social, and environmental aspects. Organizations are often analyzed with a "Triple Bottom Line" approach to evaluate the social, economic, and environmental performances of a company.

The first aspect of sustainability can measure the impacts of products and processes on the society. The societal impact of using a material and manufacturing process can be measured by the effects on the population and the roles of the workers in the community.

The second aspect of sustainability can measure the economic impacts of using a material and manufacturing process to produce products. Sustainable manufacturing processes are defined as providing proper wages for the workers and clean and safe work environments.

The third aspect of sustainability can measure the environmental impacts of producing a product or system in terms of usage of natural resources for raw materials, energy, and real estate land. The production of plastic products can generate GHGs, solid and liquid waste, air pollution, water pollution, and toxic chemicals.

Green chemistry principles can be used to develop chemical products and processes that reduce waste generation, energy, and production of toxic chemicals during the creation of chemicals. Green engineering principles are based on maximizing product throughput, quality, efficiency, productivity, space utilization, as well as, reducing hazards, pollution, and costs.

Sustainable products, processes, and systems minimize the generation of GHGs, waste, and pollution. LCAs are an essential component of sustainability and can be used to scientifically determine the environmental effects of products, processes, and systems.

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REVIEW QUESTIONS

Q.1.1 Sustainability is only defined for environmental effects? T or F?

Q.1.2 Life cycle assessment can be used to measure sustainability? T or F?

Q.1.3 Sustainable products are produced with lower carbon footprint only? T or F?

Q.1.4 Reducing greenhouse gases produce at a company will always increase costs? T or F?

Q.1.5 Methane gas has 22 times for global warming potential than carbon dioxide? T or F?

Q.1.6 Green chemistry is used to create chemicals that made from renewable resources? T or F?

Q.1.7 Green chemistry is used to create chemicals that are less expensive than traditional chemicals? T or F?

Q.1.8 Green engineering is used to create products that are used for multiple generations? T or F?

Q.1.9 Providing workers with living wages is a component of sustainability? T or F?

Q.1.10 Sustainability can be defined as the ability to produce products today with materials, and resources in 50 years? T or F?

REVIEW PROBLEMS

P.1.1 Sustainability is defined as which of the following?

- **a.** Environmental impacts of products, materials, or services on the planet.
- **b.** Economic impacts of products, materials, or services on the planet.
- **c.** Environmental and economic impacts of products, materials, or services on the planet.
- **d.** Environmental, social, and economic impacts of products, materials, or services on the planet.

P.1.2 How can environmental impacts of products, materials, or services best be measured?

- **a.** Generation of greenhouse gases
- **b.** Generation of waste products

- **c.** Generation of pollution
- **d.** All of the above

P.1.3 Which of the following is not an example of green chemistry?

- **a.** Biobased solvents
- **b.** Biobased plastics
- **c.** LDPE virgin plastics
- **d.** Paper cup with polylactic acid liner

P.1.4 Which of the following is an example of sustainable manufacturing?

- **a.** Production of products with recycled plastics for reduced carbon footprint
- **b.** Production of plastic bags with heavy yellow ink
- **c.** Production of paper bags with limited recycled content
- **d.** Production of aluminum bike frame from pure aluminum

P.1.5 Life cycle assessments can be used to measure which of the following?

- **a.** Total environmental impacts per pound of metal produced
- **b.** Environmental and economic impacts of plastic bags
- **c.** Environmental impacts of 1000 bags made from paper and plastic
- **d.** Environmental and social impacts of plastic bags per kilogram of plastic bag

REVIEW EXERCISES

E.1.1 Provide a list of your company's goals for being more sustainable?

E.1.2 Is sustainability a priority for your company? Explain why or why not.

E.1.3 What will it take for your company to produce more sustainable products, processes, or systems?

E.1.4 How sustainable are the largest beverage manufacturers? How can sustainability be measured?

E.1.5 How sustainable are the largest automotive manufacturers? How can sustainability be measured?

CHAPTER 2

Environmental Issues

2.1 THE PLANET IS WARMING

According to the World Meteorological Organization, the average temperatures of the planet in 2011 were the second highest "strong La Niña" temperatures in recorded history. Measurements on land and sea from over 10,000 locations in the world found that an average global temperature was 14.41 ± 0.11°C (World Meteorological 2012). In 2010, the National Oceanic and Atmospheric Administration's (NOAA) National Climatic Data Center (NCDC) published a report, which found that 2010 was the warmest of the average yearly temperature on record for the planet (State of the Climate 2012).

In the Northern Hemisphere, the snow cover from December to February melted in May to the lowest area covered as recorded by satellites. The mountain glaciers on the Earth lost size and mass from the previous year. This trend of glacier reductions has continued since 1990 (State of the Climate 2012).

The air temperatures over the land of the Earth, especially in the Artic, have increased in 2010 from the previous year. The NOAA report found that the average temperature in the United States in 30-year timespan from 1981 to 2010 was a half degree Fahrenheit warmer than from the previous 30-year timespan from 1971 to 2000 (State of the Climate 2012). As shown in Figure 2.1, greenhouse gases (GHGs) can cause the temperatures of the land and sea to increase.

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FIGURE 2.1 Graphic of planet warming with a blanket of greenhouse gases. Artwork courtesy of Ms. Vanessa Vaquera of Chico, CA.

Figure 2.2 shows the average worldwide surface temperature difference of land and sea as compared to the average 20th century temperature of 13.9°C (Global Analysis 2013). The temperature data on the graph were estimated from the information provided by the NOAA (Global Analysis 2013).

The actual temperature is shown in Figure 2.3 from the temperature data in Figure 2.2.

In 2011, the yearly averaged temperature over global land and ocean water surfaces was 0.51°C (0.92°F) above the 20th century average

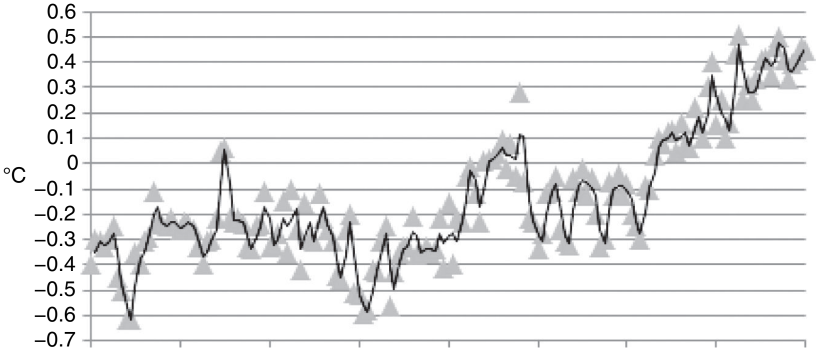

FIGURE 2.2 Average worldwide temperature anomaly of land and sea versus a 20-year average.

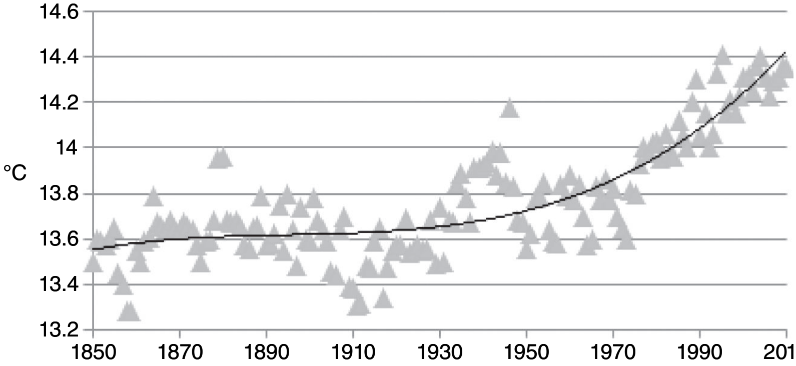

FIGURE 2.3 Average worldwide temperature of land and sea.

of 13.9°C (57.0°F). Figure 2.3 shows that since 1976 the difference between the average temperature and the 20th century average was greater than 0. Figure 2.3 shows that since 1976 the yearly average temperature was warmer than the 20th century average of 13.9°C. Figures 2.2 and 2.3 clearly show that the planet is warming.

The surface temperature is warming at a faster rate than the water temperature. In 2011, the global average land surface temperature was 0.8°C (1.49°F) above the 20th century average of 8.5°C (47.3°F). In 2011, the global average ocean and sea temperature was 0.40°C (0.72°F) above the 20th century average of 16.1°C (60.9°F) (Global Analysis 2013).

2.2 MELTING OF GLACIERS

One consequence of the warmer surface temperatures is the melting of glaciers worldwide, as shown in Figure 2.4. Glaciers are found throughout the northern and southern hemispheres, including Africa, North and South America, Asia, Europe, New Zeeland, and Antarctica. Over 130,000 glaciers are listed in the World Glacier Index (WGI; World Glacier Inventory 2012). The WGI includes information about the glaciers including area, elevation, geographic location, length, and classification. In Norway, information on 1627 glaciers was published in 1988. The average temperature in Norway is expected to rise by 2.3°C by 2100. The climate change scenario can result in approximately

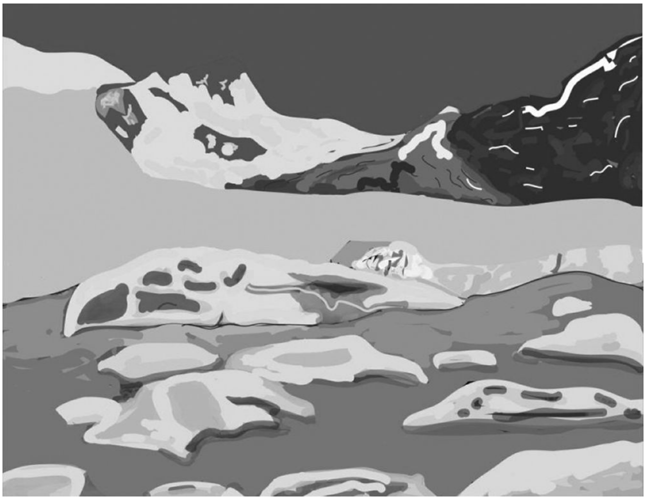

FIGURE 2.4 Melting glaciers illustration. Artwork courtesy of Ms. Vanessa Vaquera of Chico, CA.

98% of the Norwegian glaciers will be disappeared and approximately 34% of the glacier area will be reduced by 2100 (Nesje et al. 2008).

In Asia, glaciers in the Everest region have lost mass in recent years. Between 1999 and 2004, satellite measurements found that the rate of ice loss is twice as much as from 1977 and 1999. Good agreement was found between satellite measurements and field measurements between 2002 and 2004 (Berthier et al. 2007).

In South America, 72 glaciers in Northern and Southern Patagonia were studied for glacier retreat. Twenty of the 72 glaciers were found to retreat from 3% to 37.9%. Glacier retreat is attributed to average air temperature, basin geometry, glacier dynamics, and response time (Lopez et al. 2010).

In North America, Mendenhall Glacier in Alaska is undergoing substantial recession and thinning. The glacier has retreated 3 km during the 20th century. The glacier has thinned 5.5 km^3 in the last 50 years. The shrinking of the glacier is attributed to surface melting and to lake calving. Lake calving can be defined as when an edge of an iceberg or glacier separates from the iceberg or glacier. Mean temperatures in Juneau, Alaska, decreased slightly from 1947 to 1976 and then increased since then. The average temperature in Juneau increased 1.4°C since 1943.

Glacier melting in Alaska flows into the Mendenhall River. Approximately 50% of the total river discharge in the summer is due to glacier melting (Motyka et al. 2002).

An important feature of the Arctic Ocean is its floating sea-ice cover that has traditionally ranged from 16 million km^2 in March to a minimum coverage of 7 million km^2 at the end of summer melt season on September. Based on regression analysis during the period between 1979 and 2006, the ice extent (fractional ice cover) has declined every month. The decline is the largest during September with a retreat of 8.6 ± 2.9% per decade or approximately 10,000 km^2 per year (Serreze et al. 2007).

2.3 RISING SEAS

The levels of the oceans are rising. This can be attributed to thermal expansion of the water, land water storage change, and melting of glaciers and icebergs. Sea levels are measured with satellite altimetry or with *in situ* and remote sensing equipment. Recent ice mass loss and melting glaciers have increased the rate of sea-level rise to 3.1 mm per year (Cazenave et al. 2008). Between the years of 1993 and 2010, melting glaciers and polar ice caps can account for approximately 30% of the sea-level rise (Cogley 2009).

Sea-level rise in the tropical Pacific and Indian Oceans has been studied in recent years. The sea level is influenced by thermal expansion of the oceans from the warmer temperatures, melting polar ice caps and glaciers, and the atmospheric changes caused by El Niño. Large variability during El Niño years and the shortness of many of the individual tide-gauge records contribute to uncertainty of historical rates of sea-level rise.

From 1993 to 2001, the western Pacific and eastern Indian Oceans experienced large rates of sea-level rise that approached 30 mm per year, whereas, the eastern Pacific and western Indian Oceans experienced a sea-level fall approaching −10 mm per year (Church et al. 2006).

From 1950 to 2001, the average sea-level rise (relative to land) from the six longest tide-gauge records is 1.4 mm per year. After correcting for glacial isostatic adjustment and atmospheric pressure effects, the rate of sea-level rise is 2.0 mm per year, which is close to the estimates of the global averages. The relative sea-level rise at Funafuti, Tuvalu,

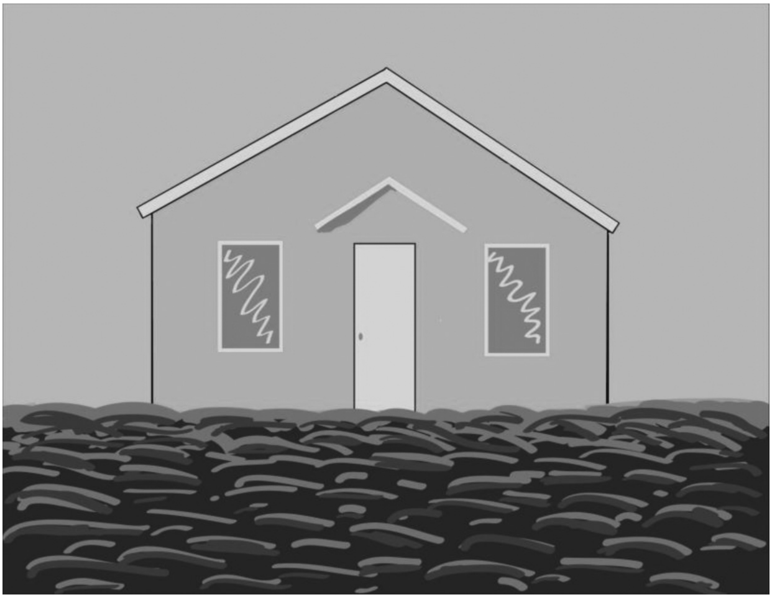

FIGURE 2.5 Rising sea waters example causing flooding of a home. Artwork courtesy of Ms. Vanessa Vaquera of Chico, CA.

is 2 ± 1 mm per year over the period 1950–2001. The analysis clearly indicates that sea levels in this region are rising (Church et al. 2006).

The rising of the sea levels can cause flooding in low-lying areas in Los Angeles, New Orleans, New York City, among others. Figure 2.5 displays the consequence of flooding for homes. In addition to global warming and melting of the ice caps, increase in GHG concentrations can also alter the planet's hydrologic cycle (Mitchell et al. 1987; Held and Soden 2006). If changes in rainfall intensity and spatial distribution are substantial, then significant amounts of rainfall can occur and pose a serious risk caused by climate change (Wentz et al. 2007).

2.4 CAUSES OF GLOBAL WARMING

2.4.1 Increased Greenhouse Gases

The National Climate Data Center report from the NOAA found that the levels of GHGs in the atmosphere increased in 2010 from the previous year (Global Warming: Frequently Asked Questions 2012). In fact, the rate that the GHG increased from 2009 to 2010 was the largest yearly rate of increase since 1980. Many scientists have concluded that carbon dioxide and other GHGs can trap heat in the Earth's lower atmosphere (Viola et al. 2010; Majorowicz and Skinner 1997; Golovanova et al. 2001; Beltrami and Bourlon 2004).

2.4.2 Sources of CO_2eq Emissions

The sources of CO_2eq emissions are from burning of fossil fuels. "Carbon dioxide equivalents" refer to the amount of carbon dioxide that would give the same warming effect as the effect of the greenhouse gas or GHGs being emitted. According to the EPA from 2006 as shown in Figure 2.6, 40% of the CO2 emissions are from burning fossil fuels for electricity, 31% from transportation, 14% from industrial sources, 10% from residential or commercial sources, and 5% from other sources (EPA Inventory of Greenhouse Gas Emissions and Sinks 2013).

In the industrial sector, steel and concrete industries have the highest CO_2eq emissions. Petrochemical industry, including plastics, has the 10th largest contribution. Table 2.1 lists the contributions to CO_2eq emissions from industry (EPA Inventory of Greenhouse Gas Emissions and Sinks 2013).

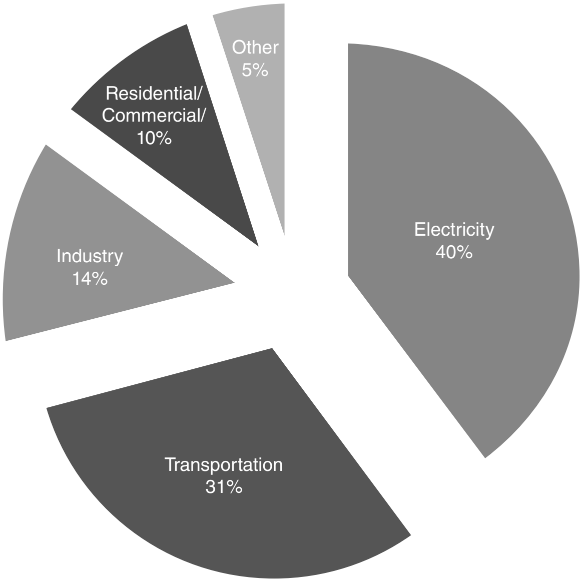

FIGURE 2.6 Sources of CO_2eq emissions for the US per market segment.

TABLE 2.1
Industrial GHG Emissions for 2010

Industry	CO_2eq emissions for 2010 (million tons of CO_2eq)	Percentage of emissions
Iron and steel production	139	67.87
Cement production	30	14.65
Lime production	13.2	6.45
Ammonia production	8.7	4.25
Urea consumption for non-agriculture production	4.4	2.15
Petrochemical production	3.3	1.61
Aluminum production	3	1.46
Carbon dioxide production	2.2	1.07
Others	1	0.49
Total	204.8	100

The importance of reducing CO_2 emissions is a significant feature of sustainable products for industry. This will be discussed in detail in Chapter 9.

2.4.3 Anti-warming Theory

Theories are established to refute the claims of GHG causes for climate change and the climate change as a balance of nature. The warming of the planet can be caused by Milankovitch climate oscillations. Periodical changes in the orbit of the Earth cause climatic changes termed “Milankovitch oscillations”, leading to large changes in the size and location of species’ geographical distributions (Dynesius and Jansson 2000). Climate has fluctuated widely during the history of the Earth. Climatic variability increases in amplitude toward longer time scales, but have a marked peak on the time scale of 10,000–100,000 years caused by Milankovitch oscillations (Berger 1989). The oscillations of the earth axis can cause temperature variations on the planet that is beyond seasonal variations.

The increased temperatures for the planet may be part of repeating cycle over the last 500,000 years (Gregory 2012). We may be part of global warming that began over 18,000 years ago. The increased carbon dioxide may also be part of a repeating cycle over the last 400,000 years.

GHG warming can cause an increase in the temperature in the middle of the troposphere, about 5 km up. However, from 1999 to 2002, the temperature of the mid-troposphere has actually decreased slightly and surface temperatures have ceased warming, even as CO_2 concentrations have continued to increase (Tropospheric 2012).

2.5 OCEAN POLLUTION AND MARINE DEBRIS

Marine debris or ocean litter is a worldwide problem. One study found that 60–80% of ocean litter is comprised of plastics (Derraik 2002). Plastic ocean debris is most often litter that was brought to the beach by beach visitors or from storm drains that collect litter on the ground and then empty into the oceans. Beach litter is comprised of cigarette butts, plastic packaging, bottles, caps, or bags that are discarded after use. Ocean plastic litter can include, as well, pre-production plastic pellets that flow to the ocean from unintended release in ocean container ships or from plastic manufacturing facilities. Recent reports have identified plastics as a significant source of ocean litter throughout the world and the physical danger that the plastic litter represents to sea life. This section describes the plastic debris problem in more detail and identifies the types of plastics that are found on beaches throughout the world.

2.5.1 Plastic Marine Debris

Oceanic gyres are circulating water zones in the world composed of large-scale ocean currents. The size of the 11 continental scale gyres ranges from 1000 nautical miles along the major axis in the Arctic Ocean to 5000 nautical miles along the major axis in the South Pacific. The gyres are designated by traditional oceanographic designations, for example, Beaufort, North Pacific Subtropical, Pacific Subarctic, South Pacific Subtropical, North Atlantic Subtropical, Atlantic Subarctic, South Atlantic Subtropical, Antarctic Circumpolar, and Indian Subtropical gyres. Two gyres in the Arctic Ocean do not have designations (Ebbesmeyer and Scigliano 2009).

Five gyres around the world, as shown in Figure 2.7, are known to collect excessive marine debris. The five gyres include the North and South Pacific gyres, North and South Atlantic gyres, and the Indian Ocean gyre.

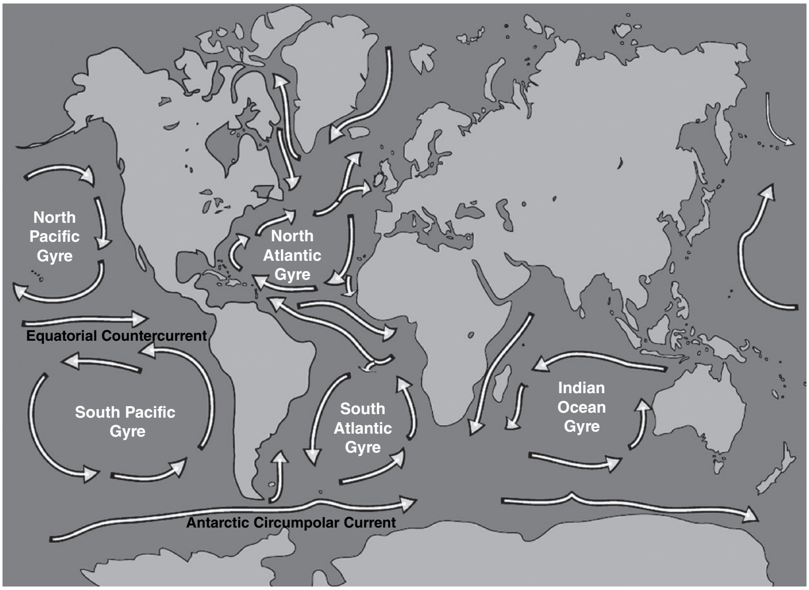

FIGURE 2.7 Worldwide gyres. Artwork courtesy of Ms. Vanessa Vaquera of Chico, CA.

The North Pacific gyre, shown in Figure 2.8, is the most studied of the five gyres. It also can be described as the "Great Pacific Garbage Patch," the "Eastern Garbage Patch," or the "Pacific Trash Vortex." The North Pacific gyre is a gyre of marine litter in the central North Pacific Ocean located approximately between 135° to 155°W and 35° to 42°N.

The gyre is characterized by exceptionally high concentrations of floating plastic and other debris that have been trapped by the currents of the North Pacific Gyre. In the gyre, plastic pieces are usually broken into fragments due to wave action and UV exposure. The plastic debris is not continuous throughout the gyre. Instead, a series of rings with high concentrations of floating debris comprise the gyre. The rings of floating debris expand and contract based on atmospheric conditions.

In the Southern and Pacific Ocean off Japan, the amount of plastic debris has increased significantly in the last 20 years (Plastic Debris from Rivers to Sea 2009). The Southern California Coastal Water Research Project (SCCWRP) and the Algalita Marine Research Foundation (AMRF) in recent years have conducted studies to identify and

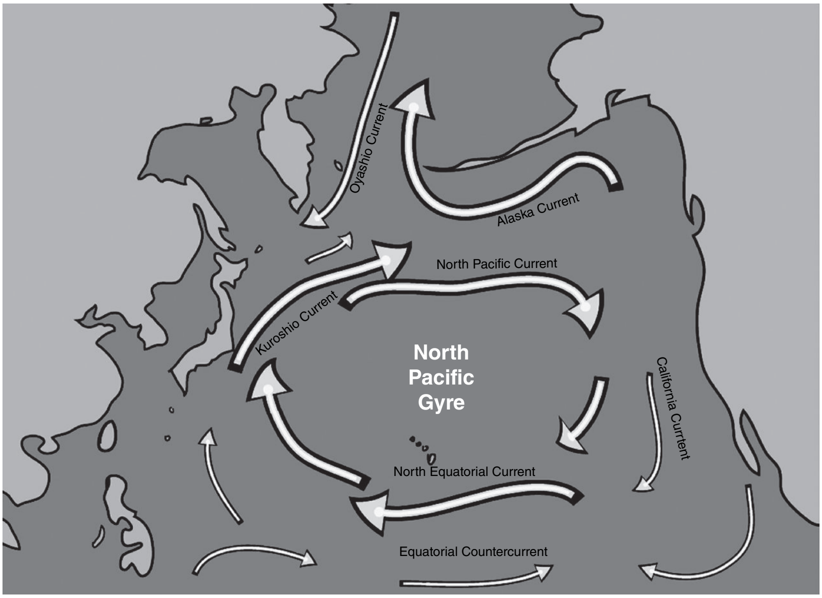

FIGURE 2.8 North Pacific gyre. Artwork courtesy of Ms. Vanessa Vaquera of Chico, CA.

quantify ocean litter in the four marine habits: beach, ocean bottom, ocean water column, and ocean surface. Plastics can accumulate in each of these four areas. The ocean bottom collects larger plastic materials, such as fishing gear and heavier objects. The water column collects plastic fragments that are suspended by ocean currents. The ocean surface collects plastic fragments, floating plastic trash, and plastic preproduction pellets. The beach environment collects several plastic materials that come from beach litter and ocean debris that can interrupt the beach experience through encounters with plastic litter on the beaches. (Figures 2.9 and 2.10).

Plastic debris can cause pollution for humans and injury to fish, seabirds, and marine mammals. Ocean litter is known to have affected at least 267 species worldwide, including 86% of all sea turtle species, 44% of all seabird species, and 43% of all marine mammal species (Plastic Debris from Rivers to Sea 2009).

Plastic fragments and floating debris can cause fatalities to marine life as a result of ingestion, starvation, suffocation, infection, drowning, and entanglement. Seabirds that feed on the ocean surface are especially prone to ingesting plastic debris that floats. Short-tailed shearwaters

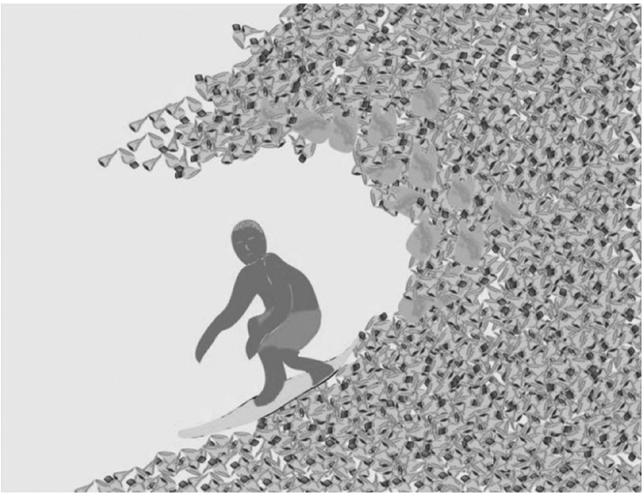

FIGURE 2.9 Surfer character riding a simulated wave of plastic debris in the ocean. Artwork courtesy of Ms. Vanessa Vaquera of Chico, CA.

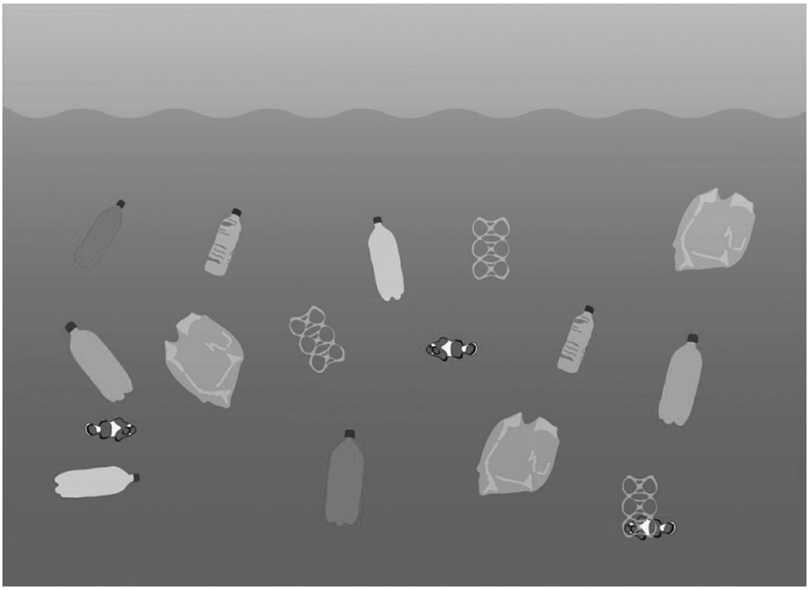

FIGURE 2.10 Plastic debris in the water column on the oceans. Artwork courtesy of Ms. Vanessa Vaquera of Chico, CA.

were found to have higher concentrations of brominated fire retardant chemicals in their stomachs than in the natural prey (fish) in the stomachs of the birds (Tanaka et al. 2013).

The Laysan albatross, black-footed albatross, and northern fulmar frequently ingest plastics including bottle caps, cigarette lighters, toys, party balloons, and fragments of consumer goods. Adults feed these items to their chicks that often die of starvation with their stomachs full of debris. Other avian species can ingest small fragments of plastic consumer products and pre-production industrial plastic pellets. Midway Islands are located very close to the North Pacific gyre. Recent reports have listed many instances of plastic debris inundating the islands. The debris includes fishing nets, computer cases, plastic bottles, plastic crates, and baskets. In addition, cigarette lighters and plastic fragments were found in deceased albatross birds on the islands (Diary from the Middle of Nowhere 2013).

2.5.1.1 Plastic Pre-production Pellet Pollution

Plastic pre-production pellets have been identified on worldwide beaches since the early 1970s (Carpenter and Smith 1972; Carpenter et al. 1972). Pre-production plastic pellets have been found in ocean waters throughout the world, such as beaches in the South Pacific (Gregory 1983) and remote islands in Hawaii (The United States Environmental Protection Agency Harbor Studies Program Survey at Honolulu, Hawaii, and Kahana Bay Beach Observations 1992). Plastic pellets were noticed on Oahu Island of Hawaii on the windward side in February 1998. Since 1998, plastic pellets that resemble plastic sand have swept onto all of Hawaiian Islands’ windward shores (Ebbesmeyer and Scigliano 2009).

In the United States, plastic pellets were identified in the Atlantic Ocean along the southern coast of New England and in the eastern seaboard (Colton 1974; Hays and Cormons 1974; Ryan 1988). In the Pacific Ocean, pellets have been reported since 1974 (Wong et al. 1974; Day et al. 1990). Most of the plastic pellets found in marine oceans have been identified as polyethylene (PE), polypropylene (PP), or polystyrene (PS) (CEE Plastics in the Ocean 1987). Those three plastics will float since they have specific gravities less than 1 (PE and PP) or near 1 (PS). All other plastics have specific gravities greater than water and can sink to the ocean floor unless they are made into a buoyant container or bottle.

Plastic pellets are approximately 5 mm in diameter and can float in the ocean water. Sea animals may ingest them as food.

Widespread pollution of plastic pellets was identified in US harbors located on the Atlantic, Pacific, and Gulf coasts (Plastic Pellets in the Aquatic Environment 2009). Pre-production pellets were found in 13 out of 14 harbors sampled. The greatest number of pellets was found in the Houston Ship Channel in Houston, Texas, where more than 250,000 pellets were collected in one sample alone. Notably, Houston has one of the greatest concentrations of plastics manufacturing facilities in the United States.

California beaches also have a higher level of these pellets. Pre-production plastic pellets accounted for more than 90% of the debris collected in a study of beach sites from Seal Beach to San Clemente in Orange County (Moore et al. 2001) and 94% of the debris items found during the EPA's Harbor Studies Program (US EPA 1992). In the Combined Sewer Overflow Studies Program, pellets were found in municipal wastewater treatment systems of Philadelphia and Boston (Plastic Pellets in the Aquatic Environment 1992).

Plastic pellets comprised more than 50% of the man-made debris collected at one Philadelphia, Pennsylvania, storm-water discharge. Pellets were also found in samples collected from four sewage treatment plants. Plastic pellet sources were not identified in research studies, but it is likely that they come from storm runoff (Plastic Pellets in the Aquatic Environment 1992).

The plastic pellets were likely released from land-based sources and could reach the Atlantic Ocean during treatment plant shutdowns or through storm-water discharges during rainy periods. Plastic pellet pollution can be removed from the water at water treatment plants with the filters that used to remove solid waste. Plastic pellet pollution on beaches, however, is very difficult to remove due to the small size of the pellets.

Plastic manufacturers sometimes lose plastic pellets on the ground during transfer of pellets from the tanker trucks or trains to the silos at the manufacturing plant. Plastic pellets can also spill during reprocessing at the recycling areas in the manufacturing plant. These pellets flow into storm drains during rainy seasons and end up in the oceans. The plastic pellets can also end up in the oceans from accidental release during ocean transportation. The loss of plastic pellets is expensive for both these groups and should be minimized. Further investigation is needed to study sources of plastic pellet release in the oceans to get a more complete picture.

The best way to reduce the plastic pellet pollution on the beaches is to have better pellet control at plastic manufacturing operations. The plastics industry is promoting ways to reduce amounts of plastic pellets released into the environment with the Operation Clean Sweep (OCS) program. The goal of OCS is to assist plastic manufacturing operations with good housekeeping and pellet containment practices to achieve zero pellet loss in the plastic manufacturing plant (Operation Clean Sweep 2007). The OCS program can help reduce the amount of plastic pellet litter in the oceans.

2.5.1.2 Persistent Organic Pollutants

Persistent organic pollutants (POPs) can be attracted to plastic pollution in the ocean. The organic pollutants that float in the oceans are absorbed onto the plastic. POPs are organic compounds that reside in the oceans and are resistant to environmental degradation through chemical, biological, and photolytic processes (Jones and de Voogt 2009).

POPs have been observed to persist in the environment and spread out over long distances. POPs can accumulate in human and animal tissue and become part of the human food chain. POPs have potential significant impacts on human health and the environment. Persistent organic pollutants in the marine environment attach to plastic debris, which then are consumed by marine animals, many of which are in the human food chain. The plastic pellets and fragments can transport toxic substances in the marine environment to animals and ultimately to humans (Rios et al. 2007).

Researchers in Morocco found polychlorinated biphenyls (PCBs) in sediments of coastal communities (Piazza et al. 2009).

Twelve different chemicals are commonly referred to as POPs, including aldrin, chlordane, dichlorodiphenyl-trichloro-ethene (DDT), dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, PCBs, polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, and toxaphene. Other POP chemicals are considered carcinogenic and include polycyclic aromatic hydrocarbons (PAHs), brominated flame retardants, as well as some organometallic compounds such as tributyltin.

Many POPs have an origin as pesticides. Some POPs are produced from natural sources. Other POPs are released from electrical equipment, or released in the production of solvents, polyvinyl chloride, and pharmaceuticals (Rios et al. 2007). Some POPs are highly toxic, carcinogenic, and can cause chronic health effects, including endocrine disruption, mutagenicity, and carcinogenicity. The toxic POPs can be collected by plastics floating in the oceans causing potential danger to sea life that ingest the plastic.

PCBs and DDTs were absorbed on polypropylene and polyethylene in high concentrations in a simulated marine environment (Mata et al. 2001).

Dioxins are present in the ocean waters due to the burning of organic materials, and can be a persistent marine pollutant. It is possible for dioxins to absorb onto plastic particles in the ocean.

In 2009, research on POPs in the world oceans were studied at an international workshop on the occurrence, effects, and fate of microplastic debris (University of Washington 2009). The workshop focused on small plastic debris in the oceans, including the amount, location, and environmental impacts of small plastics. Participants presented current research of microplastic occurrence and movement in the oceans, direct effects of micro plastics on marine organisms, interactions of POPs with plastics and the potential for plastics to adsorb and desorb these pollutants in the marine environment and to organisms, and the effect plastics could have on the cycling of POPs.

Small plastic pieces in the oceans can have high concentrations of toxic chemicals that are floating in the waters. The workshop illustrated the research, which concluded that plastic debris can absorb and transport organic contaminants, such as PCBs, up to 105–106 times the ambient seawater concentrations.

Ocean pollution can also be caused from agricultural, municipal, and industrial runoff. The pesticides, herbicides, and insecticides used on commercial, agricultural, and residential properties can flow from the ground and into storm sewers during the rainy season. The amount of pesticides, insecticides, and herbicides can be significant and cause significant environmental harm. These pollutants can be a source of POPs.

Pesticides can also be a source of environmental pollution that might migrate toward plastics in the oceans. Pesticides released from storm runoff in Australia were found to damage the Great Barrier Reef Marine

Park by creating a hazy cloud in the water over the reef and blocking out sunlight and reducing photosynthesis (Johnson and Ebert 2009).

The rural land use has changed in the last 100 years causing more pesticide use and subsequent release into the marine environment. The pesticides include organochloride, organophosphate, phenoxy, triazine, urea, mercurial, and azole group pesticides. Urban and industrial water discharges significantly pollute the marine environment. A wide variety of pesticides, including PAHs, Terbutylazine, and PCBs, were found in ocean waters of Spain with a new extraction technique that will allow measurements of semi-volatile substances (Perez-Carrera et al. 2007). The new technique will allow other researchers to study the effects of pesticides on marine life.

Chlorohydrocarbon pesticides were found in Australia sediments throughout the coastal regions in the country. DDT, in particular, was found throughout the region (Connell et al. 2002). Pesticide, herbicide, and insecticide runoff from farms and urbane dwellings can also contribute to the POPs.

2.5.2 Worldwide Coastal Cleanup

The persistence of ocean debris can be determined from the analysis of litter collected in beach cleanups around the world. The Ocean Conservancy's International Coastal Cleanup program encourages people around the world to remove trash and debris from the world's beaches and waterways, and identify the sources of debris. Trash can migrate to the ocean from waterways and storm drains hundreds of miles inland. In 1985, the Ocean Conservancy conducted a study on plastic marine garbage for the EPA (Highlights in the Fight against Marine Debris 2010). In 1986, the first beach cleanup was conducted along the Texas coast. Volunteers collected 124 tons of trash from 122 miles of coastline. Since then the number of countries participating in the cleanup has expanded from 35 countries in 1992 to 104 countries in 2008.

The Ocean Conservancy published reports every year on the collection efforts of worldwide volunteers. In 2012, the Ocean Conservancy published "Trash Free Seas. International Coastal Cleanup 2012 Data Release" (Ocean Conservancy 2012). It represented 598,076 volunteers who covered 20,776 miles and collected 9,184,428 pounds of trash on the beaches throughout the world (Ocean Conservancy 2012). In 2009, the Ocean Conservancy published "A Rising Tide of Ocean

TABLE 2.2
Total Land and Underwater Debris Collection for Worldwide Coastal Cleanup in 2011

Country	People	Pounds	Miles
Australia	139	6839	4.7
Brazil	9197	60,772	1260.4
Canada	34,220	317,156	1857.4
China	383	656	0.8
France	56	417	5.1
Germany	79	439	2.1
Greece	2686	30,521	56.6
India	26,038	170,300	330.2
Italy	204	5582	13.7
Japan	8802	39,547	65.7
Mexico	16,426	236,931	281.1
Philippines	114,418	1,069,443	149.4
Spain	703	18,457	18.3
UK	2729	22,409	1805.8
USA	200,190	3,861,630	9573.8

Debris and What We Can Do About It." The report presented ocean debris data recorded by nearly 400,000 volunteers in 104 countries and 42 US states (Ocean Conservancy's International Coastal Cleanup 2010). In 2008, approximately 73% of cleanups were performed on ocean beaches and 27% were completed on inland waterways and lakes.

The marine report features a *Marine Debris Index* that includes a breakdown of the amount and type of trash in the ocean and waterways collected in one day. The report also emphasizes environmental impacts of ocean trash on sea life. Volunteers collected more than 11 million pieces of trash from cigarette butts to grocery bags and fast food wrappers. These were collected from beaches and the ocean floor along 17,000 miles of coastline. Beach cleanup results from 15 countries are listed in Table 2.2. For most countries, the majority of litter was found on land and not in underwater. In the United States, 99% of the litter that collected was found on the land versus underwater.

Figure 2.11 shows debris that was collected at a beach on a Northern California freshwater lake. The items are similar to items collected along beaches throughout the world. The debris included aluminum cans,

FIGURE 2.11 Debris found along a beach on a Northern California freshwater lake.

cigarette butts, plastic bottles, glass bottles, plastic fragments, clothing, plastic packaging, and plastic cups (Figure 2.11).

Table 2.2 illustrates the combination of beach and underwater litter on beaches throughout the world. The beach cleanup includes marine and freshwater lakes on land and underwater. The results show that the United States had the most volunteers collecting land and underwater litter, the greatest amount of debris collected, and the most beach distance covered. China collected the least amount of debris and covered the least amount of beach area. Table 2.2 illustrates that Canada, the Philippines, and Puerto Rico also collected large amounts of litter on the beaches and underwater.

The results from the beach cleanup can be normalized to visualize the concentrations of litter per person and per mile of beach. Thus, the amount of beach trash over the beach area can be better understood. It is preferable to have the least amount of marine litter per mile.

TABLE 2.3
Litter Ratios of Total Debris Collection for Worldwide Coastal Cleanup in 2011

Country	Pounds collected per person	Pounds collected per mile
Australia	49	1455
Brazil	7	48
Canada	9	171
China	2	820
France	7	82
Germany	6	209
Greece	11	539
India	7	516
Italy	27	407
Japan	4	602
Mexico	14	843
Philippines	9	7158
Spain	26	1009
UK	8	12
USA	19	403

Table 2.3 illustrates that the Philippines, Australia, and Spain have the highest concentrations of beach litter per mile on land and underwater.

The Australian concentration is high because of lower number of participants covering fewer miles than in 2008, where the 16 pounds of debris were collected per person and 363 pounds of debris were collected per mile. These countries are followed by China, Mexico, and Japan. The United States has significantly less beach and underwater litter density than the top six countries. Brazil and the United Kingdom had the lowest litter density and can be considered the cleanest of the group per mile of beach.

The beach collection data can be analyzed by the number of items gathered on the beaches rather than the weight of the items. In 2011, the top 10 participating countries were

1. The United States
2. The Philippines
3. Canada

4. Hong Kong
5. Dominican Republic
6. Mexico
7. India
8. Peru
9. Ecuador
10. Puerto Rico

In 2011, volunteers collected over 10.5 million items of litter on beaches throughout the world, as compared to over 11.4 million items on litter on beaches in the world that were collected in 2008. The top 10 marine debris items that were collected in 2011 are listed in Table 2.4 and include plastic, aluminum, glass, and paper. The top 10 items accounted for 81% of the debris in 2011 versus 73% in 2008. Cigarettes and cigarette filters are the most common litter items and are usually made with cellulose acetate plastic. Cigarette debris is followed by plastic debris including food wrappers, beverage bottles, trash bags, caps, lids, bottles, cups, plates, spoons, and straws. Glass bottles, aluminum cans,

TABLE 2.4
Top 10 Worldwide Marine Debris Items in 2011

Products	Materials: Plastic and other	Number of items	Percentage of total worldwide debris
Cigarette/cigarette filters	Cellulose acetate	2,117,931	20%
Food wrappers and containers	PS, PET, LDPE, HDPE, PVC	1,140,222	11%
Plastic beverage bottles	PET	1,065,171	10%
Plastic bags	HDPE and LDPE	1,019,902	9%
Caps and lids	HDPE, PP, aluminum	958,893	9%
Cups, plates, knives, spoons	PS, PP, PS foam, PP foam, paper	692,767	6%
Straw/stirrers	HDPE, PP	611,048	6%
Beverage bottles	Glass	521,730	5%
Beverage cans	Aluminum	339,875	3%
Paper bags	Paper	298,332	3%
	Total	8,765,871	81%

TABLE 2.5
Sources of Marine Debris by Regions of the World in 2008

Source	North America	Central America	South America	Caribbean	South East Asia	Worldwide
Shoreline and recreational	53.1%	23.7%	71.2%	81.5%	79.6%	61%
Smoking	35.2%	74%	19.1%	9.8%	11.1%	31%
Ocean and waterway	4.9%	1.6%	5.9%	5.3%	7.3%	5%
Dumping	2.1%	0.3%	2.4%	2.2%	1.1%	2%
Medical and personal hygiene	4.7%	0.4%	1.4%	1.2%	0.9%	1%

and paper bags round out the top 10 items. Table 2.4 also lists the common plastic materials that can be used for the debris item. Plastics can be found in seven of the top 10 marine debris items collected throughout the world.

A report in 2009 from Ocean Conservancy found that the source of the debris items is mostly related to human recreational activities and smoking (Ocean Conservancy's International Coastal Cleanup 2010). The world averages for the sources of marine debris demonstrate that 61% of the items that collected were related to shoreline and recreational activities, 31% of the items were related to smoking, 5% related to ocean and waterway activities, 2% to dumping activities, and 1% to medical and personal hygiene activities. In North America, the sources of ocean debris were similar to the world averages. The sources of marine debris by region are listed in Table 2.5.

Table 2.5 lists the sources of marine debris around the world. Littering from shoreline and recreational activities is the primary source of ocean debris in the world that accounts for approximately 61% of the worldwide marine debris items. Smoking activities contribute to approximately 31% of the worldwide marine debris items. The source of marine debris from smoking can be attributed to smokers who are on or near the beaches around the world. Very little ocean debris is caused by dumping from ocean vessels or of medical and personal hygiene products.

Shoreline and recreational activities are the most significant sources of marine debris in North America, South America, the Caribbean islands, and South East Asia. Smoking-related activities are the most significant source of marine debris in South America.

2.5.3 USA Coastal Cleanup

The persistence of marine debris in the United States is similar to the persistence of worldwide debris. The United States has a lot of beaches that are used for recreational activities, as do countries in the Caribbean, South America, and South East Asia. Increased trash collection on beaches and restricted smoking areas can reduce the amount of debris that ends up in the oceans.

Table 2.6 lists cigarettes and cigarette filters as the most common litter item in the United States that is followed by plastic debris including food wrappers, containers, caps, lids, plastic bags, bottles, cups, plates, spoons, and straws. Glass bottles, aluminum cans, and paper bags round out the top 10 items. Plastics can be found in seven of the top 10 marine debris items collected in the United States.

TABLE 2.6
Top 10 USA Marine Debris Items in 2011

Products	Materials: Plastic and other	Number of items	Percentage of total USA debris
Cigarette/cigarette filters	Cellulose acetate	1,025,044	28%
Food wrappers and containers	PS, PET, LDPE, HDPE, PVC	401,800	11%
Caps and lids	HDPE, PP, aluminum	370,252	10%
Plastic bags	HDPE and LDPE	245,773	7%
Plastic beverage bottles	PET	227,046	6%
Cups, plates, knives, spoons	PS, PP, PS foam, PP foam, paper	168,478	5%
Straw/stirrers	HDPE, PP	166,601	5%
Beverage cans	Aluminum	158,796	4%
Beverage bottles	Glass	150,344	4%
Paper bags	Paper	73,928	2%
	Total	2,988,062	82%

2.6 CHEMICAL POLLUTION FROM PLASTICS

Pollution can be created during the production of plastic products. The most common areas of pollution concern are for ozone layer depletion, atmospheric emissions, smog generation, aquatic eutrophication, terrestrial eutrophication, aquatic acidification, toxic chemical generation, and carcinogenic material generation.

Ozone depletion and atmospheric emissions can come from by-products generated during the creation of plastics. The United States Environmental Protection Agency (EPA) provides a list of two classes of ozone-depleting chemicals (EPA Ozone Protection 2013). The chemicals are primarily chlorinated and brominated compounds, for example, chlorofluorocarbons. Ozone-depleting chemicals can be used and released while producing plastic pellets and products. Atmospheric emissions include chemicals classified as pollutants. Atmospheric emissions primarily are associated with the combustion of fossil fuels for energy and transportation requirements in manufacturing of products, including plastics. Atmospheric emissions can include carbon dioxide, carbon monoxide, hydrocarbons, nitrous oxides, sulfur oxides, and particulates. Smog can be formed from many chemicals including carbon monoxide, particulates, and hydrocarbons. Life cycle assessment (LCA) software can provide emission data on the production of ozone-depleting chemicals and atmospheric emissions (LCA NatureWorks^{TM} 2009).

Chemical pollution can include production of polluting substances that can lead to aquatic eutrophication, terrestrial eutrophication, aquatic acidification, toxic chemicals, and carcinogenic substances. Eutrophication is a bloom of vegetation in aquatic or terrestrial environments. It is caused by the addition of artificial nitrates and phosphates in the ecosystem. Acidification is a reduction in the pH of the aquatic environment. It is caused by the uptake of carbon dioxide in the atmosphere. As the levels of carbon dioxide increase, more of it can dissolve in ocean water and freshwater areas. The carbon dioxide can react with the water and form carbonic acid resulting in a lower pH. Toxic chemicals can be formed during the production of energy for manufacturing facilities. The toxic chemicals can include benzene, dioxins, toluene, xylene, ethyl benzene, styrene, cyanide, etc. The toxic chemicals can also be carcinogenic. LCA software can provide generation data on the production of toxic and carcinogenic chemicals during the creation of plastic products (LCI Summary for PLA and PET 12-Ounce Water Bottles 2013).

2.7 LANDFILL TRASH

Most of the debris collected on land is placed in landfill operations. Modern landfills are well designed and engineered facilities that are operated and monitored to meet federal regulations. The landfills are designed to accept solid debris and prevent contamination of the land and groundwater from the solid debris.

Landfills are, typically, designed according to the "Cap and Seal" strategy of the EPA, as shown is Figure 2.12, to prevent the leachate from contaminating groundwater near the landfill. The area below the landfill is covered in geosynthetic clay to provide a barrier for the landfill. ASTM standards are developed to design the liner systems using geosynthetic clay liners (Koerner and Narejo 1995).

In the United States, 1908 MSW landfills were in operation during 2008. A total of 289.5 million tons of solid debris were collected and buried in landfill, recycled, or composted. Approximately, 69% of the solid debris was buried in landfill, 24% was recycled and composted, and 7% was combusted via waste-to-energy. Table 2.7 lists the regional disposal of MSW at landfills during 2008 (van Haaren et al. 2010).

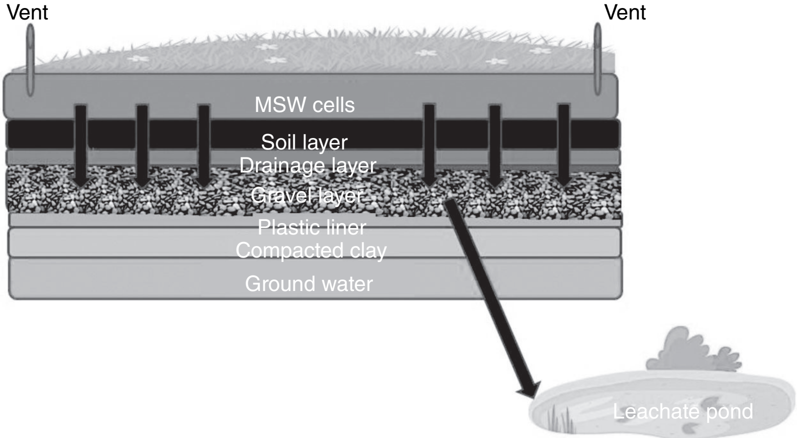

FIGURE 2.12 Cross-sectional view of cap-and-seal landfill.

TABLE 2.7
Diversion Rates of MSW in Landfills During 2008

Region	Landfills (%)	Recycling/composting (%)	Waste-to-energy (%)
Mid-Atlantic	59	27	14
Midwest	78	22	1
Rocky Mountains	88	11	1
South	79	13	8
West	52	46	2
USA total	69	24	7

The landfills are vented to release the trapped landfill gases that are made from biogas, methane, and carbon dioxide. The landfill gasses can be collected and used for energy purposes or burned. Methane can be recovered from active landfill sites called bioreactors where biodegradation is enhanced with the addition of liquids, air, and microbial processes. The bioreactor design can be of three designs that include anaerobic, aerobic, and hybrid. With anaerobic designs, moisture is added in an anaerobic environment to generate landfill gas. With aerobic designs, leachate is removed from the bottom of the reactor and recirculated with air back into the landfill. Landfill gas is removed from the landfill. With hybrid bioreactor designs, waste biodegradation is accelerated through alternating aerobic and anaerobic treatments that rapidly biodegrades organics in the landfill and collects landfill gasses at the bottom of the reactor (EPA Landfill 2013).

Landfills are capped with ground cover and grasses to provide an enclosed “tomb-like” structure for the solid debris. Very little biodegradation occurs in the landfills due to the lack of oxygen, cool temperatures, dry environment, and limited microorganisms. A study from the University of Arizona found that newspapers did not biodegrade in the landfill and could be read after 100 years from when it was first printed. Food scraps and organics found in the landfill were still recognizable after 30 years in the landfill (Rathje and Murphy 2001).

At the end of the service life, plastic products can be either collected for recycling or thrown away with the trash. Waste disposal companies usually collect the plastics with other recycled products. Plastics, metals, and glass are sorted from the refuse and sent to recyclers. The solid waste can be recycled or sent to an incinerator or landfill.

TABLE 2.8
Contents of the Landfill in USA 2008

Item	Weight%
Paper and paperboard	28.0
Food waste	14.5
Yard trimmings	13.5
Plastics	12.7
Metals	8.8
Rubber, leather, and textiles	8.2
Wood products	6.4
Glass	4.6
Other	3.3
USA total	100 (250 million tons)

For 2011 in the United States, the total waste disposed of in landfills was approximately 250 million tons. Of the MSW, approximately 53.6% was buried in a landfill, 34.7% was recycled or composted, and 11.7% was converted to energy through combustion. As shown in Table 2.8 plastics accounted for approximately 12.7% by weight of the solid debris (EPA Waste 2013).

For 2008, as reported in a California statewide waste characterization study, approximately 40 million tons of solid waste was disposed of in landfills as MSW. Plastics accounted for approximately 9.6% of the waste by weight. Plastic trash bags comprised 1% and plastic film comprised 1.7% of the waste stream. The commercial sector generated approximately 50% of the solid waste, the residential sector generated approximately 30% of the solid waste, and the self-hauled sector generated approximately 20% of the solid waste. For 2008, plastics contributed to 12% by weight of the waste stream for the commercial waste, 11.3% of the waste from residential waste, and 5.8% of the waste stream in self-hauled waste (California 2008).

Table 2.8 lists the top 10 items found in a landfill in the United States. Table 2.9 lists the top 10 items found in a landfill on average in California. For the landfills in the United States, approximately 56% of the items are organic in nature. Of the landfills in the California, approximately 50% of the items are organic in nature. Plastics accounted for 12.7 weight% of the waste in the United States and 9.6% of the solid waste in California.

TABLE 2.9
Contents of the Landfill in CA 2008

Item	Weight%
Organics and other	32.4
Inert and other	29.1
Paper	17.3
Plastic	9.6
Metal	4.6
Special waste	3.9
Glass	1.4
Other	1.6
CA total	100 (40 million tons)

2.8 SUMMARY

The land and ocean temperatures are rising over the last 100 years. The average temperatures of the planet in 2011 were the second highest "strong La Niña" temperatures in recorded history. Glaciers throughout the world are melting due to the increased surface temperature of the planet. The levels of the oceans are rising. This can be attributed to thermal expansion of the water, land water storage change, and melting of glaciers and icebergs.

Carbon dioxide and other GHGs have increased dramatically since 1960 in the world. The increase in the levels of GHGs in the atmosphere is the likely cause of the temperature rise in the planet. The primary sources of carbon dioxide emissions are from energy generation and transportation.

The predominant sources of marine debris around the world are from smoking activities and littering during shoreline and recreational activities. Very little ocean debris is caused by dumping from ocean vessels or of medical and personal hygiene products.

Plastic debris accounts for 60–80% of marine pollution. The top 10 debris items are cigarette products, plastic bags and bottles, plastic packaging and disposal cutlery, glass bottles, aluminum can, and paper bags. Cigarette and cigar products comprise the majority of solid debris items found throughout the world. Common plastic debris items are plastics bags, containers, bottles, and disposable dinnerware.

Landfills in the United States are designed according to the "Cap and Seal" strategy of the EPA, where the landfill has a liner of clay and is sealed on top with grass and vegetation. The landfills in the United States are similar to a "dry tomb" structure with very little moisture, oxygen, and microorganisms. Very little biodegradation occurs in the typical landfill.

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REVIEW QUESTIONS

Q.2.1 Recent years have registered one of the highest temperatures on land and sea. T or F?

Q.2.2 Warming of the planet is most likely caused by increased carbon dioxide concentrations in the atmosphere. T or F?

Q.2.3 Glaciers are not melting and the levels of the oceans are constant. T or F?

Q.2.4 Plastics are collecting in only one gyre in the oceans. T or F?

Q.2.5 Plastic bottles are the most common plastic debris in the ocean. T or F?

Q.2.6 Cigarette products are the most common plastic debris in the ocean. T or F?

Q.2.7 The main source of solid debris in the oceans is from dumping waste from ocean ships. T or F?

Q.2.8 POPs are chemical pollutants in the oceans from pesticides, pharmaceuticals, and other toxic sources. T or F?

Q.2.9 Landfills are designed with a Cap and Seal strategy to produce the groundwater sources from the toxic leachate. T or F?

Q.2.10 Newspapers and food waste readily biodegrade in the landfills. T or F?

REVIEW PROBLEMS

P.2.1 In a 30-year timespan from 1981 to 2010, how much did the earth's average temperature increase?

- **a.** 0 degree Fahrenheit
- **b.** 0.25 degree Fahrenheit
- **c.** 0.50 degree Fahrenheit
- **d.** 0.75 degree Fahrenheit

P.2.2 What is the highest contributor to global warming?

- **a.** Generation of electricity
- **b.** Automobile and truck transportation
- **c.** Commercial buildings
- **d.** Manufacturing production like steel mills and limestone processing

P.2.3 What can contribute the most to global warming?

- **a.** Cyclic temperatures of the earth
- **b.** Landfill operation releasing methane and CO_2
- **c.** Cows in a pasture releasing methane and CO_2
- **d.** Burning of fossil fuels

P.2.4 What is the Great Garbage Patch?

- **a.** A region in the south Pacific ocean that is filled with plastic debris
- **b.** A region the north Pacific ocean that has areas of high concentrations of floating debris including plastic and paper and areas of clear water
- **c.** A region in the north Atlantic ocean that has areas of high concentrations of floating debris including plastic and paper and areas of clear water
- **d.** A region in the south Atlantic ocean that has areas of high concentrations of floating debris including plastic and paper and areas of clear water

P.2.5 What are the most common debris items found during the worldwide ocean cleanup?

- **a.** Plastic bags
- **b.** Plastic bottles
- **c.** Plastic packaging
- **d.** Cigarette products

P.2.6 In 2011, which area of the world had the highest concentration of marine debris per square mile of shoreline?

- **a.** Australia
- **b.** Spain
- **c.** Philippines
- **d.** USA

P.2.7 What is the primary source of ocean debris?

- **a.** Dumping from ocean vessels.
- **b.** Smoking activities
- **c.** Derelict fishing containers and gear
- **d.** Leisure and recreational activities

P.2.8 What are the examples of POPs?

- **a.** DDT
- **b.** PCB
- **c.** Pesticides
- **d.** All of the above

P.2.9 How long can you expect newspapers to biodegrade in a typical landfill?

- **a.** Within 5 years
- **b.** Within 25 years
- **c.** Within 50 years
- **d.** Longer than 100 years

P.2.10 What should be done with the organic materials in a landfill?

- **a.** Leave in the landfill
- **b.** Send them to an industrial compost facility
- **c.** Recycle them
- **d.** Biodegrade them in the landfill

REVIEW EXERCISES

E.2.1 Collect and graphically plot the temperature of the land and oceans of the world for the last 100 years, 200 years, and 500 years.

E.2.2 Visit a local beach (freshwater or ocean) and record the number and types of debris in a 5 m × 5 m area. Repeat this at three other locations.

E.2.3 Determine the level of ocean rise for five coastal cities in your country over the last 50 years and then determine the sea-level rise in the next 100 years. How much of the town or city will be flooded?

E.2.4 From the latest Ocean Conservancy published report on worldwide ocean cleanup, what are the 10 most common marine debris items in the world, country, and state. What are the ways to reduce the debris for your local community and state?

E.2.5 What are the most common POPs in your region? What are the sources of the POP contamination? How can they be eliminated?

CHAPTER 3

Life Cycle Information

3.1 LIFE CYCLE ASSESSMENT FOR ENVIRONMENTAL HAZARDS

Life cycle assessments (LCAs) include many of these environmental hazards. LCA can be used to compare the environmental impacts of producing plastic products. Sustainability for manufacturing can be categorized into generation of GHGs, solid and liquid wastes, and air and water pollution.

The United Nations Environment Program and the Society for the Environmental Toxicology and Chemistry provide a Web site with information on LCA including approaches for capability development, methodologies, data, resources, and impacts. The Life Cycle Initiative includes LCA publications and manual. The goal of the initiative is to enable people around the world to use LCA more frequently and efficiently. The Life Cycle Initiative can establish a global network of LCA experts to establish and manage best practices of LCA across multiple industries and product sectors (Life Cycle Initiative 2013).

The U.S. National Energy Laboratory (NREL) created a U.S. life cycle inventory database to provide support for developers of LCA models of products and services. (U.S. NREL 2014). The database provides "cradle-to-gate" and "cradle-to-grave" LCI information to account for energy and material flows into and out of environments for products and services. The goals of the LCI database are to maintain data quality of

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Sustainable Plastics: Environmental Assessments of Biobased, Biodegradable, and Recycled Plastics, First Edition. Joseph P. Greene.

critically reviewed LCI data for US materials, products, and process, maintain compatibility with international LCI databases, and to support US industry competiveness.

3.2 LIFE CYCLE ASSESSMENT DEFINITIONS

LCA is a methodology to assess the environmental impacts of a product, process, or service. ISO 14040:2006 is an international standard for LCA. LCA is performed with a four-step process that includes:

1. Definition of goal and scope.
2. Inventory of relevant energy, material, and transportation inputs and related liquid, gas, and solid generated outputs.
3. Evaluation of the impacts of releases on the environment associated with the emissions and waste generation by viewing the environmental impacts per functional unit.
4. Interpretation of the LCA results.

The integrated four-step LCA process is described in Figure 3.1.

3.2.1 LCA Step 1: Goal and Scope Development

The first step in the LCA process is to establish the goal and scope of the LCA. The purpose, assumptions, and functional unit are established for the LCA. The functional unit is used to compare different materials, processes, or services. The functional unit ensures that comparisons can be made between different materials, processes, or services. Assumptions can include transportation by truck or rail, end-of-life is recycled, waste to energy, landfill, or composting process. The scope in the LCA will be determined if end-of-life environmental effects are considered or if the LCA will end after the manufacturing process. "Cradle-to-gate" LCA is one where the materials and energy required to produce a product from raw materials to final product are used in the LCA calculations. Likewise, the "cradle-to-gate" LCA will provide environmental emissions, waste generation, and pollution generated during the production of a product from raw materials to final product. An LCA that considers manufacturing, product use, and end-of-life is referred to as "cradle to grave." An LCA that includes chemical recycling or reuse can be

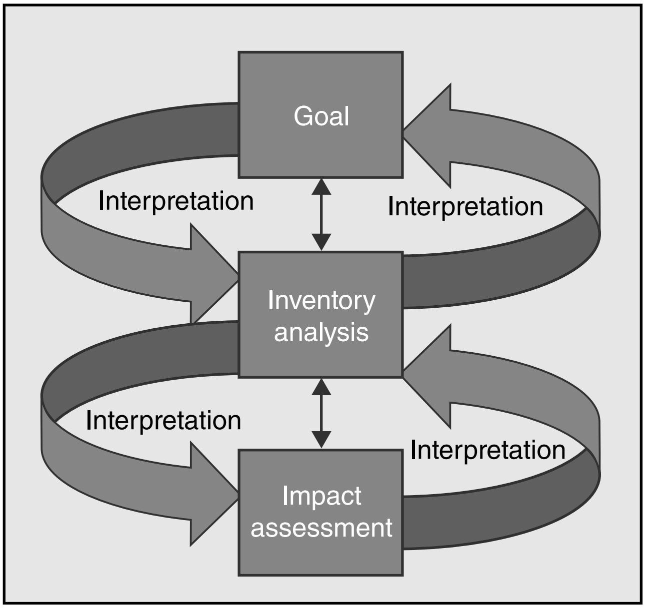

FIGURE 3.1 Life cycle assessment four-step definition.

referred to as “cradle to cradle.” “Cradle-to-gate” and “cradle-to-grave” analysis will be discussed later in this chapter.

3.2.2 LCA Step 2: LCI Development

The second step in the LCA process, called Life Cycle Inventory, catalogs all of the various material, energy, and transportation inputs needed to produce the raw materials and manufactured products or systems. The LCI also catalogs the emissions and wastes generated in the production process or system. Figure 3.3 lists the inputs and outputs for the LCI.

The US Department of Energy provides a US LCI database roadmap (US Department of Energy 2009). The goals of the database project are to:

- Maintain LCI data quality and transparency.
- Provide LCI data for common industrial materials, products, and processes in the United States.
- Be compatible with international LCI databases.
- Provide LCI resources for US industry and data accessibility.

The US LCI tool can help US companies integrate LCA into business plans and environmental analysis for new products and services. The US LCI tool can provide LCI data for many US manufactured processes and provide an expanded database of LCI information. The US LCI tool had contributions from the US Department of Energy, US General Services Administration, US Environmental Agency, US Forest Service, US Navy, US Green Building Council, American Chemistry Council (ACC), Athens Institute, CORRIM, Franklin and Associates, Institute for Environmental Research and Education, Portland Cement Association, Sylvatica, and Vehicle Recycling Partnership of USCAR.

The LCI database provides LCI information for many industries including:

- Air transportation
- Chemical manufacturing
- Crop production
- Electric component and computer manufacturing
- Fabricated metal product manufacturing
- Forestry and logging
- Mining
- Nonmetallic mineral product manufacturing
- Oil and gas extraction
- Paper manufacturing
- Petroleum and coal products
- Plastics product manufacturing
- Plastics and rubber products manufacturing
- Primary metal manufacturing
- Rail transportation
- Transit and ground passenger transportation
- Truck transportation
- Utilities
- Waste management and remediation
- Wood products manufacturing
- Biomass

For plastics manufacturing, the LCI database provides LCI information for all major plastics. The database provides references of LCI data from the ACC.

3.2.3 LCA Step 3: LCA Development

The third step in the LCA process is to assess the environmental impacts from the inventory collection of Step 2. The assessment step typically normalizes the input and outputs to the LCI as per the normalized unit.

Thus, the environmental effects can be viewed as per a grouping of the product, for example, 1000 grocery bags, 10,000 cellular phones, and 100,000 vehicles. For example, the environmental impacts can be viewed as 10,000 cellular phone cases made from Acrylonitrile butadiene styrene (ABS) versus 10,000 cellular phone cases made from PP. Then, the amount of energy required to produce 10,000 cellular phone cases from ABS can be compared to the amount of energy required to produce 10,000 cellular phones from PP. Likewise, the carbon footprint, solid waste, and pollution can be calculated as per the common grouping.

3.2.4 LCA Step 4: Interpretation of Results

The fourth step is the interpretation of the data and is involved in all of the previous three steps. The data should be analyzed in each of the three steps for consistency and accuracy. The scope and assumptions should be reviewed in each of the steps of the LCA process to ensure thoroughness. The last step interprets the results from the LCA and provides conclusions and recommendations for minimizing environmental impacts of products, processes, and services.

3.3 ISO 14040/14044 LIFE CYCLE ASSESSMENT STANDARDS

The International Organization for Standardization (ISO) published standards for LCA. LCA compares environmental performance of products in terms of greenhouse gas emissions, pollution generation, waste generation, energy consumption, water consumption, and other resource consumption. LCA compares these items in terms of a measurable quantity of the products.

ISO 14040: 2009 is an international standard of the LCA with a focus on principles and framework. ISO 14040 provides a summary of the LCA practice and applications for LCA. It also includes limitations of the LCA process. ISO 14040 describes the four-step process to develop an LCA that includes goal, LCI, LCA, and interpretation. ISO 14040 also provides reporting aspects of an LCA and the critical review and limitations of the LCA. ISO 14040 does not specify methodologies of the individual LCI and LCA phases of the LCA (ISO 14040:2006).

ISO 14044:2006 is an international standard of the LCA with a focus on requirements and methodology of conducting an LCA. ISO 14044 provides guidance on the preparation of the LCI and assessments of the LCI through the LCA. ISO 14044 provides guidance on the interpretation of the LCA results as well as sensitivity analysis of the data used in the LCA (ISO 14044:2006 2006).

LCI can be used to evaluate the material, energy, and raw materials necessary to produce a product or system, as well as the environmental impacts of the product or system. If the scope of the LCA ends with the creation of a product or system, then it is referred to as "cradle-to-gate" assessments as shown in Figure 3.2. The energy requirements, raw materials, and water consumed are tabulated to produce a product or system. Likewise, the air and water pollution, waste generation and GHG emissions are calculated for the product or system. Cradle-to-gate LCA can be used to evaluate the environmental impacts of producing a product or system. This can be beneficial to manufacturing companies who are looking into ways to produce a product or system with lower environmental impacts.

FIGURE 3.2 Life cycle inventory process for "cradle-to-gate" analysis.

LCA can be created with dedicated software packages, for example, GaBi Software, SimaPro, and Sustainable Minds (GaBi Software Product Sustainability 2013; SimaPro 2013; Sustainable Minds 2013).

LCI can be used to evaluate the raw materials, energy, and water requirements to create a product or system that includes transportation and end-of-life options for the products. This LCA process is referred to as "cradle to grave" and is shown in Figure 3.3. Likewise, the air and water pollution, waste generation, and GHG emissions are calculated for the product or system. Cradle-to-grave LCA can be used to evaluate the overall impacts of producing a product or system on the environment. This can be beneficial to manufacturing companies who are trying to reduce the transportation energy and environmental costs on a product. Also, companies can evaluate different end-of-life

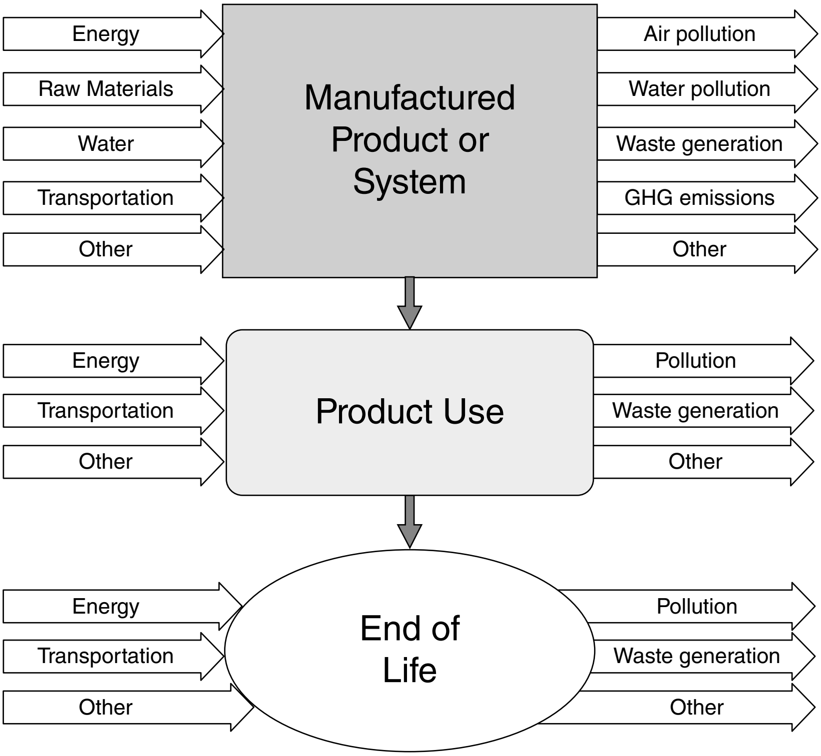

FIGURE 3.3 Life cycle inventory process for "cradle-to-grave" analysis.

scenarios for the product for composting, recycling, waste-to-energy, or landfilling options. Cradle-to-grave LCA can be helpful for companies to establish triple bottom line accounting for the development of sustainable products and to incorporate design for sustainability principles in the design of a product or system.

3.4 SENSITIVITY ANALYSIS

The results in an LCA study can be affected by many sources of uncertainty. The sources of uncertainty can be found in the choices used for assumptions, scope, boundaries, impact assessment methods, and the quality of the available data. In addition, assumptions made for the inclusion of end-of-life, transportation, and pollution can significantly affect the results in an LCA.

Key to the relevance of any LCA study is the quality of data. This can be measured with sensitivity analysis (Cellura et al. 2011).

LCA studies should include a section on sensitivity analysis and identify areas in the LCA that may be unreliable or inaccurate. The uncertainty in the LCA study should require the data to be calculated with critically reviewed methods. LCA results should include a range of results that incorporate variations in the input data.

Three procedures of analysis can be used to estimate the uncertainty in an LCA study (May and Brennan 2003):

- Gravity analysis to determine the data with the highest contribution.
- Uncertainty analysis to determine the range of possible results based on data uncertainty.
- Sensitivity analysis that assesses the influence of a parameter, or independent variable, on the value of another parameter, or dependent variable.

As an example, sensitivity analysis was used to determine the uncertainty in an LCA on Italian roof tiles (Cellura et al. 2011). In the study, uncertainty was found in several sources of data in the LCA. The results revealed that in some cases significant differences in energy usage and environmental impacts can be obtained with different assumptions. The research found that uncertainty can be of the following types:

- Parameter uncertainty due to incomplete input data.
- Model uncertainty due to linear assumptions for environmental relationships.
- Methodological uncertainty due to assumptions made with LCA parameters.
- Spatial uncertainty due to short- and long-term time scales.
- Data uncertainty due to the use of secondary input data.

The Italian tile LCA case found that significant variability in the LCA was due to the use of secondary data to calculate the environmental impacts of clay tiles. Assumptions for transportation and electricity sources caused variation in the LCA data, as well as the use of subjective choices in the LCI data from different evaluators.

Standard databases and site-specific inventories can be used to reduce the inconsistencies in the LCA and provide a more reliable LCA. Primary energy, electricity, transportation, and fuel usage data should be provided by local databases and evaluated for consistency by LCA experts.

3.5 MINIMAL ACCEPTABLE FRAMEWORK FOR LIFE CYCLE ASSESSMENTS

LCA can be produced from a variety of sources and provide a variety of results. Standardization of LCA inputs and outputs would benefit the usefulness of LCA. Minimal acceptable features of an LCA are that it follows ISO 14040/14044 standards and uses a four-step process indicated previously. In addition, the LCA should include several items listed in the definition of sustainability, that is, GHG emissions, waste generation, and pollution. The LCA should also include at a minimum end-of-life considerations. Water usage is an important consideration for some areas of the world but not in all areas, and thus is not included in the minimal framework. The pollution areas that are most commonly evaluated in LCAs are water eutrophication and acidification. Thus, an acceptable methodology for LCA should include the following at a minimum:

- Equivalent functional unit for the LCA,
- Energy required LCI calculation per functional unit,
- Equivalent carbon footprint LCI calculations per functional unit,
- Waste generation LCI calculation per functional unit,
- Eutrophication generation LCI calculation per functional unit,
- Acidification generation LCI calculation per functional unit,
- Transportation per functional unit from raw materials to plastics conversion operations,
- End-of-life scenarios,
- ISO 14040 and 14044 compliant, and
- Uncertainty analysis.

3.6 LIFE CYCLE INVENTORY FOR PETROLEUM-BASED PLASTICS

LCI can be used to calculate the environmental impacts of producing petroleum-based plastics. The LCI for petroleum-based plastics is based on ISO 14040 and 4044 and provided by the ACC for nine plastic resins and four polyurethane procurer resins. The cradle-to-gate analysis can provide a foundation for understanding the energy requirements, GHG emissions, waste generation, and pollution with the most common petroleum-based plastics. The LCA process for polyethylene terephthalate (PET) plastic can be used as an example (ACC LCA 2011; Nine resins).

3.6.1 LCI for PET Pellets

The LCI for the production of PET pellets in a cradle-to-gate analysis was provided by Franklin and Associates in 2011. PET plastic was produced from crude oil in a five-step process outlined in Figure 3.4. The LCA provides energy and water requirements, greenhouse gas emissions, waste generation, and pollution production.

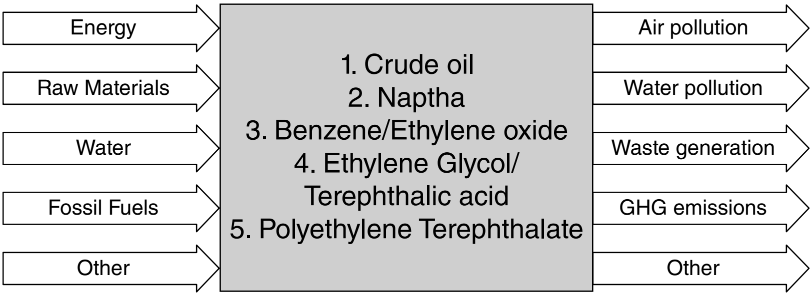

FIGURE 3.4 "Cradle-to-gate" process of producing PET plastic pellet.

For PET plastic, the pellet production process includes the following:

1. Extracting crude oil
2. Producing naptha
3. Producing benzene and ethylene oxide
4. Producing ethylene glycol and terephthalic acid
5. Polymerizing PET and producing pellet.

The LCA process takes into account all of the energy, raw materials, water, and fossil fuels required in the production of PET pellets. The first step is the extraction of crude oil. The process requires electricity, fossil fuels, natural gas, water, and other materials. The second step is the production of naptha with the use of fossil fuels, electricity, water, and other materials. The third step is the production of benzene and ethylene oxide with the use of electricity, fossil fuels, water, and other materials. The fourth step is the production of ethylene glycol and terephthalic acid with the use of fossil fuels, electricity, water, and other materials. The last step is the polymerization of PET and conversion into PET pellets with the use of electricity, fossil fuels, water, and other materials.

The air and water emission, waste generations, and pollution were calculated based on data compiled by Franklin Associates from surveys from 17 resin and precursor manufacturers in North America. Other upstream information was provided by Franklin internal database. Fuels and energy databases are from the US LCI database. All calculations followed ISO 14040 and 14044 requirements (Cradle to Gate Life Cycle 2011).

The assumptions in the LCA analysis are as follows:

Assumptions

- 1000 kg of plastic resins.
- Plastic resins were produced from crude oil and natural gas.
- Fuels used to transport plastic resins are included.
- Offgas fuel is reused in the production process.
- ISO 14040 and 14044 guidelines were used.
- Energy and fuel data included US LCI database from 2003 database.
- Data collected came from plants in the United States, Mexico, and Canada.
- Cradle-to-gate analysis was used. End-of-life options, conversion to plastic products, product use, and transportation to retail outlets are not considered.
- Water consumption was not calculated due to the lack of corresponding data for the raw materials and intermediate chemicals.
- Land use and erosion were not considered due to lack of quality data sources.

The LCA considers environmental impacts of the process, fuel, end-of-life, and energy material resource. For appropriate comparisons with other LCA studies, we will consider only the environmental effects of the process of each material. The environmental categories considered are:

- Greenhouse gas emission
- Energy usage
- Waste generation
- Water usage

3.6.2 LCA Sensitivity Analysis

The analysis has limitations for cradle to gate and not cradle to grave. The fuel production, energy values are for data from one particular year of 2009 and not 0 averages for 3–5 years. The LCA did not consider

TABLE 3.1
LCI of Environmental Impacts of Four Plastic Resins

Environmental impact	PET	GPPS	HDPE	PP
Mass (kg)	1	1	1	1
Specific gravity	1.37	1.06	0.92–0.95	0.9
Energy consumed (GJ)	0.0704	0.0952	0.0783	0.077
Carbon footprint (kg CO_2eq)	2.733	3.242	1.897	1.860
Solid waste generated (kg)	0.141	0.110	0.0771	0.085

creation of chemicals that cause eutrophication, acidification, or other chemical pollution.

3.6.3 LCA for PET, GPPS, HDPE, and PP Pellets

LCI can also be calculated for other plastic resins and used as a comparison. Table 3.1 presents “cradle-to-gate” analysis of the environmental impacts of four plastic resins that can be used for plastic applications (Cradle to Gate Life Cycle 2011).

Table 3.1 demonstrates that PP and HDPE produce lower GHG emissions per kilogram of resin and solid waste per kilogram of resin than PET and GPPS.

Additional LCAs will be calculated for PET, PP, PS, and other plastic products in Chapter 7. The LCA of plastic products can be used based on the information in Table 3.1 to calculate the cradle to grave of plastic products made.

3.7 LIFE CYCLE ASSESSMENT FOR BIOBASED POLY LACTIC ACID

LCA can be used to calculate the environmental impacts of producing biobased PLA plastic.

The LCA for the production of PLA pellets in a cradle-to-gate analysis was provided with an LCA on Ingeo® PLA. The PLA was produced with the new lactic acid production process with reduced environmental impacts for the Ingeo production system. The LCA provides energy and water requirements, greenhouse gas emissions, waste generation, and pollution production (Vink, Davies, and Kolstad in 2010) (Madival, Auras, Singh, and Narayan 2009).

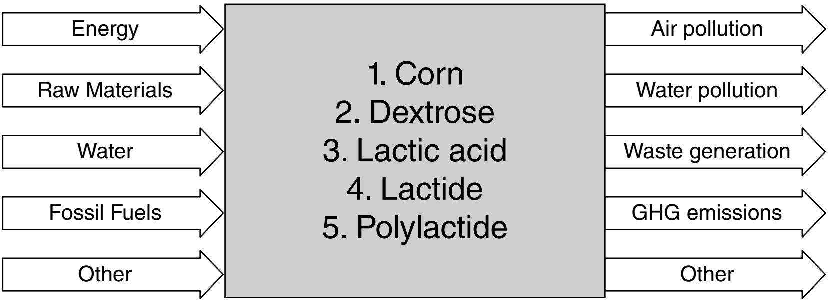

FIGURE 3.5 "Cradle-to-gate" process of producing Ingeo® PLA plastic pellet.

For PLA, the manufacturing process includes the following:

1. Harvesting corn
2. Isolating starch
3. Converting starch to dextrose
4. Fermenting glucose to lactic acid via bacteria
5. Polymerizing lactic acid to poly lactide pellets

The process of producing PLA is described in Figure 3.5

The LCA process takes into account all of the energy, raw materials, water, and fossil fuels required in the production of Ingeo® pellets. The first step is the harvesting of the corn in the fields where the corn is grown, harvested, dried, and transported to the corn wet mill. The process requires fertilizers, electricity, fossil fuels, natural gas, and other materials. The second step is the production of starches and dextrose sugars with the use of fossil fuels, electricity, steam, water, and other materials. The third step is the fermentation to lactic acid with the use of electricity, fossil fuels, water, steam, and other materials. The fourth step is the production of lactide from lactic acid with the use of fossil fuels, electricity, steam, water, and other materials. The last step is the polymerization of polylactide and conversion into PLA pellets with the use of electricity, fossil fuels, water, and other materials.

Lactic acid can be produced from chemical or biotechnological methods. Chemical synthesis is based on the hydrolysis of lactonitrile by strong acids, or by base catalyzed degradation of sugars, oxidation of propylene glycol, or by chemical reactions of acetaldehyde, carbon monoxide, and water at elevated temperatures (Mussatto et al. 2008). Most of lactic acid is produced from biochemical processes and polymerized to PLA. PLA is usually produced from lactic acid through fermentation of the sugars in corn (Natureworks 2013). PLA can also be produced from sugars from other carbohydrate sources, including organic waste. L-Lactic acid was produced from spent grain by controlling the pH and other process parameters (Shindo and Tachibana 2004). Researchers in Japan successfully produced lactic acid from spent grains with immobilized lactic acid bacterium (Lactobacillus). They were able to produce 60 grams of sugar (glucose, xylose, and arabinose) from 210 grams of spent grains (79% water), which was converted to lactic acid after 5 days.

The air and water emissions, waste generations, and pollution can be calculated based on the software developed with Plastics Europe and a series of published EcoProfiles for traditional petroleum-based polymers. The same methodology, software, and core databases developed an Ecoprofile for Ingeo. All calculations followed ISO 14040 and 14044 requirements (Vink et al. 2010).

The assumptions in the LCA analysis are as follows:

Assumptions

a. 1 kg of Ingeo®.
b. Cradle-to-gate analysis was used.
c. End-of-life options, conversion to plastic products, product use, and transportation to retail outlets are not considered.
d. Boustead 5.0 methodology and software were used to calculate the LCI and LCA of PLA (Boustead Model 5.0 2013).
e. All LCI and LCA calculations based on ISO 14040 and 14044.

The LCA considers environmental impacts of the energy, materials, processes, and end-of-life. For appropriate comparisons with other LCA studies, we will consider only the environmental effects of the process of each material. The environmental categories considered are:

- Greenhouse gas emissions
- Energy usage

TABLE 3.2
Environmental Impacts to Produce 1 kg of Ingeo® PLA

Environmental impact	Ingeo®
Mass (kg)	1
Density	1.22
Energy consumed (GJ)	0.06784
Carbon footprint (kg CO_2eq)	1.24
Solid waste generated (kg)	0.266968
Water consumed (L)	48.787674
Eutrophication, water (g PO_4eq)	0.0000316

- Waste generation
- Water usage

Table 3.2 provides the environmental impacts of producing 1 kg of Ingeo® PLA.

Additional LCAs will be calculated for PLA in Chapter 7. The LCA of plastic products can be used based on the information in Table 3.2 to calculate the cradle-to-grave LCA of plastic products made with Ingeo® plastic.

3.7.1 LCA Sensitivity Analysis

The analysis has limitations for cradle to gate and not cradle to grave. One limitation is that the energy usage is for one year and not the averages of three to five years.

3.8 SUMMARY

Life cycle assessment is a methodology to assess the environmental impacts of a product, process, or service. ISO 14040 and 14044 are international standards for developing LCA, which has four steps that include definition of goal or scope, inventory of relevant material and energy inputs and relevant environmental outputs, evaluation of environmental impacts per functional unit, and interpretation of results.

"Cradle-to-gate" LCA calculates the environmental impacts of products, processes, or systems based on energy, material, transportation, and other inputs. "Cradle-to-gate" LCA is one where the materials and energy required to produce a product from raw materials to final product are used in the LCA calculations. Likewise, the "cradle-to-gate" LCA will provide environmental emissions, waste generation, and pollution generated during the production of a product from raw materials to final product. "Cradle-to-grave" LCA includes all of "cradle-to-gate" calculations, but also includes product use and end-of-life areas of the life cycle.

LCA for four plastics demonstrates that PP and HDPE produces lower GHG emissions per kilogram of resin and solid waste per kilogram of resin than PET and GPPS.

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REVIEW QUESTIONS

Q.3.1 LCA refers to life cycle assessments of products, processes, or systems. T or F?

Q.3.2 LCA has three steps in its process, namely creation of goal, LCI, and LCA. T or F?

Q.3.3 "Cradle-to-gate" and cradle-to-grave" LCAs provide the same information and are similar approaches to LCA. T or F?

Q.3.4 "Cradle-to-gate" LCA includes transportation, product use, and end-of-life life cycles. T or F?

Q.3.5 PP and HDPE resins require the same amount of energy to produce 1 kg of resin and emit same CO_2 emission to produce 1 kg of plastic. T or F?

Q.3.6 The carbon footprint of PLA plastic resin per kg of PLA is less than the carbon footprint of PET plastic per kg of PET. T or F?

Q.3.7 The solid waste generated from producing 1 kg of PLA plastic is less than the solid waste generated from producing 1 kg of PET plastic. T or F?

Q.3.8 ISO 14040 and 14044 are international standards for developing LCAs. T or F?

Q.3.9 Cradle-to-grave LCAs calculate the environmental impacts of producing products and include manufacturing, product use, and end-of-life aspects of the product. T or F?

Q.3.10 Sensitivity analysis is needed in an LCA to evaluate only the quality of the raw data. T or F?

REVIEW PROBLEMS

P.3.1 Life cycle assessment methodology has four steps that include which of the following:

- **a.** Scope, goal, inventory, and evaluations of the environmental impacts of products, materials, or processes.
- **b.** Scope, goal, inventory, interpretation, and evaluations of the environmental impacts of products, materials, or processes.
- **c.** Scope, inventory, and evaluations of the environmental impacts of products, materials, or processes.
- **d.** Scope, goal, interpretation, and evaluations of the environmental impacts of products, materials, or processes.

P.3.2 The US Department of Energy provides an LCI tool for which industries?

- **a.** Air transportation
- **b.** Chemical manufacturing
- **c.** Oil and natural gas
- **d.** All of the above

P.3.3 Which of the following plastics has the lowest carbon footprint to produce 1 kg of plastic?

- **a.** PET
- **b.** GPPS
- **c.** PP
- **d.** HDPE

P.3.4 When is the preferred time to perform a cradle-to-gate LCA?

a. After producing a product for comparison with competing products.

b. Never. LCA cannot help sales

c. After the design phase of the product development and before production.

d. During the production phase so the process can be optimized for low environmental impacts.

P.3.5 Which of the following plastics are produced with the least amount of energy per kilogram of plastic resin?

a. PET

b. HDPE

c. PLA

d. GPPS

REVIEW EXERCISES

E.3.1 Create a “cradle-to-gate” LCA process using the ISO 14040/14044 standards for the creation of a product that you use every day.

E.3.2 List all of the energy, transportation, wastes, and pollution of a product that you use every day during the use of that product.

E.3.3 List all of the energy, transportation, wastes, and pollution of a product that you use every day during the end-of-life options of that product.

E.3.4 Create a cradle-to-gate LCA of producing a reusable steel bottle and a cradle-to-gate LCA of producing a plastic bottle. How many times do you have to use the reusable steel bottle to equal the environmental impacts of plastic bottles?

E.3.5 Create a cradle to gate of producing a paper and plastic bag. Which is more sustainable?

CHAPTER 4

Biobased and Biodegradable Polymers

4.1 BIOBASED AND BIODEGRADABLE DEFINITIONS

Biobased and biodegradable polymers have two different meanings. Biobased products are materials made from some amount of biobased materials (Narayan 2006). Biobased products were defined in the 2002 Farm Bill as commercial or industrial products that are composed in whole, or in significant part, of biological products, renewable agricultural materials, or forestry materials. The definition was expanded with the 2008 Farm Bill that incorporated biobased intermediate ingredients or feedstock (Biobased 2013).

The USDA established minimum biobased content standards for many product categories. Products must meet or exceed the minimum biobased content in its category to be certified as biobased products. ASTM D6866 provides a test method to measure the biobased content of products. This will be explained more in Chapter 8 (ASTM D6866 2013).

Biodegradable polymers are converted to biomass, CO_2, and water through a thermochemical process in a specified time frame and in a specified disposal environment. Biodegradable polymers meet ASTM or ISO standards for biodegradation in a biodegradation environment,

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Sustainable Plastics: Environmental Assessments of Biobased, Biodegradable, and Recycled Plastics, First Edition. Joseph P. Greene.

for example, industrial compost or marine environments. This will be explained in more detail in Chapter 8. Many biobased polymers are biodegradable, but not all biodegradable polymers are biobased products. Some biodegradable or compostable polymers are made from petroleum products. Compostable polymers are those that meet the ASTM requirements for biodegradation under industrial composting conditions.

In Europe, biobased polymers can be certified as biobased with the OK Biobased certification program from VinCotte (OK Biobased Certification 2013). Biobased plastics are made with a renewable resource that can offer lower environmental impacts than petroleum-based plastics (Bastioli, C. (2005)). Replacing petroleum-based carbon with organic carbon from today can reduce the carbon footprint of the plastic material based on life cycle assessments (LCA; Narayan 2006a, 2011b).

The biobased content of the plastic material can be established by tests that measure carbon isotopes of the polymer material. In the United States, the ASTM D6866 standard establishes the procedures, equipment, materials, and conditions to measure the 14C content of the plastic sample through radiocarbon analysis. ASTM D6866 biobased standard establishes that a material can be certified as biobased if greater than 99% of the carbon in the plastic sample is made from organic sources and is characterized by a 14C isotope. This will be further explained in Chapter 8.

Biodegradable polymers are defined as polymers that undergo chemical conversion of the carbon in the polymer sample to carbon dioxide or methane, water, and other organic residue (Tokiwa, Calabia, Ugwu, and Aiba 2009). Biodegradable polymers can be made from biobased materials or petroleum-based materials. The biodegradable polymers are used in packaging, agricultural, medicine, and other applications (Vroman and Tighzert 2009). Biodegradation occurs in an environment during a specified timespan. In the United States and Europe, biodegradation testing is defined for industrial compost, home compost, anaerobic digestion, and marine environments. However, biodegradation performance is only defined for industrial compost and marine water environments with ASTM standards in the United States and for industrial compost and home compost ISO standards in Europe. Thus, plastics can claim biodegradability for industrial compost, home compost, or marine environments, but not for anaerobic digestion or landfill environments. Biodegradable Products Institute (BPI World 2013) provides biodegradation certification as compostable in the United States, and Vinçotte (OK Compost) and DIN CERTO provide biobased and biodegradation certification for plastics in Europe. Compostable is defined as meeting the requirements of biodegradation of plastic materials under industrial composting conditions specified in ASTM D6400 standard specifications. This will be further explained in Chapter 8.

Compostable plastics are those that pass the ASTM D6400 biodegradation requirements of greater than 90% carbon conversion to CO_2 after 180 days while exposed primarily to hot composting conditions of 58°C and 50% moisture. Marine biodegradable plastics are those that pass the ASTM D7081 of greater than 30% carbon conversion to CO_2 after 180 days while exposed to cool marine water of 30°C for 180 days. This is explained in more detail in Chapter 8.

4.2 BIOBASED POLYMERS

Biobased polymers are those made from natural or organic ingredients, such as starch from corn, potato, tapioca, rice, or wheat (Narayan 2006a, 2011b). Biobased polymers can also be made from oils, such as palm seed, linseed, soy bean, or fermentation products, like polylactic acid (PLA), polyhydroxyalkanoate (PHA), and polyhydroxybutyrate (PHB). BPI World provides a listing of compostable plastic resins, bags, cutlery, and packaging (BPI World 2013).

Many types of biodegradable polymers are available to biodegrade in a variety of environments, including soil, air, or compost. Biodegradable polymers are primarily made from corn in the United States, but can be made from sugarcane, wheat, cellulose, collagen, casein, soy, or triglycerides.

Biodegradable polymers can be used for packaging, containers, bottles, bags, agricultural pots, and ground coverings. With plastic packaging, compostable and biodegradable polymers are formed into candy trays, bottles, cups, and clear clamshells for food service products as listed in Table 4.1. Environmental impacts of biodegradable plastic bags were found to vary with a variety of biobased, petroleum based, oxodegradable, and reusable plastic bags (The Impacts of Degradable Plastic Bags in Australia 2003).

TABLE 4.1
Commercially Available Biodegradable and Compostable Polymers

Material	Type	Resin supplier	Biodegradation environment
Bagasse	Sugarcane	Asean Corporation, China Various others	Industrial compost
Bionolle®	Poly(butylene succinate)	SK Polymers, Korea, www.skchemicals.com Showa Highpolymer, www.shp.co.jp	Industrial compost
Bionolle®	Poly(butylene succinate-co-adipate) copolymers	Showa Highpolymer, www.shp.co.jp	Industrial compost
Biotec Bioplast®	Thermoplastic starch, blended with additives (e.g., plasticizers)	Novon International (USA) Eco-FOAM (National Starch) Paragon (Avebe)	Industrial compost
Biotec Bioplast®	Thermoplastic starch, blended with additives (e.g., plasticizers)	Novon International (USA) Eco-FOAM (National Starch) http://www.biotec.de/en/index	Industrial compost
Ecoflex	Polyester, poly(butylene adipate-co-terephthalate)	BASF http://www.bioplastics.basf.com/ecoflex.html	Industrial compost
EnMat	PHBV	Tianan Ltd., http://www.tianan-enmat.com/}	Industrial compost
GreenBio	P3HB/P4HB	Tianjin Ltd., http://www.tjgreenbio.com/en/	Industrial compost
Ingeo®	Polylactic acid	NatureWorks www.natureworksllc.com/	Industrial compost
Mater-Bi™	Corn starch/PBAT or acetate derivatives	Novamont www.biobagusa.com/mater_bi.htm	Industrial compost
Mirel™	P3HB/P4HB	Metabolix Inc. www.metabolix.com/	Industrial and home compost, marine, anaerobic digester
Plantic®	Starch/PVOH	Plantic Technologies Ltd, http://www.plantic.com.au/about/history.html	Industrial compost

Trash bags, films, and sheet can be made from compostable plastics for household purposes. The bags, film, and sheet products can be composted into high quality compost along with other composting materials (Rudnik 2008).

4.2.1 Bagasse-Based Polymers

Bagasse is a sugarcane-based polymer that can be made into paper-like products for packaging, disposable tableware, and containers (Liyana et al. 2012). Bagasse is a fiber-pulp product that is part of the sugarcane stalk. Bagasse fibers can be processed similar to paper pulp to produce compostable products for stationary, paper products, food packaging, and disposable service ware (Daud et al. 2007).

4.2.1.1 Bagasse Composition

In general, 1 ton of sugarcane can generate 280 kg of bagasse fiber. The composition of bagasse is as follows (Sun et al. 2004):

- Cellulose: 42%
- Hemicellulose: 25%
- Lignin: 20%
- Ash: 1.64%
- Extractives (water + ethanol): 8.38%
- Other: 3.98%

4.2.1.2 Chemical Structure of Bagasse

The conversion of bagasse from sugarcane waste to compostable plastic does not involve a chemical change, but rather a mechanical change in form. Cellulose has glucose groups in its linear crystalline structure. Hemicellulose has a branched amorphous structure and can contain many sugar groups including xylose, glucose, and galactose (Penga et al. 2010). The chemical structures of cellulose $(C_6H_{10}O_5)_n$ are displayed in Figure 4.1. The molecular structure of lignin has aromatic rings and consists of various substructures that appear to repeat in a random pattern (Davé et al. 1993).

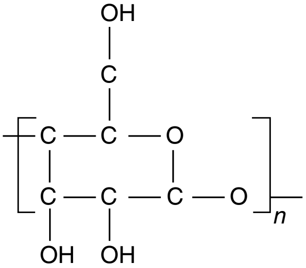


FIGURE 4.1 Chemistry of cellulose.

4.2.1.3 Manufacturing Methods and Fiber Pulping Operation

Bagasse is converted into a paper product with a modified paper pulping process (Zhao et al. 2011). Typically, strong acids or bases are used to remove the lignin from the bagasse mixture. Recently, wood pulp and bagasse were treated with steam explosion and a laccase enzyme to remove the lignin rather than with toxic chemicals (Martín-Sampedro et al. 2011).

4.2.1.4 Properties

The properties of bagasse-based polymers are similar to cardboard. The mechanical properties of bagasse are dependent in part on the aspect ratio of the bagasse fiber. The average diameter and length of bagasse fibers were measured to be 13.0 μm and 61.0 μm, respectively (Tewari et al. 2012). The aspect ratio of these results would be 4.69, which is much less than a typical short glass fiber of approximately 100. Short glass fiber has an average fiber diameter of 12.7 μm and an average fiber length of 1500 μm. Typically, an aspect ratio of 100 is needed to obtain structural properties of a fiber. Wood fibers have an average diameter between 0.016 and 0.030 mm and an average length between 1 and 3 mm resulting in an average aspect ratio between 60 and 100. The bagasse fiber can be considered as a filler that is similar in mechanical properties of talc. Glass fibers can be added to bagasse-based fiber boards to increase strength and stiffness. Fiberboards made with 30% bagasse and 5% glass fibers had higher strength and stiffness as commercially available 100% Bagasse boards (Tewari et al. 2012).

Bagasse food service products can be a replacement for Styrofoam and paper products. PLA and PHA coatings can provide a water barrier for bagasse and paper products. This can provide a compostable fiber product for disposable plates, containers, and food packaging.

4.2.2 PHA-Based Polymers

Polyhydroxyalkanoates can be made from over 100 monomers based on poly(3-hydroxyalkanoates) (P3HB), poly(4-hydroxybutyrate) P4HB, PHB, and PHV. PHA is produced in the cells of bacteria from at least five different PHA biosynthetic pathways (Park and Lee 2005; Madison and Huisman 1999). PHA is harvested from the cells and made into plastic pellets. Poly(3-hydroxyalkanoates) are the most common PHA and are the basis of PHAs produced by Metabolix Company and Tianjin Company. The P3HB can be copolymerized with P4HB to produce a flexible polymer based on PHAs. Polyhydroxyalkanoates have hydroxy-acid repeat units that are produced by bacterial fermentation with sugars or lipids to create linear polyesters.

The PHA biopolymer can be made with increased ductility with changes to the polymer structure (Yu and Stahl 2008). Chemical structures of PHA can affect the physical, mechanical, and processing properties of the plastic resin. In addition, the molecular weight or polymer size of the PHA molecule can influence the mechanical and processing properties. Hence, some PHAs are more suited for injection molding applications and some PHAs are more suited for blow molding and thermoforming applications due to their chemical structure and molecular weight.

PHA plastics can be made into bottles, bags, containers, and other consumable plastic applications. PHA typically has biobased and biodegradable additives that can assist in thermoplastic processing. PHA is biodegradable under industrial composting conditions and is marine biodegradable (Greene 2007; Greene 2009).

4.2.2.1 Chemical Structure of PHA

PHA is a family of several plastics that included P3HB, P4HB, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and others. P3HB and P4HB are the most common form of PHA and the chemical basis of two commercially available PHAs. The structures are listed in Figure 4.2.

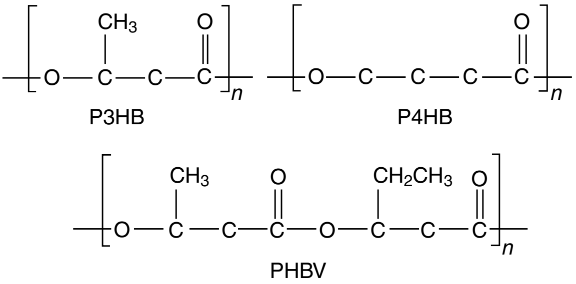


FIGURE 4.2 Structures of poly(3-hydroxybutyrate) (P3HB), poly(4-hydroxybutyrate) (P4HB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV).

P3HB has a short methyl side chain and is a very crystalline and very brittle polymer. P4HB provides a less brittle component for P3HB and is an essential part of the P(3HB-4HB) copolymer that is less brittle and stronger than P3HB. PHBV, a copolymer of hydroxybutyrate and hydroxyvalerate, is also commercially available. PHBV is a random copolymer that has high crystallinity.

Metabolix Company produces injection and thermoforming grades of P(3HB-4HB). Metabolic recently reorganized the product line and developed a rubber grade PHA (Metabolix 2011).

Tianjin Company produces Green Bio P(3HB-4HB) in Tianjin Economic-Technological Development Area, China. Tianjin produces injection molding, film, and rubber grades of P(3HB-4HB) (Tianjin Biodegradable Plastics 2011).

Tianan Company produces Enmat PHBV at Ningbo Tianan Biologic Material Ltd in Ningbo, China. Tianan produces injection molding grade of PHBV (Tianan Biological PHBV 2011).

4.2.2.2 Mechanical Properties

The mechanical properties of P(3HB-4HB) and PHBV are similar to polypropylene. The mechanical properties of commercially available P(3HB-4HB) and PHBV are listed in Table 4.2. As a comparison, the mechanical properties of PP and HDPE are provided in Table 4.3 (Mirel^{TM} P1004 Injection Molding Grade PHA Bioplastic 2013; MatWeb 2013; Tianjin Biodegradable Plastics 2011; Tianan Biological PHBV 2011).

TABLE 4.2
Mechanical Properties of PHA Injection Molding Grade Plastics

Description	Mirel 1004	Tianjin Sogreen P(3,4) HB	Tianan ENMAT Y1000P
Specific gravity	1.3	1.2	1.25
Yield strength (MPa)	24	14–33	31–36
Elongation at break (%)	7	10–775	2.5–4
Flexural modulus (GPa)	1.3	0.5–1.8	3.5–4.2
Heat distortion temperature (°C) (66 psi)	123	85–134	N/A

4.2.2.3 Injection Molding Process

Mirel P(3HB-4HB) plastics can be molded via injection molding, extrusion, thermoforming, and blow molding thermoplastic processes. The injection molding, extrusion, and blow molding processes are explained in more detail in Appendices A, B, and C.

Tianjin P(3HB-4HB) and Tianan PHBV can be molded via injection molding. The temperature profile in the injection molding barrel is different than conventional thermoplastics with the hottest temperature at the first zone and the coolest temperature at the nozzle. PHAs can be exposed to a temperature range between 160°C and 190°C. PHAs viscosity is too large for injection molding at temperatures below 160°C. PHAs can thermally decompose at temperatures above 190°C. PHAs also require a heated mold to enhance crystallinity. The injection molding parameters for P(3HB-4HB) are displayed in Table 4.4. Injection molding process conditions are similar for PHBV.

TABLE 4.3
Mechanical Properties of PP and HDPE Injection Molding Grade Plastics

Description	PP	HDPE
Specific gravity	0.91	0.92–0.98
Tensile yield strength (MPa)	33	21–35
Elongation at break (%)	14	3–2000
Flexural modulus (GPa)	1.34	0.28–1.8
Heat distortion temperature (°C) (66 psi)	101	47–93

TABLE 4.4
Typical Injection Molding Parameters for Mirel P(3HB-4HB) (MatWeb 2013)

Zone	Value
Feed section	175°C
Compression section	170°C
Metering section	170°C
Nozzle	165°C
Injection speed	25 mm/s
Injection time	1.25 seconds
Injection pressure	7200 kPa
Hold time	10.0 seconds
Hold pressure	4000 kPa
Screw speed	55 rpm
Back pressure	500 kPa
Cooling time	10.0 seconds
Mold temperature	60°C

Typically, the injection molded article has low crystallinity upon molding with increased crystallinity within 24 hours. Polyethylene plastic is an excellent purge material for injection molding machines. PHA plastics should be dried for 4 hours at 85°C prior to molding for improved mechanical properties.

4.2.2.4 Extrusion Process

Mirel P(3HB-4HB) can be extruded into sheets with single screw extruders and compounded with additives in a twin screw extruder. Tianan P(3HB-4HB) and Tianan PVHB can be compounded with additives in a twin screw extruder. Currently, Tianan P(3HB-4HB) and Tianan PVHB do not provide an extrusion grade plastic and thus are not typically extruded, blow molded, or thermoformed.

Compounding is necessary to convert P(3HB-4HB) and PHBV powders into plastic pellets for the injection molding process. Virgin P(3HB-4HB) and PHBV materials are typically blended with a nucleating agent (boron nitride) and acrylic impact modifiers in a twin screw extruder. A twin screw extruder from American Leistritz Model ZSE-18HP with 40:1 L/D was used to compound P(3HB-4HB) and PHBV powder with additives (Greene 2013). The temperatures of the eight

TABLE 4.5
Typical Twin Screw Process Parameters for P(3HB-4HB) and PHBV

Zone	Value
Rear	190°C
Middle	180°C
Front	170°C
Nozzle	160°C
Screw speed	60 rpm
Side stuffer speed	30 rpm
Water bath temperature	40°C

zones were between 190°C in the feed zone and 160°C at the nozzle. The screw rpm was 60. The water bath was warmed to 50°C. Table 4.5 lists the process conditions for compounding P(3HB-4HB) and PHBV on a twin screw extruder. The P(3HB-4HB) and PHBV extrudate was cut into pellets at the take-up roll (Greene 2013).

Single screw extrusion of Mirel P(3HB-4HB) is similar to twin screw process conditions. Table 4.6 lists the process conditions for a single screw extruder.

4.2.2.5 Blow Molding Process

Mirel P(3HB-4HB) is available in injection grade and thermoforming grade. The plastic pellets from injection and thermoforming grades were made into bottles using an extrusion blow molding process at molding

TABLE 4.6
Typical Single Screw Process Parameters for Mirel P(3HB-4HB) (MatWeb 2013)

Zone	Value
Rear barrel temperature	175°C
Middle barrel temperature	170°C
Front barrel temperature	165°C
Die temperature	165°C
Melt temperature	165–170°C
Drying temperature	80°C
Drying time	4 hours

FIGURE 4.3 Blow molded bottles of P(3HB-4HB) on a Rocheleau R4 extrusion blow molding machine.

conditions (Greene 2013). P(3HB-4HB) and PHBV polymers were blow molded on a Rocheleau R4 extrusion blow molding machine. Minimizing residence time to less than 5 minutes was a key for producing good quality bottles. Figure 4.3 shows the examples of P(3HB-4HB) bottles.

Typical molding conditions are listed in Table 4.7 (Greene 2013). Optimal conditions are rear temperature of 160°C, front temperature of 150°C, block temperature of 150°C, injection pressure of 7000 kPa,

TABLE 4.7
Optimum Blow Molding Processing Information for Mirel P(3HB-4HB)

Molding parameter	Setting
Injection pressure	7000 kPa
Blow pressure	400 kPa
Rear temperature	160°C
Front temperature	150°C
Shut-off block temperature	150°C
Head temperature	154°C
Mold temperature	50°C

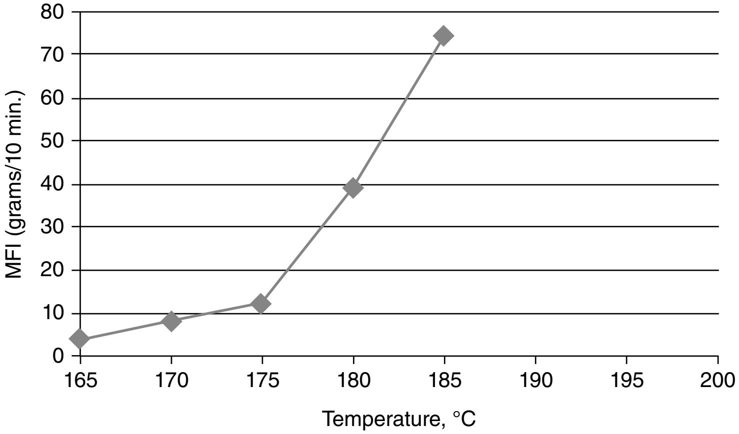


FIGURE 4.4 Melt Flow Index (MFI) for Tianjin P(3HB-4HB).

blow pressure of 400 kPa, mold temperature of 50°C, and mold close time of 60 seconds.

4.2.2.6 Melt Index Testing

Melt index is an indication of the viscosity of the material or the ability of the material to flow at temperature while under load of a 2.060-kg mass. Melt index is similar to zero-shear viscosity in melt rheometry. Melt index is a measure of flow at temperature in 10 minutes (grams of flow in 10 minutes). The melt index can be measured at several temperatures to indicate the thermal stability of the plastic during heated plastic processing conditions. The melt index of the Tianjin injection grade P(3HB-4HB) is listed in Figure 4.4 and the melt index of the Mirel thermoforming grade P(3HB-4HB) is listed in Figure 4.5 using an LMI 4002 series melt flow indexer (Greene 2013). Figure 4.5 clearly shows that Mirel PHA is very thermally stable over a range of temperatures from 170°C to 195°C.

4.2.3 PLA-Based Polymers

Polylactic acid, which is manufactured and supplied by NatureWorks LLC, is a very important biobased polymer. NatureWorks LLC produces a certified biobased and compostable polymer (Schimmel et al. 2004).

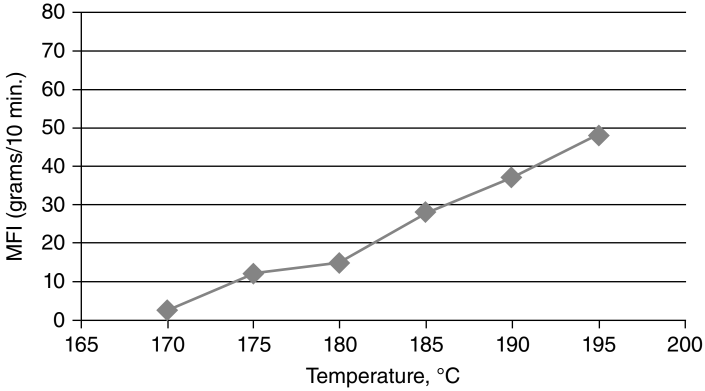
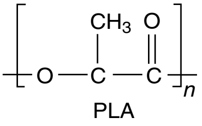


FIGURE 4.5 Melt Flow Index (MFI) for Mirel P(3HB-4HB).

NatureWorks LLC applies its proprietary technology to process natural plant sugars into a family of polylactide biopolymers, which are marketed under the Ingeo^{TM} brand name. Ingeo^{TM} biopolymers are used for rigid packaging, food service ware, films and cards, fibers and nonwoven applications, and durables. NatureWorks LLC has a 150,000 metric tons manufacturing capacity in Blair, Nebraska, and is exploring a building, a second polymer plant, in South East Asia.

4.2.3.1 Chemical Structure of PLA

The chemistry of polylactide $(C_3H_4O_2)_n$ is similar for organic-based polyesters. Polylactide can occur in two forms, L and D. Poly-L-lactide is the most common form of PLA and is biodegradable while exposed to industrial composting conditions. PLA is created in the United States from corn. The corn starch is converted to glucose and then to lactic acid through bacterial fermentation. The lactic acid is fermented to lactide that is polymerized through a ring-opening process. The molecular structure of PLA is shown in Figure 4.6.



$$\left[-O-\overset{\overset{\Large CH_3}{|}}{C}-\overset{\overset{\Large O}{\|}}{C}- \right]_n$$

FIGURE 4.6 Molecular structure of PLA.

4.2.3.2 Manufacturing Methods

Lactic acid is a very important commercial product. Lactic acid is a chemical compound that plays a role in several biochemical processes. Lactic acid is a carboxylic acid with a chemical formula of $C_3H_6O_3$. Lactic acid has a hydroxyl group adjacent to the carboxyl group, making it an alpha hydroxy acid. It is miscible with water or ethanol, and is hygroscopic. Lactic acid is chiral with two optical isomers namely L (+) lactic acid, the most common isomer, and D (−) lactic acid.

Two molecules of lactic acid can be dehydrated to lactide, a cyclic lactone, Then, polymerized to lactide to either heterotactic or syndiotactic polylactide, which is also called PLA. Lactic acid can be produced from chemical or biotechnological methods. Chemical synthesis can be based on the hydrolysis of lactonitrile by strong acids, or by base-catalyzed degradation of sugars, oxidation of propylene glycol, or by chemical reactions of acetaldehyde, carbon monoxide, and water at elevated temperatures (Mussatto et al. 2008).

Most of lactic acid is produced from biochemical processes and polymerized to PLA. PLA is usually produced from lactic acid through fermentation of the sugars in corn starches (NatureWorks LLC PLA 2013). PLA can also be produced from sugars from other carbohydrates sources, including organic waste. L-Lactic acid was produced from spent grain by controlling the pH and other process parameters (Shindo and Tachibana 2004). The research project successfully produced lactic acid from spent grains with immobilized lactic acid bacterium (*Lactobacillus*). The researchers were able to produce 60 grams of sugar (glucose, xylose, and arabinose) from 210 grams of spent grains (79% water), which was converted to lactic acid after 5 days.

Polylactic acid can be produced from a four-step cellulosic-based process:

1. Pretreatment of the carbohydrate to release sugars.
2. Fermentation of sugars to lactic acid.
3. Purification of lactic acid.
4. Polymerization of lactic acid to PLA.

The first step involves treating the carbohydrate in the starch or biomass with an acid mixture. Agricultural products like corn and agricultural waste such as rice hulls can be the primary carbohydrate

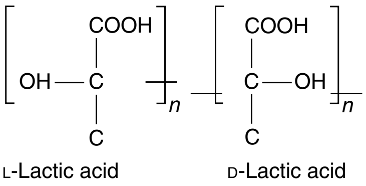


FIGURE 4.7 L-Lactic acid and D-lactic acid molecular structure.

source. The pretreatment can include sulfuric acid. The sulfuric acid breaks the chemical bonds of the starch 3D structure and opens up the structure to release glucose molecules.

The second step in the process ferments the glucose to lactic acid with a bacterium, *Lactobacillus rhamnosus*. The *L. rhamnosus* bacterium consumes the glucose and provides only lactic acid as a product. The lactic acid can be either L or D lactic acid. The molecular structure of lactic acid is shown in Figure 4.7.

The third step in the manufacturing process is to purify the lactic acid from the fermentation broth. Very pure lactide acid with approximately 95% purity is essential for the polymerization to PLA products with high mechanical properties, such as tensile strength, tensile modulus, heat deflection temperature, and rate of biodegradation under industrial composting conditions. Lactic acid can be purified with ion exchange techniques, for example, chromatographic column ion exchange (Hofvendahl and Hahn-Hagerdal 2000).

The fourth step in the manufacturing process is the polymerization of lactic acid to polylactide, or PLA. PLA can be polymerized via direct polycondensation reaction through azeotropic dehydration. High molecular weight polymers are difficult to synthesize due to the equilibrium between the free acids, water, and the polymer. Dean-Stark trap can be used to remove excess water during the reaction. *m*-Xylene can be added to lactic acid that added together in a flask at 138°C for 30 hours. After water is removed, the Dean-Stark trap can be replaced with a molecular sieve to recycle the azeotropic mixture. The resultant mixture can be polymerized to PLA at 138°C (Kim and Woo 2002).

4.2.3.3 Mechanical Properties

The mechanical properties of PLA are similar to PET plastic. PLA is available in many grades including injection molding, extrusion/thermoforming, sheet extrusion, fibers and nonwovens, blow molding,

TABLE 4.8
Mechanical Properties of PLA Injection Molding Grade Plastic

Description	Ingeo 3801X	PET
Specific gravity	1.25	1.41
Tensile modulus (GPa)	2.98	2–2.7
Tensile yield strength (MPa)	25.9	14–33
Elongation at break (%)	8.1	10–775
Flexural modulus (GPa)	2.85	0.5–1.8
Heat distortion temperature (°C) (66 psi)	65	85–134

and foam (PLA Technical Resources 2012). The mechanical properties of injection molding grade Ingeo® and PET are listed in Table 4.8 (NatureWorks™ 2012).

4.2.3.4 Injection Molding Processing Conditions

Polylactic acid plastics should be dried with standard desiccant drying conditions of 4 hours at 45°C for amorphous PLA and of 2 hours at 60°C for crystalline PLA. Typical injection molding parameters for PLA are listed in Table 4.9 (NatureWorks™ 2012).

4.2.3.5 Extrusion Processing Conditions

Polylactic acid can be extruded into sheets with Ingeo™ AW 240D at a thickness between 0.2 mm and 1.3 mm. The pellets should be stored at

TABLE 4.9
Typical Injection Molding Parameters for NatureWorks PLA

Zone	Value
Feed section	177°C
Compression section	188°C
Metering section	188°C
Nozzle	188°C
Injection pressure	7200 kPa
Hold pressure	4000 kPa
Screw speed	125 rpm
Back pressure	1700 kPa
Mold temperature	85–105°C

TABLE 4.10
Typical Resin Properties for Extrusion Grade NatureWorks LLC 2003 D PLA

Mechanical property	Value
Specific gravity	1.24
Tensile strength at yield (MPa)	60
Tensile modulus (GPa)	3.5
Tensile elongation (%)	6
MFI at 190°C and 2.16 kg	6 g/10 min
Flexural modulus (GPa)	1.65
Heat distortion temperature (°C) (66 psi)	55

a cool temperature of 50°C. Typical properties of extrusion grade AW 240 are listed in Table 4.10 (NatureWorks LLC 2013).

A general purpose single screw extruder can extrude PLA into sheet. Typical processing conditions of extrusion grade PLA are listed in Table 4.11 (NatureWorks LLC 2013).

4.2.3.6 Blow Molding Processing Conditions

Polylactic acid can be blow molded into bottles with an injection stretch blow molding process (NatureWorks LLC 2012). The mechanical properties of blow molding grade are listed in Table 4.12 (NatureWorks LLC 2013).

Polylactic acid resin pellets should be dried 4–6 hours to less than 400 ppm prior to blow molding into bottles. Blow molded preforms are injection molded with standard PLA injection molding conditions.

TABLE 4.11
Typical Processing Conditions for Extrusion Grade NatureWorks LLC PLA

Zone	Temperature
Rear (°C)	160–175
Center (°C)	168–185
Front (°C)	168–185
Die (°C)	170–185
Chill roll top (°C)	21
Chill roll middle (°C)	49
Chill roll bottom (°C)	57

TABLE 4.12
Mechanical Properties of PLA Blow Molding Grade Plastic

Description	Ingeo 3801X
Specific gravity (g/cc)	1.24
Crystalline melt temperature (°C)	145–155
Glass transition temperature (°C)	52–58
Crystalline temperature (°C)	100–120
Transmission rates, oxygen, CO_2 water vapor	550 cc-mil/m^2/24-h atm 3000 cc-mil/m^2/24-h atm 325 cc-mil/m^2/24-h atm
Clarity	Transparent

Preform design is critical on producing high quality PLA blow molded bottles. Reheating of the PLA preforms is critical on achieving high quality bottles with good clarity and mechanical properties. The typical preform temperatures are 80–95°C (NatureWorks LLC 2012).

4.2.4 Thermoplastic Starch Polymers

Starch-based polymers can be produced from potato, corn, wheat, cassava, or tapioca. In the United States and Europe, corn starch is the predominate source for starch-based polymers. Corn starch is mostly used for animal feed. Starch-based polymers can be processed on traditional thermoplastic forming operations of injection molding, extrusion, blow molding, compression molding, rotational molding, etc. Starch can be made from corn or vegetable oils and other renewable sources. The most common plasticizers for starch are water and glycerol.

Starch-based plastics can be classified as compostable if the additives are also biodegradable under industrial compost environment conditions. Starch can be an additive for petroleum-based plastics like polyethylene, polypropylene, polyurethane, and polyester. However, these starch-filled petroleum-based plastics are not included in this book since they would not biodegrade under industrial composting conditions and would not be recyclable with commercial mechanical recycling operations.

4.2.4.1 Composition

The composition of Thermoplastic Starch (TSP) is starch, aliphatic polyester, glycerol, and water. Linear aliphatic polyesters that are

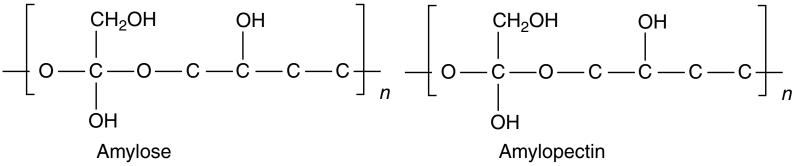


FIGURE 4.8 Molecular structures of amylose and amylopectin.

compostable are added to starch to create compostable plastics for film, sheet, plastic bags, liners, and film. Starch, though, can be blended with aliphatic polyesters, like Polycaprolactone (PCL), polylactide (PLA), PHA, or polyesteramide (Teixeira et al. 2012; Ren et al. 2009).

Polycaprolactone can increase the tensile strength and impact strength but reduce the ultimate elongation, tensile modulus, and shrinkage of the thermoplastic starch (TPS) polymer (Avernous et al. 2000). Montmorillonite clay can improve the properties of TPS and create a biobased nanocomposite (Bordes et al. 2009; Aouada et al. 2011).

4.2.4.2 Chemical Structure of TPS

The chemistry of starch involves blends of two molecular structures of amylose and amylopectin shown in Figure 4.8. Amylose and amylopectin have very similar monomer repeating unit. Amylopectin is a highly branched molecule that dissolves very quickly in enzymes due to the multiple end points. Amylose is a linear molecule with very little branching and very limited end points. High amylose starch can be produced with grades of up to 90% amylose. High amylose starch crystallizes rapidly and can produce a TPS with higher mechanical properties than typical TPS with amylose content of approximately 25% (Lescher et al. 2012).

4.2.4.3 Manufacturing Methods

Thermoplastic starch is manufactured with corn starch. Corn starch can be produced with a six-step process (International Starch Organization 2013). The steps include:

1. *Steeping*: Cleaned corn is placed into steeping tanks where the corn is soaked in hot water for 30–48 hours. The kernel swells to twice its original size with moisture content between 15% and 45%.

2. *Steepwater evaporation*: Steepwater containing approximately 10% solids is drained from the kernels and condensed with a multistep condenser. The steepwater is condensed to a solid product and then used commercially in the fermentation industry.
3. *SO_2 addition*: SO_2 that can be added to the process to produce SO_2 improves fermentation and reduces destructive molds, yeast, and fungi.
4. *Germ separation*: Soften kernels are broken up with attrition mills to loosen the hulls and break bonds between the germ and endosperm.
5. *Germ drying*: Surface water is removed with the use of a tapered screw press and then dried in a rotary steam bundle dryer. The moisture level is reduced to approximately 4%.
6. *Storage in germ silo*: The germ is transported to a germ silo.
7. TPS is produced in a twin screw extruder and then cut into resin pellets.

Typically, glycerol and water are added to potato or corn starch with a gravimetric feeder and then compounded in a single crew extruder. The semi-crystalline starch polymer is heated and pressurized to convert starch polymer into an amorphous phase for processing. Glycerol can influence the onset of gelatinization and increase the activation energy for melting the starch crystals (Mościcki et al. 2012).

High amylose starch can have a more stable extrudate flow, increased melt tenacity (bubble strength), and reduced die clogging by increasing the moisture content, increasing the compression ratio of the screw, and increasing the screw revolutions per minute (rpm) (Thuwall et al. 2006).

Compounded TPS pellets can be blown into a film with 45 parts glycerol per 100 parts dry starch and 13 weight% moisture at a blow up ratio of 2–3 (Thurnwall et al. 2008).

Film blowing was accomplished with a compact extruder characterized by a 19 mm diameter and length of 25D. TPS can also be injection molded at barrel temperatures between 100°C and 180°C.

4.2.4.4 Mechanical Properties

The properties of TPS and polyethylene film are provided in Table 4.13 (Novamont S.p.A. 2013). Mater-Bi® grades of TPS are compostable.

TABLE 4.13
Mechanical Properties of Novamont TPS and LDPE Plastic Films

Description	Mater-Bi® AB05H TPS	LDPE film
Melt flow index (g) (10 min)	3 at 190°C and 2.16 kg	0.1–22 at 190°C and 2.16 kg
Specific gravity	1.28	0.92–0.95
Tensile modulus (MPa)	1103.2	100–200
Tensile strength (break) (MPa)	18.409	8–10
Tensile elongation (break) (%)	160	150–600

Blends of starch and polyethylene films are not compostable, however, due to the polyethylene plastic.

4.3 PETROLEUM-BASED COMPOSTABLE POLYMERS

Synthetic aliphatic polyesters can be created to produce many different types of compostable products for packaging, film, and disposable service-aware applications that biodegrade under industrial composting conditions (Kint and Munoz-Guerra 1999).

The majority of petroleum-based compostable plastics belong to the polyester family, including Ecoflex®, polycaprolactone (PCL), Ecovio®, poly-butyrate adipate terephthalate (PBAT), and aliphatic copolyesters (The Impacts of Degradable Plastic Bags in Australia 2003). Table 4.14 lists several commercially available biodegradable or compostable plastic products.

4.3.1 Ecoflex®

Ecoflex® is an aromatic-aliphatic copolyester that is produced from petroleum-based products, for example, terephthalic acid, adipic acid, and 1,4-butanediol. The compostable plastic is an excellent biodegradable material for blown film and sheet products, for example, grocery bags, lawn and leaf bags, agricultural mulch films.

Ecoflex® can be used to produce blown film applications such as packaging films, agricultural films, hygienic films, and organic waste bags. Ecoflex® has similar film properties to an LDPE. Ecoflex® is classified as compostable, which is biodegradable under industrial

TABLE 4.14
Commercially Available Biodegradable and Compostable Petroleum-based Polymers

Material	Chemical type	Resin supplier	Products	Biodegradation environment	Production capacity (tons)
Ecoflex	Aromatic-aliphatic copolyester PBAT	BASF Inc. http://www.bioplastics.basf.com/ecoflex.html	Film, sheet, bottles, molded products, durable fibers	Industrial compost	74,000
Ecovio	Ecoflex and PLA blend	BASF/NatureWorks^{TM} http://www.basf.com/group/corporate/en/brand/ECOVIO	Trash bags, agricultural films	Industrial compost	Less than 10,000
PCL	Aromatic-aliphatic copolyester	Multibax Public Company Limited http://www.multibax.com/Products.html	Additive for starch, PLA, and other bioplastics	Industrial compost	Less than 10,000

composting conditions in 180 days or less, for Australia, Europe, Japan, and the United States (BPI World 2013).

4.3.1.1 Composition

The composition of ecoflex® is an aliphatic-aromatic copolyester based on the monomers 1,4-butanediol, adipic acid, and terephthalic acid in the polymer chain. The composition of each is proprietary for the company. Ecoflex® can be blended with PLA to produce ecovio® compounds for specific film and molding applications.

4.3.1.2 Chemical Structure of Ecoflex®

The molecular structure of ecoflex® is listed in Figure 4.9.

4.3.1.3 Properties

The properties of ecoflex®, ecovio®, and LDPE plastic film materials are provided in Table 4.15 (Biopolymers Inspired by Nature: Ecoflex® and Ecovio® 2013).

4.3.1.4 Processing Methods

Ecoflex® and ecovio® can be processed on conventional thermoplastic extrusion, injection molding, and blown film equipment (Biopolymers Inspired by Nature: Ecoflex® and Ecovio® 2013). Ecoflex® can be dried at temperatures similar to LDPE, but generally does not require pre-drying. Process equipment can be purged with LDPE. The temperature zones should be between 140°C and 190°C. The grooved feed section of the extruder should be kept cool. The screw speed should be 35% of typical LDPE speeds. Large film thickness should be used during the start-up phase. Ecoflex® has excellent draw-down capabilities. Ecoflex® can be printed with standard printing equipment.

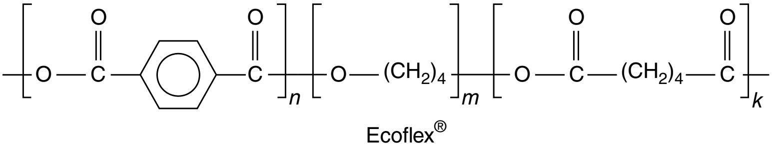


FIGURE 4.9 Molecular structure of ecoflex®.

TABLE 4.15
Mechanical Properties of Ecoflex®, Ecovio®, and LDPE Plastic Films

Description	Ecoflex® F Blend C1200	Ecovio® F2224	LDPE film
Melt flow index (g) (10 minutes)	2.7–4.9	2	0.8–1.2
Specific gravity	1.25–1.27	1.24–1.26	0.92–0.95
Melt temperature (°C)	110–115	140–155	110
Shore D hardness	32	59	48
Tensile strength (break) (MPa)	36–42	27–36	8–10
Tensile modulus (MPa)	80–95	520–750	200–240
Tensile elongation (break) (%)	560–720	250–320	300–600
Impact strength (Dyno test) (J/mm)	24	38	5.5
Transparency (%)	82	58	89

4.3.2 Polycaprolactone

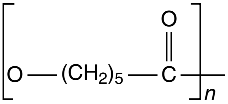
Poly(ε-caprolactone) is an aliphatic polyester produced from petroleum products. PCL is compatible with human tissues and an excellent additive for starch polymers. PCL is used by Novamont with the Mater-Bi biodegradable plastic. PCL can be used for adhesives, compatibilizers, plasticizers, and films for the packaging and for the biomedical industries.

4.3.2.1 Chemistry of PCL

Polycaprolactone is produced from ring-opening polymerization of ε-caprolactone. The molecular structure of PCL is listed in Figure 4.10.

4.3.2.2 Properties

PCL can have several polymerization extent based on the polymerization method. The mechanical properties of PCL are listed in Table 4.16 (LACTEL PCL 2013).



$[O-(CH_2)_5-C(=O)-]_n$

FIGURE 4.10 Molecular structure of polycaprolactone.

TABLE 4.16
Mechanical Properties of PCL

Description	PCL
Specific gravity	1.11
Tensile elongation (%)	300–500
Tensile strength (MPa)	21–35
Tensile modulus (MPa)	207–345

4.3.3 Poly(Butylene Succinate)

Poly(butylene succinate) (PBS) is an aliphatic polyester produced from petroleum products. PBS can be used to produce biodegradable sheets, film, bottles, and molded products. PBS can be blended with PLA, PHA, and TPS (Tan et al. 2010; Xu and Guo 2010).

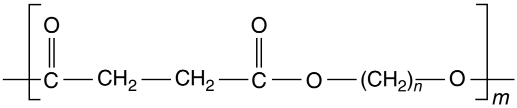
4.3.3.1 Chemical Structure of PBS

Poly(butylene succinate) can be produced from a poly condensation reaction of succinic acid and butanediol in the presence of catalysts (Xu and Guo 2010). Poly(butylene succinate) can also be produced from biomass-based furfural that oxidized to fumaric acid. The fumaric acid can be hydrogenated under high pressure to produce 1,4-butanediol and succinic acid and then ultimately poly(butylene succinate) (Tachibana et al. 2010).

The molecular structure of PBS is listed in Figure 4.11.

4.3.3.2 Properties

The mechanical and physical properties of PBS are similar to PP and LDPE. The mechanical properties of PBS, PP, and LLDPE are listed in Table 4.17 (Xu and Guo 2010).



$$\left[\overset{O}{\overset{\|}{C}} - CH_2 - CH_2 - \overset{O}{\overset{\|}{C}} - O - (CH_2)_n - O \right]_m$$

FIGURE 4.11 Molecular structure of poly(butylene succinate).

TABLE 4.17
Mechanical Properties of PBS and LLDPE

Description	PBS Bionelle	PP	LDPE
Specific gravity	1.260	0.90	0.92
Glass transition temperature (°C)	−32	−5	−120
Melting temperature (°C)	114	163	110
Tensile strength (MPa)	34	33	10
Tensile elongation (break) (%)	560	415	300
Izod impact strength (J/m)	300	20	>400
Crystallinity (%)	35–45	56	49

4.3.3.3 Processing Methods

Poly(butylene succinate) can be molded on conventional thermoplastic processing equipment, including blown film, mono-filament extrusion, blow molding, and injection molding. PBS pellets should be dried to a water content of less than 0.1% to prevent hydrolysis (Xu and Guo 2010).

Poly(butylene succinate) can be injection molded at barrel temperatures between 140°C and 160°C, injection pressure of 90 bar, and mold temperature of 20°C (Qi et al. 2013).

4.4 LIFE CYCLE ASSESSMENT OF COMPOSTABLE AND BIODEGRADABLE POLYMERS

Life cycle assessment can be used to determine the environmental impacts of producing the biobased and petroleum-based compostable polymers. As a comparison, LCA can consider the energy and GHG generation for producing compostable polymers from the raw materials to the plastic pellet. The "cradle-to-factory gate" approach can be useful for comparing biopolymers for plastic packaging, bags, and other products. The "cradle-to-gate" LCA of biobased and petroleum-based biodegradable polymers is listed in Table 4.18.

The environmental effects of producing PHA, TPS, and PLA are provided from three sources mentioned previously. The first LCA source for PHA was created with simulation of producing P(3HB-3Hx) from

TABLE 4.18
LCA of Compostable Polymers per kilogram of Plastic

Polymer type	Energy (GJ)	kg-CO_2eq
PHA from soybeans bacterial fermentation[a]	50	0.26
Polylactic acid[b]	67.8	1.24
TPS/(52.5%PCL)[c]	48.3	3.3

[a] Akiyama et al. (2003).
[b] NatureWorks LLC (2012).
[c] Rudnik (2008).

soybean oil. The production costs and cradle-to-gate LCI were calculated based on data from the USDA and DOW Company with a SuperPro Designer v4.5 software. The assumptions were based on the values of energy in kg-CO_2 per kWh of electricity and kg-CO_2 per kg of steam, cooling water, and process water. The functional unit was 1 kg of PHA. The assumptions in the LCA analysis are cradle-to-gate analysis and end-of-life options are ignored.

The second source of LCI data for PLA polymers was produced for NatureWorks™. The LCI data were calculated based on software developed with Plastics Europe and a series of published EcoProfiles for traditional petroleum-based polymers. All calculations followed ISO 14040 and 14044 requirements (Vink et al. 2010). The functional unit was 1 kg of Ingeo® PLA. The assumptions in the LCA analysis are for cradle-to-gate analysis, where end-of-life options are not included. Boustead 5.0 methodology and software were used to calculate the LCI and LCA of PLA. All LCI and LCA calculations were based on ISO 14040 and 14044 (Boustead Model 5.0 2013). The LCA calculations included the following environmental impacts: greenhouse gas emissions, energy usage, waste generation, and water usage.

The third source of LCI data for starch-based polymers was produced for a Swiss Federal Agency for the Environment (Patel et al. 2003). The assumptions were "cradle-to-gate" LCI and end-of-life options are ignored. The functional unit was 1 kg of plastic.

Table 4.18 lists the environmental impacts of compostable polymers.

Additional LCAs will be calculated for PLA in Chapter 7. Very little LCA information is available for PHA- and TPS-based plastic components, for example, bottles, bags, or packaging.

4.5 SUMMARY

Biobased products are defined as commercial or industrial products that are composed in whole, or in significant part, of biological products, renewable agricultural materials, or forestry materials. Biodegradable polymers are converted to CO_2 and water through a thermochemical process in a specified time frame and in a specified disposal environment. Biodegradable polymers meet ASTM or ISO standards for biodegradation in a biodegradation environment, for example, industrial compost or marine environments.

The three most common biobased biodegradable polymers are PLA, PHA, and TPS. PLA, PHA, and TPS can be made into plastic containers, packaging, bags, and bottles. All three biobased polymers can be processed with traditional plastics processing equipment. Polyhydroxyalkanoates can be made from over 100 monomers based on P3HB, P4HB, PHB, and PHV. PHA is produced in the cells of several types of bacteria. Polylactide, or polylactic acid, is made from starch and bacteria. Thermoplastic starch is a blend of starch and other additives.

The three most common petroleum-based biodegradable polymers are ecoflex®, ecovio®, and PCL. Ecoflex® and ecovio® can be processed into plastic bags. PCL is an additive that can be blended with TPS or PLA to produce plastic bags and containers.

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REVIEW QUESTIONS

Q.4.1 Biobased polymers are the same as biodegradable polymers. T or F?

Q.4.2 PLA is an abbreviation for polylactide polymer. T or F?

Q.4.3 PHA is a biopolymer made in the cells of bacteria. T or F?

Q.4.4 TPS, PHA, and PHA are all examples of pure biobased polymers. T or F?

Q.4.5 TPS, PHA, and PHA require special plastics processing equipment. T or F?

Q.4.6 Biobased polymers are those made from in part from organic sources, for example, corn, sugarcane, biomass, wheat, vegetable oil. T or F?

Q.4.7 Bagasse is a biobased plastic made from sugarcane. T or F?

Q.4.8 Ecoflex is a biobased polymer made from corn. T or F?

Q.4.9 PHA is a biobased polymer made only from a few monomers based on P3HB, P4HB, and PHBV. T or F?

Q.4.10 PLA has two forms of molecular structures, for example, L- and D-type. T or F?

REVIEW PROBLEMS

P.4.1 What is the biggest difference between biobased and biodegradable polymers?

- **a.** None. Biobased polymers are biodegradable and vice versa.
- **b.** Biobased polymers are made entirely of organic ingredients and biodegradable polymers are ones that break down under certain conditions.
- **c.** Biobased polymers are made mostly or entirely of organic ingredients and biodegradable polymers are ones that are converted to CO_2 in a specified time frame and under specified biodegradation conditions.
- **d.** Biobased polymers are made entirely of organic ingredients and biodegradable polymers are ones that break into small enough pieces that are consumed by microorganisms.

P.4.2 Ecoflex biodegradable polymer is made from which ingredients?

- **a.** Entirely from petroleum-based materials.
- **b.** 50% from corn and 50% from petroleum-based materials.
- **c.** Entirely from corn and other organic materials.
- **d.** Partially from corn that is subsequently converted to Ecoflex polymer via bacteria.

P.4.3 What material is the composition of bagasse most similar?

- **a.** Plastic bag material.
- **b.** Paper material.
- **c.** Plastic bottle material.
- **d.** Cotton material.

P.4.4 What is the most common molecular structural form of PLA?

- **a.** D-lactide
- **b.** E-lactide
- **c.** L-lactide
- **d.** M-lactide

P.4.5 The mechanical properties of PLA are most similar to which thermoplastic resin?

- **a.** LDPE
- **b.** PP
- **c.** PS
- **d.** PET

P.4.6 The mechanical properties of PHA are most similar to which thermoplastic resin?

- **a.** LDPE
- **b.** PP
- **c.** HDPE
- **d.** PS

P.4.7 The mechanical properties of PBS are most similar to which thermoplastic resin?

- **a.** PS
- **b.** HDPE
- **c.** PP
- **d.** PVC

P.4.8 The mechanical properties of TPS are most similar to which thermoplastic resin?

- **a.** LDPE
- **b.** PP
- **c.** HDPE
- **d.** SBR

P.4.9 What liquids are added to starch to produce TPS?

- **a.** Glycerol
- **b.** Water
- **c.** Glycerol and water
- **d.** Glycerol, water, and butanol

P.4.10 Ecovio biodegradable plastic is made from what materials?

1. PLA
2. Ecoflex
3. PLA and ecoflex
4. PHA and ecoflex

REVIEW EXERCISES

E.4.1 Acquire plastic bottles made from PLA and PET. Weigh each bottle and fill them with water. Then, drop the bottles at different heights to determine the fracture height for each bottle. Are they similar in properties?

E.4.2 Acquire a TPS plastic bag and an LDPE trash bag from a local health food store. Tie the top end of the bag to a post. Fill each bag with weights until breakage occurs. Are the bags similar in properties?

E.4.3 PHA is compostable, home compostable, and biodegradable in marine waters. If coffee cups at a local coffee shop or restaurant were to use PHA cups, how much of your waste be reduced if you composted the cups at home?

E.4.4 Place leaves, sticks, and/or grass in plastic bags made from polyethylene, starch Biobag, and BioTuf ecoflex . Add one quart of water and place the bags outside on the concrete. Evaluate the amount of water leaking from the bags after 1 hour, 4 hours, 8 hours, 1 day, and 7 days. What can be the causes of the leakage.

E.4.5 Acquire plastic bottles made from PLA and PET. Measure the dimensions and weight of plastic bottles made from PLA and PET. Measure the thickness of each bottle. What material properties would cause the thickness to be different.

CHAPTER 5

Biobased and Recycled Petroleum-Based Plastics

As defined in Chapter 1, sustainable plastics are those plastics made with lower energy, lower carbon footprint, lower waste, and lower pollution than conventional plastics. Plastics that are made from plants and biobased sources or from recycled plastics can be considered sustainable plastics.

5.1 BIOBASED CONVENTIONAL PLASTICS

Several conventional plastics can be produced from organic sources. Biobased polyethylene and biobased PET resins are currently available. Other plastics can be produced with biobased sources Table 5.1 lists the biobased plastics that are commercially available.

5.1.1 Biobased Polyethylene

Biobased polyethylene is currently available from Braskem and DOW Chemical Company. Biobased polyethylene can be made from sugarcane or other agricultural materials.

Sustainable Plastics: Environmental Assessments of Biobased, Biodegradable, and Recycled Plastics, First Edition. Joseph P. Greene.

TABLE 5.1
Biobased Conventional Plastics

Material	Type	Resin supplier	Products
Biobased polyethylene	Polyethylene	Braskem, DOW Chemical	Blown film, sheet, bottles, packaging products, fibers, etc.
Biobased PET	Polyethylene terephthalate	Many	Bottles, packaging products, fibers, etc.
Biobased polypropylene[a]	Polypropylene	Braskem	Blown film, sheet, bottles, packaging products, fibers, etc.

[a] Launch date expected in 2014.

5.1.1.1 Composition

The composition of biobased polyethylene is the same as conventional polyethylene. Typically, polyethylene is produced from natural gas or petroleum products, for example, naptha. Biobased polyethylene is produced from biobased ethanol as depicted in Figure 5.1.

5.1.1.2 Chemistry

Biobased ethylene can be produced from biobased ethanol. The ethanol can be fermented from sugars found in organic sources like corn, sugarcane, potatoes, etc. The two common sources of bioethanol are from corn in the United States or sugarcane in Brazil. Bioethanol is converted to ethene with an aluminum oxide catalyst. The ethene is polymerized to polyethylene. Figure 5.1 lists the molecular formula of ethanol, ethane, and polyethylene.

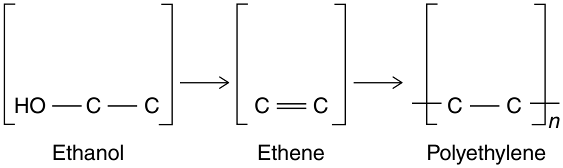

FIGURE 5.1 Molecular structures of ethanol, ethane, and polyethylene.

TABLE 5.2
Mechanical Properties of Bio-based HDPE Injection Molding Grade Plastics

Description	Biobased Braskem SHC7255 HDPE	Petroleum-based DOW 17450N grade HDPE
Specific gravity	0.954	0.950
Melt flow index (grams) (10 minutes)[a]	4.5	17
Tensile modulus (MPa)	1270	593
Tensile strength (yield) (MPa)	27	18.6
Tensile elongation (break) (%)	880	660

[a] Tested at 190°C with 2.16 kg plunger mass.

5.1.1.3 Mechanical Properties

The mechanical properties of polyethylene made from sugarcane or corn are the same as conventional polyethylene. Polyethylene is a very versatile plastic and can be made into many different types of products that are injection molded, extruded into profile or sheet, blown into film or bottles, rotation molded into hollow parts, or compression molded into molded products. Braskem Company produces seven grades of plant-based high density polyethylene (HDPE) and eight grades of plant-based LDPE for use in blow molding, injection molding, extrusion, and thermoforming applications. Table 5.2 lists some mechanical properties of one grade of sugarcane-based HDPE (MatWeb 2014).

5.1.1.4 LCA for Biobased Polyethylene

Life cycle assessment (LCA) can be used to determine the environmental impacts of producing the biobased polyethylene. The LCA will consider the energy and GHG emission for producing biobased polyethylene from the raw materials to the plastic pellet. The “cradle-to-factory gate” approach can be useful for plastic packaging, bags, and other products. The “cradle-to-gate” LCA of biobased polyethylene and petroleum-based polyethylene are listed in Table 5.3 (Hunter et al. 2008).

The LCA results for biobased polyethylene demonstrate the ability of sugarcane to absorb CO_2 during the growing season resulting in a net reduction in greenhouse gases. Additional LCA calculated including end-of-life options are presented in Chapter 7.

TABLE 5.3
LCA of Biobased and Petroleum-based Polyethylene per 1000 kg

Polymer type	Energy (MJ)	GHG (ton) CO_2eq
Biobased polyethylene	10	−2000
Petroleum-based polyethylene	65	1800

5.1.2 Biobased Polypropylene

Polypropylene (PP) can also be produced from sugarcane and other organic plant-based materials. Braskem Company planned to produce polypropylene from sugarcane in 2013 (Braskem Green Products 2013).

5.1.2.1 Composition

The composition of biobased polypropylene is the same as conventional polypropylene. Typically, polypropylene is produced from natural gas or petroleum products. Biobased polypropylene is produced from ethanol.

5.1.2.2 Chemistry

Biobased polypropylene can be produced from biobased ethanol as depicted in Figure 5.2. The ethanol can be fermented from sugars found in organic sources like corn, sugarcane, potatoes, etc. Polypropylene can be produced form several different techniques. One method includes converting sugarcane to polypropylene by fermenting the sugars in sugarcane to ethanol, then to butylene as an intermediate, and finally to polypropylene through a metathesis reaction of butylene and ethylene.

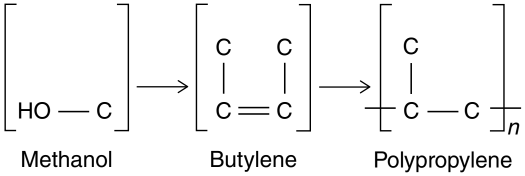

FIGURE 5.2 Molecular structures of ethanol, butylene, and polypropylene.

TABLE 5.4
Mechanical Properties of Petroleum-based Polypropylene Injection Molding Grade Plastics

Description	Polypropylene
Specific gravity	0.954
Melt flow index (grams) (10 minutes)[a]	4.5
Tensile modulus (MPa)	1270
Tensile strength (yield) (MPa)	27
Tensile elongation (break) (%)	880

[a] Tested at 190°C with 2.16 kg plunger mass.

Another method involves gasifying sugarcane to syngas and methanol that is polymerized to polypropylene via "methanol-to-olefins" technology (Liu and Liang 1999).

5.1.2.3 Mechanical Properties

The properties of polypropylene made from sugarcane or corn are the same as conventional polyethylene. Polypropylene is a very versatile plastic and can be made into many different types of products that are injection molded, extruded into profile or sheet, blown into film or bottles, rotation molded into hollow parts, or compression molded into molded products. The properties of polypropylene are listed in Table 5.4 (MatWeb 2014).

5.1.3 Biobased Polyethylene Terephthalate

Polyethylene terephthalate (PET) plastic can also be made from plant sources. PET is typically produced from terephthalic acid and monoethylene glycol (MEG) that are made from petroleum products. MEG can also be fermented from sugarcane, corn, soy, or other organic ingredient. Biobased PET, then, can be produced with approximately 30% from organic sources and 70% from petroleum sources. Coca-Cola, Ford Motor, Heinz, Nike, and Proctor & Gamble combined forces in a consortium to develop a 100% plant-based PET product. The plant-based PET consortium will collaborate on PET research projects with universities, suppliers, and research and development companies. The plant-based PET can be used to produce plastic bottles, plastic packaging, clothing, shoes, automotive carpets, fibers, and other durable goods made currently from traditional PET (Nova 2013).

5.1.3.1 Composition

The composition of biobased PET is the same as conventional PET. Typically, PET is produced from natural gas or petroleum products. Biobased PET is produced from MEG and terephthalic acid. Recently, terephthalic acid can be produced from organic sources through selective oxidation with a special Co/Mn catalyst (Chavan et al. 2001).

Toray Company in Japan and Virent Company in the United States have produced terephthalic acid from para-xylene and MEG, which were made from organic sources. Gevo Company in the United States can produce terephthalic acid and MEG from sugars, starches, and cellulosic materials via para-xylene and isobutanol intermediates (Gevo 2011; Toray 2011; Virent 2011).

5.1.3.2 Chemistry

Biobased PET can be produced from biobased MEG and terephthalic acid. Figure 5.3 lists the molecular structures of MEG, terephthalic acid, and PET.

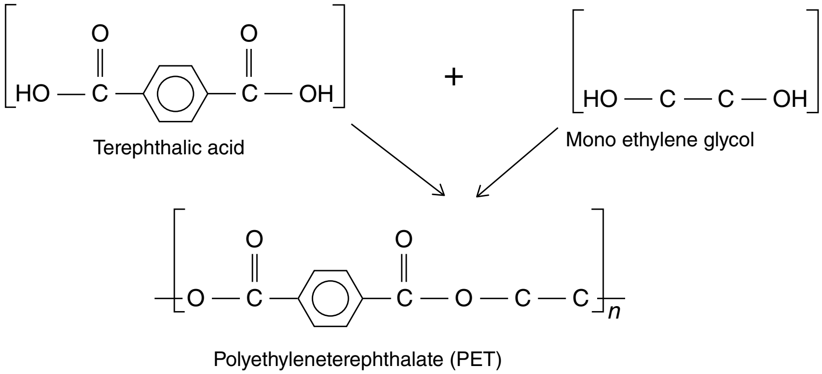

FIGURE 5.3 Molecular structures of terephthalic acid, mono-ethylene glycol, and PET.

TABLE 5.5
Mechanical Properties of Petroleum-based PET Blow Molding Grade Plastics

Description	PET
Melt flow index (grams) (10 minutes)[a]	4.5
Specific gravity	0.954
Tensile modulus (MPa)	1270
Tensile strength (yield) (MPa)	27
Tensile elongation (break) (%)	880

[a] Tested at 190°C with 2.16 kg plunger mass.

5.1.3.3 Mechanical Properties

The properties of PET made from sugarcane or corn should be the same as conventional PET. PET is a very versatile plastic and can be made into many different types of products that are injection molded, extruded into profile or sheet, blown into film or bottles, or compression molded into molded products. The properties of PET are listed in Table 5.5 (MatWeb 2014).

5.1.3.4 LCA of Biobased PET

Life cycle assessment can be used to determine the environmental impacts of producing the biobased PET. The LCA will consider the energy and GHG generation for producing biobased PET from the raw materials to the plastic pellet. The “cradle-to-factory gate” approach can be useful for plastic packaging, bags, and other products. Currently, 30% of the PET can be made from biobased sources. Future research can increase the development of a 100% biobased terephthalic acid and 100% PET. Very few LCA studies have been conducted on biobased PET but it is an active area of research.

5.2 RECYCLED PETROLEUM-BASED PLASTICS

Petroleum-based plastics can also be sustainable if they are made with plastics that produce less GHG emissions, less waste, and less pollution than conventional plastics. Recycled plastics can be produced with lower energy, lower GHG emissions, and lower pollution than conventional plastics since they are converting the recycled plastics into pellets and not polymerizing the plastic from petroleum or natural gas sources (Franklin and Associates 2010).

5.2.1 Mechanical Recycling

Plastics are seemingly ubiquitous in the world today. A key feature of thermoplastics is the ability of the plastic to be heated and formed multiple times. Recycling is one of the advantages of managing thermoplastics at the end-of-life. Thermoplastic types include PET or PETE (Type 1), HDPE (Type 2), PVC (Type 3), LDPE (Type 4), PP (Type 5), PS (Type 6), and other (Type 7).

The majority of recycled plastic is PET (or PETE) or HDPE. PET is used for bottles of soda pop and other beverages. Recycled PET can be remolded for strapping materials and fibers for clothing or carpeting. HDPE is most commonly used for plastic milk jug containers. HDPE can be used as a plastic material in plastic pipe, bottle, and lumber applications.

The gross recycling rate of PET bottles was 29.3% in the United States for 2011 (National Association for PET Container Resources (NAPCOR) 2013). In California, the recycling rate of PET bottles is greater than 60% (CalRecycle PET 2013).

Polyethylene terephthalate and HDPE bottles continue to comprise over 96% of the United States plastic bottle market. In 2011, the total annual post-consumer plastic bottles recycled in the United States increased to an all-time high of 2624 million pounds. The total bottle collection rate was 28.9% for 2011. Plastic bottles with recycling codes #3 to #7 make up only 3.5% of the plastic bottle market. Of these bottles, polypropylene bottles were recycled at a rate of 2.2% and PVC recycled bottles were recycled at a rate of 0.8% in 2011 (Association of Postconsumer Plastic Recyclers and the American Chemistry Council 2011).

Plastics can be recycled with two methods: mechanical recycling or chemical recycling. Chemical recycling will be discussed in Chapter 6. The mechanical recycling is the most common recycling method for plastics and is discussed in the following section.

5.2.1.1 Plastics Mechanical Recycling Process

The manufacturing process of converting recycled plastic into a new plastic product is daunting. Converting recycled plastics to plastic pellets involves sorting, washing, drying, and pelletizing. The most common processing steps include granulation, air classification, washing, separation, rinsing, and drying. The plastics are sorted by either manual or automated identification methods.

Mechanical recycling makes great sense for petroleum-based plastic and biobased plastics. Mechanical recycling has the appropriate recycling infrastructure established in the United States, Europe, Australia, and Asia. The recycling system requires a collection system for plastic products labeled as #1 through 7.

The recycling process has two major steps. The first step is with the materials recycling facility (MRF) that collects the recycled materials and separates them into bales of plastic products by resin type. The second step is with the recycling company who converts the bales of plastic products into plastic pellets.

The first step can be broken down into the following recycling sequences:

- Consumer places plastic item in a recycling container.
- Waste management company collects recycled materials from the recycling container.
- Materials recovery facility collects the recycling container and segregates the plastics by type into collapsed pallets.

The segregation process to segregate the plastic from the debris can be broken down into the following steps:

- Remove large cardboard items from the recycled stream.
- Remove other paper products from the waste stream.
- Separate the glass and ferrous metals from the plastic bottles, bags, and other plastic products.
- Separate aluminum from the plastic stream with an automated “eddy current” process.
- Segregate the plastic stream into plastic type.
  - Separate bottles from other plastics and separated into green bottle (PET), opaque bottle (HDPE), and clear bottle (PET) streams with an automatic method.

  - Compress plastic bottles of each type into a baled form with a metal strap.
  - Compress other plastics that are not bottles into a baled form with a metal strap.

The cycled plastic bales are sent to recyclers for the next step in the process. The recyclers convert the bales of plastic bottles into plastic pellets of HDPE, PET, and PP. The pallets with the mixed plastics of 3–7 are sent to recyclers for additional sorting and then conversion to pellets of plastics from 3 to 7.

The manual sorting method is labor intensive and requires operators to monitor an assembly line and sort out clear plastic bottles (PET) from the milk containers (HDPE) and colored plastic containers (LDPE, PP, PVC). The automated method can employ one of several analytical techniques, including X-ray fluorescence, mass spectroscopy, Fourier Transform Near Infrared (FT-NIR) spectroscopy, Fourier Transform Medium Infrared (FTIR) spectroscopy, or tribo-electric analysis, on the recycled plastic materials. The state of Rhode Island has a single stream process to sort out the recycled materials with optical sorting technology. The recycled materials include cardboard, paper, glass, metal, and plastics (Rhode Island 2013).

The automated sorting method efficiently and quickly sorts the plastic. Researchers reported the speed at which spectroscopic techniques can identify plastics with the use of a computer and tabulated spectra. Hundreds of identifications per second can help sort plastics with more than 99% accuracy (Wienke 1995). Throughput rates can be significantly increased with automated sorting techniques (Dvorak et al. 2000). The sorting efficiency was improved with the development of an automated sensor cleaning system.

The second step in the recycling process transforms the recycled plastic products into plastic pellets. The bales of plastic bottles are converted into pellets with the following process:

- Plastic bottles are washed to remove the ink, labels, and glue from the outside of the bottle.
- The washed bottles are chopped into small pieces and then floated in a soak tank to wash the inside of the bottle plastic and to separate the PP caps from the PET bottles.

- The PET is then dried and then sent to an extruder for pelletizing into PET pellets.
- The PP cap small pieces are dried and then sent to an extruder and transformed into pellets.
- The HDPE small pieces are also dried and then sent to an extruder and converted into pellets.
- The pellets of HDPE, PP, and PET are evaluated for purity, density, and melt index for quality control.

The plastic pellets then can be sold as recycled pellets for plastic manufacturers of bottles, containers, caps, and plastic packaging.

The mechanically recycled plastic experiences several thermal cycles to the melting temperature that can reduce the molecular weight of the polymer and reduce its mechanical properties. Mechanical recycled plastics can have two forms recycled sources post-industrial or post-consumer plastics. Chemical recycling is possible for PET but not currently used in high volumes.

Post-industrial recycled plastics occur in most plastic products, wherein the plastics from the sprues runners, extrudate, etc. are added back into the virgin plastic at the plastic manufacturing plant. Post-consumer resin (PCR) refers to plastics that were made into products, for example, bottles, bags, film, packaging, used by a consumer, collected by a waste disposal company, processed into recycled pellets at an MRF, where the recycled plastic parts are converted into recycled plastic pellets. The plastic pellets are then sold to plastic companies.

5.2.2 California Plastics Recycling

According to the 2008 Waste Characterization Study, the amount of plastics disposed in California's waste stream was 3,807,952 tons, or 9.6% by weight (CalRecycle 2009). The Rigid Plastic Packaging Container Program of California, administered by the CalRecycle, mandates that companies whose products are sold in California must meet several recycling or product specifications that includes, be made of at least 25% PCR, and produce the container with reduced amount of material. If using 25% PCR is technologically infeasible, such containers could be eligible for waivers (CalRecycle Container Recycling 2013).

California's Trash Bag Recycled Content Act, passed in the early 1990s, requires plastic trash bag manufacturers selling trash bags in

California to meet one of the following requirements: either the plastic trash bags contain actual post-consumer material equal to at least 10% by weight of the regulated bags, or the trash bags must contain actual post-consumer material of at least 30% of the weight of material used in all of its plastic products (CalRecycle 2013). Light weighting of plastic bags and containers can also achieve compliance with the laws in California, if the plastic products are made with a thinner gauge.

5.2.3 Society of Plastics Industry Recycling Codes

The plastic materials can be collected and sorted based on the Society of Plastics Industry (SPI) recycling code. The recycling code was created in the late 1980s. The recycling code can help keep the recycled plastics segregated by plastic type. Then, waste management companies can sort the plastics into bins of each recycled plastic.

Typically, recycling collection companies sort the plastics into clear bottles and containers (number 1), opaque bottles (number 2), and colored bottles and plastics (numbers 3 through 7). The recycled plastic bottles and containers are crushed and then placed in pallets and shipped to MRF.

Plastic recyclers sort the plastics by plastic type and then covert the recycled product into plastic pellets. The recyclers can also provide melt index and density measurements of the recycled plastic pellets to assist the plastic converter in using the recycled plastics to produce plastic bottles, bags, packaging, or other plastic products.

ASTM D7611 committee provides a standard practice for coding plastic manufactured articles for resin identification (ASTM D7611 2013). The ASTM committee utilizes a resin identification code system to identify plastic products into resin family categories. ASTM D7611 provides codes for the six most commonly used resin types. The seventh code is reserved for plastic resins that are not in the six other plastic codes. The numeric code identifying the plastic type shall be placed in the middle of an equilateral triangle. The recycling code for plastics is listed in Table 5.6.

5.2.4 LCAs of Recycled Plastics

Recycling of plastics can make them sustainable with lower carbon footprint, lower waste generation, and lower pollution than virgin plastics.

TABLE 5.6
SPI Recycling Codes for Plastics

Code	Plastic	Typical products
1	PET, Polyethylene terephthalate	Plastic beverage containers, food containers,
2	HDPE, High density polyethylene	Plastic grocery bags, beverage containers
3	PVC, Polyvinyl chloride	Plastic containers
4	LDPE, Low density polyethylene	Plastic bags and stretch film
5	PP, Polypropylene	Plastic containers
6	PS, Polystyrene	Plastic containers, beverage containers
7	Other, Can be a mixture of plastics above or polycarbonate	Plastic containers, beverage containers

5.2.4.1 Life Cycle Inventory

The environmental impacts of recycling can be found by accounting or the accumulation of waste, CO_2 emissions pollution during each step in the recycling process.

Steps in mechanical recycling process include the following:

1. Collection by single stream, dual stream, or curbside collection.
2. Sorting and separation by manual, conveyers and separators, separator technology, or computer-aided technology.
3. Reclaiming and pelletizing operations.

The energy usage, GHG emissions, waste generation, and pollution productions are calculated for each of the above steps and combined for an overall life cycle inventory. The recycling operations can involve four types of collection including cut-off weight-based, cut-off volume-based, open-loop weight-based, or open-loop volume-based collection. The open-loop collection methods include virgin plastic collection and will be omitted from this analysis.

Thus, for cut-off collection systems, the following LCA is listed in Table 5.7 (Franklin and Associates 2010).

AS shown in Table 5.7, recycled plastics require less energy and less greenhouse gases than virgin plastics. Recycled plastics, though, require more water and produce more solid waste than virgin plastics.

TABLE 5.7
Life Cycle Assessment (LCA) of Recycled PET and HDPE per 1000 kg

LCA category	Virgin PET	100% recycled PET	Virgin HDPE	100% recycled HDPE
Energy (GJ)	15.3	3.5	17.1	1.8
GHG (kg CO_2eq)	2746	1136	1822	609
Water (L)	27.5	81.2	30.7	91.5
Waste (kg)	142	385	74.6	212

5.2.4.2 Sustainable Recycled Plastic Products

Thus, plastic products can be made with recycled plastics that can have lower energy, lower GHG, and lower waste than traditional plastic products that are made with virgin plastics. The plastic products made with recycled product, though, will have higher water usage due to the large amounts of water used in the washing process of recycled plastics. The recycled PET can be blended with virgin PET plastic to produce plastic containers and products. The recycled HDPE pellets can be blended with virgin HDPE to produce plastic products.

5.3 OXODEGRADABLE ADDITIVES FOR PLASTICS

Oxodegradable additives, typically transition metals, can be added to plastics to cause fragmentation in the plastic. Temperature and relative humidity are the key factors in polymer fracture and reducing the molecular weight in polyethylene plastic (Chiellini et al. 2006). Oxidative degradation of polyethylene samples with proprietary pro-oxidant additives resulted in increased mass, oxygen uptake, and wettability. Two bacterial strains showed increased activity with polyethylene samples that contained antioxidants and pro-oxidants. The microorganisms gained energy from the plastic substrates on the biofilm surface with slow rate over a 3-year testing period (Koutny et al. 2006).

Oxo-additives can cause the plastic to fragment into smaller pieces over a period of time depending on temperature and humidity in the disposal environment. Oxodegradable additives did not cause polyethylene samples to biodegrade under industrial compost environment according to EN 13432 or ASTM testing standards (Greene 2009; Thomas et al. 2010). The length of time for degradation of oxodegradable cannot be predicted accurately due to environmental conditions. Oxodegradable plastics are not suitable for mechanical recycling with PET, HDPE, or other petroleum-based plastics.

A position paper was released by the SPI concerning the biodegradability claims made by producers of degradable additives (SPI 2013). SPI asserts that the degradable additives were not found to result in biodegradation of the plastic, fragmentation is not equivalent with biodegradation, oxo-additives do not reduce litter, and accumulation of plastic fragments can cause risks to the environment. The plastic additive, however, can cause some concern with contamination with the plastic bottle recycling process.

5.4 SUMMARY

Sustainable plastics are those plastics made with lower energy, lower carbon footprint, lower waste, and lower pollution than conventional plastics. Plastics that are made from plants or biobased sources and from recycled plastics can be made with lower energy, lower carbon footprint, lower waste, and lower pollution than conventional plastics. Biobased polyethylene, propylene, and PET can be made from sugarcane or other agricultural materials. Biobased plastics can be made with nearly identical mechanical properties as conventional petroleum-based plastics and can be manufactured on identical plastics processing equipment.

Recycled plastics can be produced with lower energy, lower GHG emissions, and lower pollution than conventional plastics since they are converting the recycled plastics into pellets and not polymerizing the plastic from petroleum or natural gas sources. Mechanical recycling is the most common recycling method for plastics. Converting recycled plastics to plastic pellets involves sorting, washing, drying, and pelletizing.

The recycling process has two major steps. The first step is with the MRF that collects the recycled materials and separates them into bales of plastic products by resin type. The second step is with the recycling company who converts the bales of plastic products into plastic pellets.

Through LCA results, recycled plastics require less energy and less greenhouse gases than virgin plastics. Recycled plastics, though, require more water and produce more solid waste than virgin plastics.

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REVIEW QUESTIONS

Q.5.1 Biobased polyethylene can be produced from sugarcane as petroleum-based polyethylene. T or F?

Q.5.2 Biobased polypropylene will have significantly different mechanical properties as petroleum-based polypropylene. T or F?

Q.5.3 Biobased PET required special injection blow molding equipment to produce bottles than petroleum-based PET. T or F?

Q.5.4 Based on LCA, recycled HDPE plastics requires more energy to be produced than plastics made from petroleum or natural gas. T or F?

Q.5.5 Recycled HDPE plastics process generates more solid waste than plastics made from petroleum or natural gas. T or F?

Q.5.6 The GHG emitted during production of sugarcane-based polyethylene is less than zero. T or F?

Q.5.7 The density of biobased PP is greater than 1.0 like other biobased plastics. T or F?

Q.5.8 Over 90% of the recycled petroleum-based plastics are made from HDPE and PET. T or F?

Q.5.9 Oxodegradable additives for plastics are a sustainable additive. T or F?

Q.5.10 Based on LCA, 100% recycled HDPE emits approximately 66% less GHGs than production of virgin HDPE.

REVIEW PROBLEMS

P.5.1 Biobased polyethylene can be used to produce which of the following products?

a. Biodegradable plastic bottles.

b. Biodegradable plastic bags.

c. Conventional plastic bags and bottles with standard recycling codes

d. Conventional plastic bags and bottles with special codes to prevent mixing with petroleum-based plastics

P.5.2 How does the mechanical properties of biobased polyethylene compare to the mechanical properties of petroleum-based polyethylene?

a. They are very similar in mechanical properties.

b. Biobased polyethylene has lower strength, stiffness, and ultimate elongation percentage than petroleum-based polyethylene.

- **c.** They are quite different.
- **d.** Unknown since very little data have been published.

P.5.3 What could be the reasons for biobased polyethylene to emit a negative amount of GHGs during production of the biobased plastic?

- **a.** Error in calculations since biobased polyethylene should have the same carbon footprint as petroleum-based polyethylene.
- **b.** The sugarcane has lower density than petroleum.
- **c.** The sugarcane is harvested manually and without petroleum-burning engines.
- **d.** Sugarcane stalks are very tall when they grow and absorb CO_2 during the harvest season that offsets the use of fossil fuels during the production of the biobased polyethylene.

P.5.4 Biobased PET is made from materials with how much percentages of biobased and petroleum sources?

- **a.** 100% biobased
- **b.** 50% biobased and 50% petroleum
- **c.** 30% biobased and 70% petroleum
- **d.** 70% biobased and 30% petroleum

P.5.5 For recycled petroleum-based plastics, what is the most common method of separating the metals, wood, and other debris from the plastics?

- **a.** Automated sorting techniques using Infrared (FTIR) techniques
- **b.** Manual sorting methods with laborers
- **c.** Automated sorting techniques using X-ray fluorescence techniques
- **d.** Automated sorting techniques using FT-NIR techniques

P.5.6 In California, how much recycling content is required in plastic container products sold that is technologically feasible?

- **a.** None
- **b.** 10%
- **c.** 25%
- **d.** 30%

P.5.7 In California, what can a company do if the company cannot find any acceptable recycled polyethylene for plastic bags?

- **a.** Apply for a waiver to the law.
- **b.** Do not sell plastic bags in California.

c. Ignore the law and sell plastic bags without recycled content.

d. Develop your own recycling process by recycling in-house polyethylene scrap.

P.5.8 What situations can occur if the recycling code "7" is given to PLA plastic bottles?

a. It would increase the recycling rate of PLA bottles and not cause any disturbance to the PET recycling stream.

b. It would increase the recycling rate of PLA bottles and cause major disturbances to the PET recycling stream since the PLA can be accidently recycled as a PET bottle.

c. It would decrease the recycling rate of PLA bottles and significantly reduce the amount or PLA bottles that are chemically recycled.

d. It would decrease the recycling rate of PLA bottles and significantly reduce the amount or PLA bottles that are composted.

P.5.9 What would be the percentage reduction of GHG emission if 1000 PET clamshell containers had 20% recycled content? *Note*: each clamshell has a mass of 10 grams.

a. 10%

b. 12%.

c. 17%

d. 22%

P.5.10 What would be the percentage reduction of GHG emissions if 1000 HDPE shampoo bottles containers had 50% recycled content? *Note*: each bottle has a mass of 100 grams.

a. 10%

b. 18%

c. 33%

d. 50%

REVIEW EXERCISES

E.5.1 Determine the recycling process in your state and the recycling rates for plastics # 1 through #7. What could be done to increase the recycling rates of plastics?

E.5.2 What type of products is made with the recycled plastics collected at your local MRF?

E.5.3 Calculate an LCA for biobased polyethylene based on data from Braskem or DOW. How does it compare with petroleum-based polyethylene?

E.5.4 Visit the local plastic recycler in your community. Determine the method that is used to sort the recycled materials. Where do the recycled plastics go after they are sorted? What products are made from the recycled plastics?

E.5.5 Collect the plastic containers and bottles in your recycling bin. List the recycling number that is located on the plastic item. List the plastic that was used to make the plastic part. Weigh the part and perform an LCA on the part if the part was made with 100% recycled content.

CHAPTER 6

End-of-Life Options for Plastics

End-of-life options for plastics are important factors that influence the life cycle assessment (LCA) of plastics. Disposal options for plastics are to mechanically recycle the plastic, chemically recycle the plastic, compost the biobased plastic, burn the plastic into energy, or bury the plastic in a landfill.

6.1 US EPA WARM PROGRAM

The Environmental Protection Agency (EPA) provides a Waste Reduction Model (WARM) to calculate the environmental impacts of end-of-life options for products, including plastics. The US EPA WARM calculates GHG emissions for source reduction, recycling, waste-to-energy, and landfill end-of-life options. The US EPA WARM provides information about recycling, sources reduction, waste-to-energy, and landfill processes. WARM calculations are available in web-based calculator and as a Microsoft Excel® spreadsheet. WARM has databases for over 45 material types and GHG emissions are provided in metric tons of CO_2eq or metric tons of carbon equivalent (EPA Waste Reduction Model 2013).

Sustainable Plastics: Environmental Assessments of Biobased, Biodegradable, and Recycled Plastics, First Edition. Joseph P. Greene.

6.2 MECHANICAL RECYCLING OF PLASTICS

Mechanical recycled plastics can have two forms, recycled sources, post-industrial or post-consumer plastics. Post-industrial recycling of plastics can occur with most plastic products, wherein the plastic from the sprues runners and extrudate is added back into the virgin plastic at the plastic manufacturing plant. Post-consumer recycling process occurs when plastics are made into products, for example, bottles, bags, film, packaging, used by a consumer, collected by a waste disposal company, processed into recycled pellets at a materials recovery facility (MRF), and then sold to plastic companies.

6.2.1 US Plastics Recycling

The state of North Carolina developed a framework for the assessment of plastics recycling potential (Barlaz et al. 1993). It includes estimations of the quantity of waste that could be available for recycling, assessment of the state's recycling technology including the manufacturing capacity, and evaluation of potential markets for products manufactured from recycled plastics. The state's recycling manufacturing capacity was found to be adequate for the current recycling technology that does not include commingled plastics. Similarly, plastic bottle reclamation in the United States is a mature process for reclaiming plastic bottles and has a sufficient number of manufacturing companies to recycle plastic bottles.

6.2.2 Plastics Recycling Process

Mechanical recycling has the appropriate recycling infrastructure established in the United States, Europe, Australia, and Asia.

As explained in Chapter 5, the recycling process is as follows:

- Consumer places plastic item in a recycling container.
- Recycling container is collected by a waste management company.
- Materials recovery facility collects the recycling container and segregates the plastics by type into collapsed pallets.
- Recycling company collects the segregated plastic from the MRF and converts the recycled plastic parts into plastic pellets.

The manufacturing process of converting recycled plastic into a new plastic product was explained in Chapter 5 and will not be repeated here.

6.3 CHEMICAL RECYCLING

Chemical recycling is a process by which the polymer chemicals are retrieved from the plastic and then used for primary chemicals to produce new polymers. The chemical conversion process is usually done at high heats with the absence of oxygen. Some typical processes are as follows:

- Pyrolysis
- Glycolysis of PET to bis(2-hydroxyethyl) terephthalate (BHET) monomer
- Methanolysis of PET to dimethyl terephthalate (DMT) monomer
- BASF thermal cracking
- Degradative extrusion
- Steam gasification
- Polymer cracking in fluidized bed
- Battelle high temperature gasification
- Destructive distillation
- Catalytic cracking
- Cracking by hydrogenation
- Texaco gasification

Four chemical recycling methods from the above list are further explained in the following sections. Other resources can be used to describe the other chemical recycling processes.

Pyrolysis is a very common thermochemical decomposition of carbon-based materials at elevated temperatures of 700°C in the absence of oxygen. Pyrolysis of plastic waste can yield gases and oils (Williams and Williams 1997; Pinto et al. 1999). The oils can be polymerized back to polymers.

PET can be chemically recycled with glycolysis of PET to BHET monomer. The supercritical glycolysis reaction occurs at 450°C and 15.3 MPa. The chemical reaction recovers BHET (Imran et al. 2010).

PET can be chemically recycled with methanolysis to recover dimethyl terephthalate and ethylene glycol. The chemical reaction occurs at 200°C and achieved yields of 64% (Kurokawa et al. 2003).

PLA can be chemically recycled in a process called LOOPLA hydrolysis (NatureWorks^{TM} 2013). During hydrolysis, the Ingeo PLA plastic is broken down into lactic acid. The lactic acid can then be polymerized back into Ingeo PLA.

6.4 COMPOSTING

Industrial composting process is a thermophilic chemical process to convert organic materials to carbon dioxide, water, and biomass. Industrial compost occurs at thermophilic temperatures between 50°C and 60°C. The compost environment is hot and moist with a moisture content between 45% and 55%. The industrial compost uses a windrow method to biodegrade organic materials, for example, leaves, grass, sticks, yard waste food waste, and compostable plastics. The US Composting Council provides a wealth of information about composting (U.S. Composting Council 2013).

Industrial compost is a viable end-of-life option for compostable plastics but not traditional plastics. Compostable plastics biodegrade under industrial composting conditions (Greene 2007b; Greene 2008; Greene 2009).

The composting process involves the following steps:

- Collect yard or food waste at an anaerobic compost facility.
- Place the compost with a proper mixture of green and brown organic materials in a row approximately six feet high and six feet wide at the bottom and 100 feet long.
- For in-vessel composting, an 8-mil plastic film is typically placed over the compost row. Alternatively, in-vessel composting can include a concrete enclosure with control over temperature, airflow, moisture accumulate, and others (Greene 2007a).
- The composting row is flipped over or turned several times per week to introduce air and oxygen to the compost via mixing process.

- After 60–90 days, the compost row is sent to a trammel sorter to remove contaminants like plastic, rocks, large sticks, and other debris, and to produce a fine compost dirt.

PLA, PHA, starch, and other compostable plastics biodegraded in an industrial compost and an in-vessel industrial compost (Greene 2007a).

6.4.1 LCA of Composting Process

The use of green yard waste compost on farmland can lead to a positive environmental impact with lower water usage, lower fertilizer usage, lower herbicide usage, and sequestration. Life cycle impact assessments of environmental concerns from production and application of composted products provide a net positive environmental impact. The use of composting process and products provides a reduction in GHG, human toxicity potential, ecotoxicity potential, and eutrophication potential due to lower use of fertilizers, herbicides, water, and electricity (LCA for Windrow Compost 2006).

Industrial composting in Ireland had positive environmental impacts. Use of industrial compost rather than fertilizer can significantly reduce the global warming potential, eutrophication, and acidification. Irish composting operations had 50% less CO_2eq than equivalent fertilized systems. Sequestration occurs from the soil absorbing the carbon (Irish Composting Study 2013).

6.5 WASTE TO ENERGY

Solid waste can be burned to create energy in waste-to-energy facilities. The carbon sources in plastic can be a fuel source for several types of waste-to-energy processes. Four types of waste-to-energy facilities can use the plastic waste as a fuel in the combustion chamber. The types of waste-to-energy municipal solid waste (MSW) combustion include the following:

- Municipal solid waste combustion
- Blast furnace
- Cement kiln

6.5.1 Municipal Solid Waste Combustion

The US EPA provides a website for guidelines for generating electricity from MSW (EPA 2010). The MSW is unloaded at the waste-to-energy facility. Metals, glass, and other recyclables are separated out. The remaining burnable waste is fed into a combustion chamber and burned. The released heat produces steam that turns a steam turbine and generates electricity.

The United States has approximately 87 MSW-fired power generation plants, generating approximately 2500 MW, or about 0.3% of total national power generation. The burning of MSW can create air emissions of 1671 kg of CO_2/MWh, 0.54 kg of SO_2/MWh, and 3.0 kg of nitrogen oxides/MWh. Emission and effluents can be minimized with efficient design (Fodor and Klemes 2012).

The energy potential of various sources of fuel in an MSW is provided in Table 6.1 (DOE 2007).

Plastics have a stored energy for combustion due to their inherent material source is petroleum. One kilogram of plastics can generate twice as much energy as Wyoming coal and almost as much energy as fuel oil (SPI 2013). When combusted in a modern waste-to-energy

TABLE 6.1
Typical Heat Content of Materials in Municipal Solid Waste

Materials	Energy (M BTU/ton)	Energy (GJ/ton)
PET	20.5	23.85
HDPE	38	44.20
PVC	16.5	19.19
LDPE	24.1	28.03
PP	38	44.20
PS	35.6	41.41
Other	20.5	23.85
Rubber	14.4	16.75
Leather	13.8	16.05
Wood	10	11.63
Food	5.2	6.05
Yard trimmings	6	6.98
Newspaper	16	18.61
Cardboard	16.5	19.19
Mixed paper	6.7	7.79

facility, plastics can assist other solid waste burn more completely due to their intrinsic heat value and result in less residual ash in the furnace.

6.5.2 Blast Furnace

The blast furnace is used in the metal-processing industry. Plastics can be a fuel source and a reducing agent to replace coke as a carbon source. The blast furnace is used in the process of producing iron ore and has temperatures exceeding 2000°C. The higher temperatures can generate less emissions and less particulate matter. The use of waste plastics in a blast furnace can reduce the energy and material costs and provide for improved combustion efficiencies (Ziebik and Stanek 2001; Kim et al. 2002). Polystyrene and PET were found to have negative effects on coke reactivity with CO_2 and with coke strength (Melendi et al. 2011). Polyolefins were also found to reduce coking pressure.

6.5.3 Cement Kiln

Cement kilns are used to create cement under temperatures of approximately 1350°C. Recently, cement kilns can also replace petroleum coke with refuse-derived fuel (RDF). Plastic waste can be a component of RDF. The quality of the cement was not affected by the use of blends of RDF and petroleum coke. The emissions from the blends of RDF and petroleum coke were within the industrial limits. Plastic waste that is used as a fuel source can offer environmental and economic advantages for the cement industry (Kara 2012).

6.5.4 Pollution Issues with Waste-to-Energy Process of Plastics

Incineration operations can produce toxic emissions including dioxins, furans, NO_x, SO_x, CO, CO_2, polychlorinated dibenzo-*p*-dioxins and dibenzofurans, and heavy metals. Incineration of plastic waste can produce HCl and other toxic emissions if PVC is burned. The World Health Organization provides best practices for the operators of incineration facilities, including small scale and large scale. The organization recommends removing PVC and vinyl products from the plastic waste stream to avoid generating HCl emissions. Continuous emissions monitoring is required on large incinerators. The emissions standards in the

TABLE 6.2
United States and European Regulatory Limits for Pollutant Emissions at Large Incinerators

Pollutant	Units	US EPA limits	European limits
Cadmium	mg/m^3 (dry normal)	0.04	0.05
Carbon monoxide	ppm	40	100
Dioxins/furan	mg/m^3 (dry normal)	25	0.1
Hydrogen chloride	ppm	15	10
Lead	mg/m^3 (dry normal)	0.07	N/A
Mercury	mg/m^3 (dry normal)	0.55	0.05
Nitrogen oxides	Ppm	250	200
Organics	mg/m^3 (dry normal)	N/A	10
Particulate matter	mg/m^3 (dry normal)	34	10
Sulfur dioxide	ppm	55	50

Note: (1) EPA defines a large incinerator as one that burns more than 227 kg per hour. (2) European council defines large incinerator as one that produces 50 MW or more of thermal output. (3) EU standards not shown for thallium, copper, manganese, nickel, arsenic, antimony, cobalt, vanadium, tin, oxygen.

United States are regulated by the EPA. The emissions limits for the combustion of waste materials in an incinerator are listed in Table 6.2 (World Health Organization 2013).

6.6 LANDFILL OPERATIONS

Plastics can be discarded and sent to local landfills for disposal. In 2010, the United States collected over 250 million tons MSW. In 2010, 34.1% or 85 million tons of solid waste was recycled or composted. Residential waste comprises approximately 64% of the MSW and commercial waste comprises 35% of the waste. Table 6.3 lists the materials collected at a typical landfill in the United States in 2010. Organics are the largest component of the waste stream sent to landfills. Paper and cardboard account for 29%, food and yard trimmings account for 27%, plastics comprise 12%, metals are at 9%, rubber and textiles are at 8%, wood at 6%, glass at 5% miscellaneous at 3% (EPA Municipal 2010).

According to the EPA during 2010, 250 million tons of MSW was collected in the United States. Of that total, 34.1% (85.1 million tons) of the MSW was composted or recycled. Thus, 65.9% (164.9 million tons) of the MSW was sent to landfills or incinerated. The MSW before

TABLE 6.3
Weight Percentage of MSW Before Recycling or Composting

Materials	Weight percentage of total waste
Paper and paperboard	28.5%
Food scraps	13.9%
Yard trimmings	13.4%
Plastics	12.4%
Metals	9%
Rubber, leather, and textiles	8.4%
Wood	6.4%
Glass	4.6%
Miscellaneous	3.4%

recycling or composting is comprised of the following materials by weight percentage (EPA Municipal 2010).

In general, landfills in the United States and Europe utilize a cap and seal strategy, wherein the bed of the landfill is lined with clay and then the top sealed to prevent contamination with ground water and to capture gases in the landfill. Landfill gases can be burned or collected to reduce dangers associated with overpressure. Methane can be captured in a bioreactor landfill for energy utilization.

6.7 LIFE CYCLE ASSESSMENT OF END-OF-LIFE OPTIONS

LCA can be used to determine the environmental effects of various end-of-life scenarios for plastic waste. A review of a number of LCAs found that when single polymer plastic waste fractions with little organic contamination are recycled, and replace virgin plastic at a 1:1 ratio, mechanical recycling has the lower environmental burden than incineration of MSW (Lazarevic et al. 2010).

Landfill, incineration, pyrolysis–gasification, and anaerobic digestion are evaluated for environmental effects atmospheric emissions per unit electricity generation from solid waste using SimaProLCA software (Zaman 2009). Landfill and incineration generated the highest global warming emissions. Incineration and pyrolysis–gasification had the significant impact on respiratory inorganics and acidification categories.

Anaerobic digestion had the lowest impacts on respiratory inorganics and acidification. Anaerobic digestion and pyrolysis–gasification had least overall environmental impact.

LCA for the end-of-life was used for seven plastic components that are commonly used in automotive applications. The parts included the bumper cover made from polypropylene (PP), windshield washer fluid container made from polyethylene (PE), air-intake manifold made from 30% glass-filled nylon, air duct made from 20% talk-filled PP, seat cushion made from polyurethane foam, head lamp lenses made from polycarbonate, and mirror housing made from acrylonitrile butadiene styrene (Jenseit et al. 2003).

The LCA analysis included an eco-efficiency portfolio for each plastic part compared with a cost analysis. Plastics can be recovered as recycled plastics, used for energy source in a furnace, or sent to the landfills. The end-of-life scenarios included landfill, municipal incineration, cement kiln, blast furnace, syngas production, and mechanical recycling.

The LCA study evaluated the eco-environment portfolio and costs of sending the plastic waste to one of the end-of-life scenarios. The environmental burdens included considerations for 10 different environmental indicators including the following:

1. Fuel resources depletion potential
2. Mineral resources depletion potential
3. Cumulative energy requirement
4. Global warming potential
5. Photochemical ozone creation potential
6. Acidification potential
7. Water pollution
8. Final waste
9. Risk and misuse potential
10. Human toxicity potential

The LCA compared the environmental burdens and costs associated with each plastic part. The plastics are removed from the car for the recycling scenario versus being shredded into plastic fluff and sent to the waste-to-energy or landfill scenarios. The costs for dismantling were accounted for in the mechanical recycling option.

Mechanical recycling of the plastics obtained the lowest cost and lowest environmental burden than energy recovery and landfill options. The LCA work determined that in the cases with minimum disassembly time of plastic parts and 1:1 substitution with virgin plastics (PP bumper, HDPE fluid container, and glass-filled nylon air-intake manifold) mechanical recycling of the plastics obtained the lowest cost and lowest environmental burden than energy recovery and landfill options.

Mechanical recycling showed the worst eco-efficiency for parts with high disassembly costs. The parts included air duct, seat cushion, and headlamp lens. Eco-efficiency was also low if part thickness is increased for recycled plastics. The increased thickness of recycled plastic parts can led to increased weight of the plastic parts and ultimately the vehicle.

In all cases of plastic parts, use of landfills was the highest cost and highest environmental burdens. Energy recovery of the plastic through a blast furnace process had the lowest cost and lowest environmental burden of all energy recovery methods that included cement kiln, municipal incineration, and syngas production. This is due to the higher temperatures in a blast furnace compared with other waste-to-energy processes.

6.8 SUMMARY

Disposal methods for plastics have resulted in environmental impacts that can be evaluated with LCAs. The disposal options for plastics are to mechanically recycle the plastic, chemically recycle the plastic, compost the biobased plastic, burn the plastic into energy, or bury the plastic in a landfill. Use of landfill is the most common disposal method for plastics.

Post-consumer recycling process occurs when plastics are made into products, for example, bottles, bags, film, packaging, used by a consumer, collected by a waste disposal company, processed into recycled pellets at an MRF, and then sold to plastic companies. Mechanical recycling is the most common recycling method for plastics.

Chemical recycling is a process by which the polymer starting chemicals are retrieved from the plastic with high temperatures and in the absence of oxygen. The chemical recycling process can produce primary chemicals to produce new polymers. Chemical recycling process can be used for petroleum-based and biobased plastics.

Industrial composting process is a thermophilic chemical process to convert organic materials to carbon dioxide, water, and biomass. The composting process can be used for biobased plastics if they are certified as compostable.

Plastics can be burned to create energy in waste-to-energy facilities. The carbon sources in plastic can be a fuel source for several types of waste-to-energy processes, including municipal waste to energy, blast furnace, and cement kiln.

Plastics can be discarded and sent to local landfills for disposal. The landfill process is the most common end-of-life option for plastics and most solid waste.

Mechanical recycling of plastic parts can provide the least environmental burdens than waste to energy and sending the plastics to landfill. Use of landfill for plastic parts can provide the highest environmental burdens.

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REVIEW QUESTIONS

Q.6.1 Chemical recycling of plastics involves heating the plastics to high temperatures in the presence of oxygen. T or F?

Q.6.2 Composting can be used for PET and LDPE. T or F?

Q.6.3 Waste-to-energy processes can generate toxic emissions including dioxins, furans, NO_x, SO_x, CO, CO_2, polychlorinated dibenzo-*p*-dioxins and dibenzofurans, and heavy metals. T or F?

Q.6.4 Mechanical recycling of plastics can have lower environmental impacts than waste to energy and sending the plastics to landfill. T or F?

Q.6.5 Sending plastic waste to landfills always has the lowest environmental impacts. T or F?

Q.6.6 US EPA WARM provides useful information about end-of-life options for plastics that include recycling, waste-to-energy conversion, and landfill processes. T or F?

Q.6.7 The plastic bottle recycling industry is limited by the number of recycling companies. T or F?

Q.6.8 Pyrolysis is a chemical recycling process that recovers the chemicals from carbon-based materials by heating materials to very high temperatures, for example, 700°C or higher, in the absence of oxygen. T or F?

Q.6.9 The heat content of PET is approximately twice that of wood in municipal solid waste. T or F?

Q.6.10 Industrial composting process is a thermophilic chemical process to convert organic materials into carbon dioxide, water, and biomass at low temperatures. T or F?

REVIEW PROBLEMS

P.6.1 PET can be chemically recycled with methanolysis and result in which of the following chemicals?

- **a.** Ethylene glycol and dibasic acid.
- **b.** Ethylene glycol and dimethyl terephthalate.
- **c.** Dibasic acid and dimethyl terephthalate.
- **d.** Ethylene glycol and BHET monomer.

P.6.2 Industrial composting is a process to convert organic materials into carbon dioxide, water, and biomass. Which of the following conditions are required for composting?

- **a.** Cool temperatures (below 100°F), dry compost (less than 10% moisture), and anaerobic microorganisms.
- **b.** Hot temperatures (above 140°F), dry compost (less than 10% moisture), and anaerobic microorganisms.
- **c.** Hot temperatures (above 140°F), wet compost (approximately 50% moisture), and aerobic microorganisms.
- **d.** Cool temperatures (below 100°F), wet compost (approximately 50% moisture), and aerobic microorganisms.

P.6.3 During a waste-to-energy furnace, which three MSW materials have the highest heat content (GJ/ton)?

- **a.** Wood, food, and yard trimmings.
- **b.** LDPE, HDPE, and PET plastics.
- **c.** Newspaper, cardboard, and wood.
- **d.** PP, HDPE, and PS plastics.

P.6.4 What are the EPA regulatory limits for NO_x and SO_x?

- **a.** 10 ppm and 50 ppm
- **b.** 250 ppm and 55 ppm
- **c.** 200 ppm and 100 ppm
- **d.** 100 ppm and 100 ppm

P.6.5 According to the EPA in 2010, how much of the solid waste in a landfill is recycled and composted?

- **a.** 11%
- **b.** 20%
- **c.** 34%
- **d.** 43%

REVIEW EXERCISES

E.6.1 Determine the end-of-life options for the plastics made into your cell phone. Can they be recycled? What type of plastic is used for the cell phone? What is the recycling rate of that plastic? Where can you take the cell phone at the end of its useful life?

E.6.2 Determine the end-of-life options for grocery bags that you use? What type of plastic is used for the plastic bag? What is the recycling rate of that plastic? Should the plastic bag be sent to a waste-to-energy facility? Why or why not?

E.6.3 What are the environmental effects of using a landfill to dispose of broken TV sets? What should be the best way to dispose of broken TV sets? Should the plastics and metals in the TV be recycled? Why or why not?

E.6.4 Determine the amount of energy that can be recovered from 1 ton of MSW in an incinerator that has the composition listed in Table 6.3 based on the heat content of materials from Table 6.1.

E.6.5 Determine which of the following materials in 1 ton of MSW can be composted in an industrial compost.

CHAPTER 7

Sustainable Plastic Products

7.1 INTRODUCTION

As defined in Chapter 1, sustainable plastic products can be created with lower carbon footprint, lower waste, and lower pollution than conventional plastic products. Plastic products can be used for sustainable plastic packaging, bottles, and bags. Life cycle assessments (LCAs) can be used to compare the different options for plastic packaging, bottles, and bags. Those three plastic products account for approximately 40% of all of the plastic products sold, but approximately 10% of the plastic products in a typical landfill and approximately 30% of the plastic waste in the oceans.

Sustainable plastic products are made from recycled or biobased plastics and are produced with minimum environmental and social impacts. Sustainable plastic products can be defined as being produced with:

- Lower carbon footprint than virgin petroleum-based plastics.
- Lower waste generation than virgin petroleum-based plastics.
- Lower pollution generation than virgin petroleum-based plastics.
- Minimum levels of regulated heavy metals.

Sustainable Plastics: Environmental Assessments of Biobased, Biodegradable, and Recycled Plastics, First Edition. Joseph P. Greene.

- Clean manufacturing principles.
- End-of-life using composting or recycling processes rather than being sent to landfill.
- Fair worker wages.
- Safe worker environment.

Further information on sustainable plastic products is available at the Sustainable Plastic Products (2013) website.

7.2 SUSTAINABLE PLASTIC PACKAGING

Plastic packaging can be produced with sustainable plastics through the use of the definitions presented above. Plastic packaging products account for approximately 30% of the plastics sold in the United States, and approximately 27% of the plastic products sold in Europe (Beswick and Dunn 2002). Sustainable plastic packaging can be made from recycled plastics or biobased plastics, like PHA, PLA, starch, and others. Life cycle assessments can be used to compare environmental impacts of using recycled or biobased plastic materials for plastic packaging products.

7.2.1 LCAs of Sustainable Plastic Packaging

Sustainable plastic packaging can include plastics made from recycled plastics and biobased plastics. Biobased plastics for packaging can be made from PLA, PHA, and thermoplastic starch. Recycled plastics for packaging can be made from PET, PS, PP, HDPE, or PLA. Currently, recycled plastics are predominately PET and HDPE. The following sections include LCA studies of PET, PLA, PP, HPPS, and HDPE.

7.2.1.1 LCA Step 1. Creation of the LCA Goal for Plastic Packaging

The goal of the LCA is to determine the LCAs of plastic packaging with biobased, petroleum-based, and recycled plastics. Sustainable plastic packaging can be compared with virgin PET, PP, and PS for packaging plastic materials.

7.2.1.2 LCA Step 2. Creation of the Life Cycle Inventories for Plastic Packaging

Life cycle inventory (LCI) methodology breaks down the plastics manufacturing of biobased plastics, recycled plastics, and virgin plastics.

The manufacturing process for PLA includes the following:

- Harvesting corn.
- Isolating starch.
- Converting starch to dextrose.
- Fermenting dextrose to lactic acid via bacteria.
- Polymerizing lactic acid to poly lactide pellets.
- Extruding PLA into plastic containers.
- Creating packaging of plastic trays.
- Transporting packaging boxes to retail outlets.
- Consumers using the PLA packaging containers.
- Collecting of compostable plastics for compost, incineration, recycling, or landfill.
- Incinerating, composting, or sending the PLA packaging to a landfill.

The manufacturing process for virgin PET containers includes the following:

- Mining of naptha.
- Producing benzene and ethylene oxide.
- Producing ethylene oxide.
- Producing ethylene glycol and terephthalic acid.
- Polymerizing PET pellets.
- Extruding PET into plastic containers.
- Creating packaging of plastic trays.
- Transporting packaging boxes to retail outlets.
- Consumers using the PET packaging containers.
- Collecting of compostable plastics for incineration or landfill.
- Incinerating or sending the PET packaging to a landfill.

7.2.1.3 LCA Step 3. Creation of the LCAs for Plastic Packaging

The third step in the LCA process is to create a functional group and then recalculate the LCI into functional groupings for environmental impacts. For example, the LCI will calculate the energy consumed during the creation of the plastic packaging products. The LCA step will group the energy information into 10,000 containers as an example. Thus, the LCA will provide the energy consumed during the creation of 10,000 plastic packaging containers. The LCA will also repeat the process for water consumed, CO_2eq emission, waste generation, pollution generated, and other environmental impacts.

7.2.1.4 LCA Step 4. Interpretation of the Three Previous Steps for Plastic Packaging

The fourth step in the LCA process is to interpret the results in the previous three steps. For instance, the first step will be reviewed to make sure the goal was reached in the LCA process. The goal was to compare the LCA results for plastic packaging made from several types of plastic materials. The goal was not changed throughout the process and was accomplished through the creation of LCI and LCA for plastic packaging products. The assumptions used in the LCA step support the goal and purpose of the LCA study. The second step was the creation of the LCI. The LCI was properly created and supported with the assumptions in the LCA step. The LCA assumptions should be reviewed for consistency. For example, the assumptions in the third step must support whether to create a cradle-to-gate or cradle-to-grave analysis. This constraint is part of the goal creation step.

The following sections provide LCA examples with the four-step LCA process.

7.2.2 Literature Review of LCAs for Plastic Packaging

Life cycle assessment can be used to evaluate the environmental impacts of several plastic materials used for clamshells. The LCAs will follow the EPA four-step process. The LCAs will provide a goal, LCI, LCA, and interpretation. The LCAs will be compared for the LCA results and the process to develop the LCAs.

7.2.2.1 Case 1: LCA of Plastic Food Service Products

The first LCA from Franklin and Associates is dated but can provide a starting point in discussing LCAs of plastics for packaging. The Franklin LCA compares the environmental impacts of PS, paper, and PLA packaging materials. Franklin and Associates use SIM Pro LCA software with a database of LCI data. Food service items were produced from polystyrene foam, paper, and PLA. The food service items included cups, plates, and clamshells. Only the clamshell data are analyzed in the following analysis (LCI Food Service Products 2006).

The assumptions are listed in two groups: product category and scope category. The assumptions are listed as follows:

7.2.2.1.1 Assumptions

Product category

- Ten thousand clamshell containers with equal carrying capacity.
- Ten thousand containers per year.
- General purpose polystyrene (GPPS) data came from Franklin and Associates' database.
- Mass of the GPPS container was 4.8 grams and PLA was 23.3 grams.
- NatureWorks LLC PLA Ingeo^{TM} LCI data were provided by a PLA report reference from 2006.
- PLA sample mass was measured from actual PLA containers.
- Sandwich-size clamshell containers made from GPPS and PLA.

Scope category

- Composting of PLA is not considered.
- Cradle-to-grave analysis was used. End-of-life options include landfilling and waste to energy.
- Eutrophication, acidification, and other pollution impacts are not considered.
- Recycling of PLA and EPPS products are not considered.
- Transportation was included for movement of containers to retail stores and for collection of post-consumer products.

TABLE 7.1
Environmental Impacts of PLA, EPS for 10,000 Clamshells

Environmental impact	Foam PS	PLA
Units	10,000	10,000
Mass (grams)	4.8	23.3
Specific gravity	0.8	1.25
Energy consumed (MJ)	3034.662	13125.7
Carbon footprint (tons CO_2eq)	0.024853	0.118367
Solid waste generated (kg)	40.41723	187.161
Water consumed (liters)	423.9648	8611.785

- Eighty percent of the PLA and GPPS clamshells are sent to landfill at end-of-life and 20% are sent to waste-to-energy incineration.

The LCA considers environmental impacts of the process, fuel, end-of-life, energy material resource, and end-of-life waste-to-energy credit. For appropriate comparisons with other LCA studies, we will consider only the environmental effects of the process of each material. The environmental categories considered are as follows:

- Greenhouse gas (GHG) emissions
- Energy usage
- Waste generation
- Water usage

7.2.2.1.2 LCA Results for Case 1 Table 7.1 lists the environmental impacts of PLA and foam PS clamshells. For 10,000 clamshells, foam PS had lower mass, energy consumption, carbon footprint, waste generation, and water consumption. The pollution aspects were not considered and no data were provided for eutrophication, acidification, smog generation, or release of toxic chemicals.

7.2.2.1.3 Sensitivity Analysis The LCA did not use an equal carrying capacity of foam PS and PLA. The analysis assumed a specific gravity of foam PS was 0.8, and the specific gravity of PLA was 1.2. Thus, with a mass of 4.8 grams for the foam PS and 23.3 grams for the PLA, the volume of the foam container was 6 cm^3 and the volume of the PLA container was 19.3 cm^3. The LCA also did not include waste generation, pollution with acidification, eutrophication, or toxic generation. Additionally, transportation was not considered.

7.2.2.2 Case 2: LCA of Plastic Packaging Products

The second LCA of packaging materials was provided by IFEU from Germany and was commissioned by LCA NatureWorks LLC (2006). The LCA is dated but can show the improvement in reduced environmental impacts of PLA in the third LCA study (LCA Packaging NatureWorks LLC 2006).

The assumptions are listed in two groups: product category and scope category. The assumptions are listed as follows:

7.2.2.2.1 Assumptions

Product category

- Thousand clamshell containers with equal carrying capacity of 500 mL.
- Thousand containers per year.
- Sandwich-size clamshell containers made from oriented polystyrene (OPS), PP, PET, and PLA.
- The masses of the clamshells were 15.2 grams (OPS), 16.9 grams (PP), 19.9 grams (PET), and 12.2 grams (PLA).
- The specific gravities of the plastic materials are 1.06 (OPS), 0.9 (PP), 1.25 (PET), and 1.22 (PLA).
- Solid waste values were calculated based on LCA per kilogram information from Franklin and Associates (2011) and Madival et al. (2009), and then extrapolated for the mass of 1000 containers.
- Water consumed values were calculated based on LCA per kilogram information from Franklin and Associates (2011) and Madival et al. (2009), and then extrapolated for the mass of 1000 containers.

Scope category

- Composting of PLA is not considered.
- Cradle-to-grave analysis was used.

- End-of-life options include mechanical recycling of 80% for PP, PET, OPS and 20% energy recovery.
- End-of life for PLA is 80% composted and 20% chemical recycling.
- Eutrophication, acidification, and other pollution impacts are considered.
- Transportation of plastics is considered.
- Eighty percent of the PLA and GPPS clamshells are sent to landfill at end-of-life and 20% are sent to waste-to-energy incineration.

The LCA considers fossil fuel consumption, global warming potential, summer smog potential, acidification, eutrophication, carcinogenic risk, and human toxicity. The LCA did not consider waste generation or water consumption. To provide a more complete LCA, the waste generation and water consumption were calculated for each plastic based on reference sources.

The waste generation was calculated based on the mass of each material. If most of the waste is generated from the creation of the plastic clamshell, then the waste from transportation, use, and end-of-life conditions can be ignored.

7.2.2.2.2 LCA Results for Case 2 Table 7.2 provides the environmental impacts of clamshells made from plastic materials. The PLA clamshells had the lower mass, energy consumed, carbon footprint, and

TABLE 7.2
Environmental Impacts of PLA, PET, PP, OPS for Clamshells

Environmental impact	PLA	PET	PP	OPS
Units	1000	1000	1000	1000
Mass (grams)	12.2	19.9	16.9	15.2
Specific gravity	1.22	1.25	0.9	1.06
Energy consumed (MJ)	1100	1700	1500	1500
Carbon footprint (tons CO_2eq)	0.03	0.08	0.045	0.065
Solid waste generated[a] (kg)	0.83	2.72	1.44	1.67
Water consumed[a] (liters)	4.10	2.33	3.25	11.84
Eutrophication, water (g PO_4eq)	4	0.8	5.5	0.5
Eutrophication, terrestrial (g PO_4eq)	23	22	9	13
Acidification (kg SO_2eq)	0.25	0.33	0.13	0.19

[a] These values were calculated based on creation of pellets from raw materials.

waste generation than clamshells made from PET, PP, and OPS. PLA clamshells consumed more water than clamshells made with PET and PP but less water than clamshells made with OPS. PET clamshells produced the least amount of chemicals that create eutrophication in the water. PP clamshells produced the least amount of chemicals that create eutrophication in the land and the least amount of chemicals that produced acidification in the water.

7.2.2.2.3 Sensitivity Analysis The analysis included chemical pollution and production of chemicals that can lead to eutrophication, acidification, summer smog, and human toxicity. The mass of the PLA was lighter than the other plastics even though it had a higher density than PP and OPS. The LCA claims that PLA can be produced with thinner walls due to the high modulus of elasticity for PLA.

7.2.2.3 Case 3: LCA of Plastic Clamshell Products

A third LCA that calculated the environmental profiles of clamshells was created for PLA, PET, and PS plastic materials. The LCA was calculated for use as containers for strawberries. The functional unit was 1000 containers that have packaging capacity to hold 0.4536 kg of strawberries. The LCA included transportation effects and provided environmental impact results for global warming, energy consumption, aquatic acidification, ozone layer depletion, aquatic eutrophication, respiratory organics, respiratory inorganics, land occupations, and aquatic eco-toxicity. SimaPro^{TM} LCA software was used to calculate the environmental impacts of the plastic materials. The mass of the PET was calculated based on the same volume as the PLA clamshell and the density ratio of PET and PLA (Madival et al. 2009).

7.2.2.3.1 Assumptions The assumptions are listed in two groups: product category and scope category. The assumptions are listed as follows:

Product category

- Thousand clamshell containers with equal carrying capacity of 0.4536 kg of strawberries.
- Sandwich-size clamshell containers made from GPPS, PET, and PLA.
- The masses of the clamshells were 24.2 grams (GPPS), 32.55 grams (PET), and 29.6 grams (PLA).

- The dimensions of the clamshell containers, $19 \times 16.5 \times 7\ \text{cm}^3$, were the same for all three plastics.
- The specific gravities of the plastic materials are 1.052 (GPPS), 1.37 (PET), and 1.25 (PLA).

Scope category

- Composting of PLA is not considered.
- Consumer usage and environmental impacts are not considered.
- Cradle-to-grave analysis was used.
- End-of-life options include mechanical recycling, landfill, incineration, combinations of the three options.
- End-of-life scenario in the LCA includes: 23.5% of the clamshells were sent to incineration and 76.5% of the clamshells were sent to landfill operations.
- Eutrophication, acidification, and other pollution impacts are considered.
- Pollution is considered if they exceed governmental regulations in Greene Sustainability Index (GSI).
- Solid waste values were calculated based on LCA per kilogram information from Franklin and Associates (2011) and Madival et al. (2009), and then extrapolated for the mass of 1000 containers.
- Transportation of plastics is considered during the life cycle of the plastic clamshells.
- Water consumed values were calculated based on LCA per kilogram information from Franklin and Associates (2011) and Madival et al (2009) and then extrapolated for the mass of 1000 containers.

7.2.2.3.2 LCA Results for Case 3 Table 7.3 provides the environmental impacts of clamshells made from plastic materials when incineration and landfill end-of-life options are considered. The PLA clamshells had the lower energy consumed and waste generation than clamshells made from PET and GPPS. PLA clamshells consumed more water than clamshells made with PET but less water than clamshells made with GPPS. Clamshells made from GPPS produced the clamshells

TABLE 7.3
LCA of 1000 Clamshells with Transportation Including End-of-Life Scenarios

Environmental impact	PLA	PET	GPPS
Units	1000	1000	1000
Mass (grams)	29.6	32.55	24.2
Specific gravity	1.246	1.37	1.052
Energy consumed (MJ)	2993	4560	4090
Carbon footprint (tons CO_2eq)	0.171	0.198	0.165
[a]Solid waste generated (kg)	2.02	4.59	2.66
[b]Water consumed (liters)	0.12	0.08	0.29
Eutrophication, water (g PO_4eq)	0.01603	0.0753	0.0094
Eutrophication, terrestrial (g PO_4eq)	23	22	13
Acidification (kg SO_2eq)	.25	.33	.19
Summer smog (POCP)	12	68	8

[a] Solid waste values were calculated based on LCA per kilogram information from Franklin and Associates (2011) and Madival et al. (2009).
[b] Water consumed values were calculated based on LCA per kilogram information from Franklin and Associates (2011) and Madival et al. (2009).

with the lowest carbon footprint and with the least amount of chemicals that create eutrophication in the oceans and land.

7.2.2.3.3 Sensitivity Analysis The LCA is more complete with inclusion of end-of-life, waste generation, pollution, transportation. The LCA assumes equal stiffness of the clamshell containers and equivalent dimensions for each material. GPPS and PLA clamshells may have increased thickness and hence increased mass for the containers.

7.2.3 LCA of Sustainable Plastic Containers Made from Biobased and Petroleum-Based Plastics

Environmental impacts of sustainable plastic containers can be determined with the LCA information and the definitions of sustainable plastics. The sustainable plastic containers can be made of recycled plastic or biobased plastics. The end-of-life for the plastic is either recycled or composted. Thus, polystyrene is not considered because sufficient recycled plastic is not available. As a comparison, virgin PET is evaluated for LCA. Recycled PET and biobased PLA can be compared for clear sustainable plastic containers. The LCA information from Madival et al. 2009 is used as a starting point. Then, WARM model from EPA is used to estimate the environmental effects of composting the PLA and recycling the PET at their end-of-life.

Sustainable packaging and containers includes plastics made from biobased or recycled materials for clear packaging plastics. Currently, PS was not considered as the recycling rate is low which may be problematic for collecting of sufficient quantities of recycled PS.

The following assumptions are used with the sustainable container LCA:

Product category

- Thousand clamshell containers of equal carrying capacity are used per year.
- The masses of the clamshells were 32.55 grams (PET), and 29.6 grams (PLA).
- The specific gravity of the plastic materials is 1.37 (PET), and 1.25 (PLA).
- Cradle-to-grave analysis was used.
- End-of-life options include 40% mechanical recycling of PET and 5% composting of PLA.
- EPA WARM model was used for composting of 100 tons of PLA resulting in 20 tons of CO_2eq savings.

Scope category

- Eutrophication, acidification, and ozone layer depletion, and aquatic toxicity are equivalent for recycled PET and virgin PET.
- Transportation of plastics is considered for raw materials and containers to retail outlets.
- Consumer usage and environmental impacts are not considered.
- Pollution is considered if they exceed governmental regulations in GSI.
- No heavy metals are present in the plastic or in the inks or color concentrates.
- Five percent of the PLA clamshells are composted as an end-of-life scenario.
- Forty percent of the PET is recycled as an end-of-life scenario.

- The manufacturing process utilizes Operation Clean Sweep Practices to minimize pellet loss at plastic manufacturing operations.
- Solid waste and water consumption values were calculated based on LCA per kilogram information from Franklin and Associates (2011) and Madival et al. (2009), and then extrapolated for the mass of 1000 containers.

The goal of the sustainable packaging LCA is to develop an LCA for recycled and biobased plastics from published data. The first step in the LCA is to incorporate data from a recent LCA that considered end-of-life options (Madival et al. 2009). The research provides data for PLA and PET with 100% landfill as an end-of-life scenario. The second step is to modify the data in the LCA report to include 5% composting of PLA and 40% recycling of PET. The EPA WARM model can be used to provide carbon credits for composting of PLA of 20 tons of CO_2eq savings per 100 tons of PLA. The recycling of PET can provide reduced carbon footprint and energy usage, but results in increased waste generation and water consumption (Franklin and Associates 2010).

Table 7.4 lists the LCA for 1000 plastic containers. The data show that PLA plastic containers had lower global warming potential and

TABLE 7.4
Cradle-to-Grave LCA of 1000 Sustainable Plastic Containers

Environmental impact	PLA with 5% composting	rPET with 40% recycled content	Virgin PET
Container units	1000	1000	1000
Mass (grams)	29.60	32.5	32.5
Specific gravity	1.25	1.37	1.37
Energy consumed (MJ)	4000	3107	4500
Global warming potential (tons CO_2eq)	0.1047	0.1531	0.198
Solid waste generated (kg)	2.02	6.54	4.59
Eutrophication, water (g PO_4eq)	0.01603	0.0753	0.0753
Acidification (kg SO_2eq)	1.82	1.34	1.34
Ozone depletion (kg CFC-11)	0.0000145	0.0000179	0.0000179
Freshwater eco-toxicity (kg, TEG)	33,000	41,600	41,600

lower waste generation than virgin and recycled PET containers. Recycled PET containers had lower energy consumption than PLA or virgin PET containers. PET containers produced fewer chemicals that can cause eutrophication, acidification, and ozone depletion.

7.2.4 Greene Sustainability Index (GSI) of Sustainable Plastic Containers

The environmental impacts of the plastic materials can be calculated based on the data in Table 7.4. Environmental comparisons can be made based on the ratio of the environmental impact of the plastic material and a reference material as listed in Table 7.4. For our purposes, we will use PLA as the reference material. Thus, we will be able to compare the ways in which different plastic materials have more or less environmental impacts of global warming potential, solid waste generation, and pollution than the reference material.

The GSI can provide an overall sustainability measurement of the three sustainable plastics based on an arithmetic summing of weighted individual environmental factors (Basurko and Mesbahi 2014). An integrated quantitative approach was found to provide a holistic assessment of sustainability technologies. The methodology measured environmental, economic, and social assessments separately and then provided a single measurement of sustainability by summing the weighted assessments.

Similarly, the GSI for each of the materials can be found from the ratios of environmental impacts of the plastic material with a reference material. PLA can provide the reference material. The different environmental impact factors can be weighted with the following: 50% for GWP, 25% for waste generation, and 25% for pollution factor. The pollution factor is an arithmetic average of eutrophication, acidification, ozone depletion, and freshwater eco-toxicity. Table 7.5 provides a summary of the ratios of environmental impacts of rPET and virgin PET containers versus the reference containers made from PLA.

Table 7.5 shows that containers made from PLA had lower global warming potential and lowest waste generation than containers made from recycled PET and virgin PET. Containers made from recycled PET produced less GHGs but generated more solid waste than virgin PET containers. The GSI results are provided for 50:25:25 index of global warming ratio, solid waste generation ratio, and pollution ratio and for 60:20:20 index.

TABLE 7.5
Greene Sustainability Index for Sustainable Containers Using Cradle-to-Grave Life Cycle Assessment

Environmental impact	PLA with 5% composting	rPET with 40% recycled content	Virgin PET
Global warming potential ratio	1.000	1.115	1.456
Solid waste generation ratio	1.000	3.231	2.267
Eutrophication, water ratio	1.000	4.697	4.697
Acidification ratio	1.000	0.736	0.736
Ozone depletion ratio	1.000	1.234	1.234
Freshwater eco-toxicity ratio	1.000	1.261	1.261
Greene Sustainability Index—50:25:25	1.000	1.860	1.790
Greene Sustainability Index—60:20:20	1.000	1.711	1.723

The GSI results reveal that for the 50:25:25 split, recycled PET containers had 86% higher overall environmental impacts than PLA clamshells. Similarly, virgin PET containers had 79% higher overall environmental impacts than PLA clamshells. The GSI results reveal that for the 60:20:20 split recycled PET containers had 71% higher overall environmental impacts than PLA clamshells. Similarly, virgin PET containers had 72% higher overall environmental impacts than PLA clamshells.

Containers made from recycled PET produce less GHG emission, less waste, and less pollution than containers made from virgin PET. Containers made from recycled PET produce equivalent chemicals that result in eutrophication, acidification, ozone depletion, and freshwater eco-toxicity than containers made from virgin PET. Polystyrene was not considered because of the lack of recycled PS materials available for production of clamshells.

7.3 SUSTAINABLE PLASTIC GROCERY BAGS

Sustainable grocery bags can be made with biobased or recycled plastics, produced without regulated heavy metals or toxins, made with clean manufacturing principles, and produced fair employment and safety practices. LCA can be used to provide a sustainable plastic grocery bag. The LCA process can include key elements of LCA that features consistent functional units, energy, GHGs, waste, and pollution that include eutrophication, acidification, toxic chemical release, and end-of-life.

7.3.1 Literature Review of LCA of Plastic Bags

Environmental aspects of various bags have been analyzed by several researchers. Three LCA studies are summarized in the following. The three studies conducted the LCA per ISO standards.

The first LCA study, from Boustead Consulting and Associates, compares the LCA of single-use plastic bags with single-use paper. The "cradle-to-gate" analysis includes the environmental impacts of plastic bags from the creation of the plastic from raw materials to plastic pellets.

The second LCA study, from the paper industry in Hong Kong, compares the environmental effects of single-use paper and plastic bags. The "cradle-to-grave" analysis includes the environmental impacts of plastic and paper bags over the life cycle of the product.

The third LCA study, from Hyder Consulting Pty Ltd of Victoria, Australia, is a "cradle-to-grave" analysis that includes EOL and transportation impacts. It compares the LCA of single-use plastic and paper bags with reusable plastic and cotton bags.

The fourth LCA study, from Scottish Executive of Edinburgh, Scotland, compares the effects of a bag tax on consumers and the LCA of single-use plastic, paper, and compostable bags versus reusable rPET bags.

7.3.1.1 LCA of Plastic Bags from Boustead Consulting

The Boustead report is comprehensive in its evaluation of the LCAs of paper and plastic bags. The Boustead report was funded by the American Chemical Council Plastics Division. The Boustead report compares LCAs of 1500 plastic bags with 1000 paper bags and 1000 compostable plastic bags. The 1.5:1 ratio was determined from a Franklin report from 1990, which pointed out that consumer bagging behavior illustrates that plastic-to-paper use ranged from 1:1 all the way to 3:1, depending on the situation (Council for Solid Waste Solutions 1990). The information for the LCI was taken from Boustead database and plastic suppliers (Chaffe and Yaros 2007).

The assumptions in the Boustead LCA study are as follows:

Product category

- **a.** One-and-a-half plastic bags had equal carrying capacity as one paper bag.
- **b.** Ten bags were used per week for 52 weeks.
- **c.** Plastic bags were made from HDPE.
- **d.** The mass of the plastic bag is 6 grams and the paper bag is 52 grams.
- **e.** Paper bag has 30% recycled content.

Scope category

- **a.** Cradle-to-gate analysis was used, ignoring end-of-life impacts.
- **b.** Eutrophication, acidification, and other pollution impacts are not considered.

Plastic bags require less energy, fossil fuel, and water than an equivalent number of paper bags. Also, this LCA reports that plastic bags generate less solid waste, acid rain, and GHGs than paper bags. Paper bags weigh significantly more than the traditional thin plastic bag and use an energy and water-intensive manufacturing process to produce paper bags. The results are listed in Table 7.6.

TABLE 7.6
Life Cycle Assessments of 1500 Plastic Bags and 1000 Paper Bags

	1500 plastic bag industry average	1000 paper bag (30% recycled)	Paper/plastic bag ratio
Total energy (MJ)	763	2622	3.44
Fossil fuel used (kg)	15	23	1.53
Municipal solid waste (kg)	7	34	4.86
Greenhouse emission (tons CO_2)	0.04	0.08	2.00
Freshwater usage (gal)	58	1004	17.31
Mass (g, per paper)	6	52	8.67

7.3.1.2 Sensitivity Analysis

The Boustead report provides an acceptable LCA analysis but failed to consider recycled content for plastics and the effects of using reusable bags instead of single-use bags. The report uses 30% recycled paper content which might be low. Other paper products have higher recycled content. The Boustead report claims equal carry capacity of 1.5 plastic bags for each paper bag. The ratio might not reflect actual usage of plastic bags that might reflect two or three plastic bags for every paper bag.

7.3.2 LCA of Plastic Bags from the Paper Industry in Hong Kong

A second LCA report on plastic bags is provided by the paper industry from Hong Kong that investigated the environmental effects of paper and plastic bags. The results are based on commercial LCA software called SIMAPRO 7.1. The report used data from Franklin and Associates. The results show that paper bags had higher energy usage, higher carbon footprint, and higher material consumption than plastic bags. The study also investigated pollution generation from paper and plastic shopping bags with eco-indicator 91. The software considers creation of carcinogens, respiratory organic and inorganic, climate change, radiation, ozone layer, eco-toxicity, acidification, eutrophication land use, minerals, and fossil fuels. The LCA found that paper bags had higher pollution, higher carbon footprint, and higher waste generation. Table 7.7 describes the results of the LCA (Muthu et al. 2013).

TABLE 7.7
Life Cycle Assessment of Plastic and Paper Bags

Environmental impact	HDPE plastic bag two units	Paper bag (40% recycled content) one unit	Ratio, paper/HDPE bag
Energy consumed (MJ)	1.47	1.68	1.14
Carbon footprint (factor)	0.45	1	2.22
Solid waste generated (kg)	14	50	3.57
Air pollution (kg)	1.1	2.6	2.36
Eutrophication/acidification (factor)	0.85	1	1.18
Greene Sustainability Index	1	2.445	

The assumptions in the LCA study are as follows:

Product category

- **a.** Two plastic bags had equal carrying capacity as one paper bag. Ten bags per week for 52 weeks were used.
- **b.** Plastic bags were made from HDPE and LDPE.
- **c.** The mass of the plastic bag is 6 grams and the paper bag is 42.6 grams.
- **d.** Paper bag has 40% recycled content.

Scope category

- **a.** Cradle-to-gate analysis was used, ignoring end-of-life impacts.
- **b.** Eutrophication, acidification, and other pollution impacts are considered.

The LCA found that the lighter plastic bag had less environmental impacts than paper bags, with less energy consumed, less carbon footprint, less solid waste generated, less air pollution, and less eutrophication/acidification.

7.3.2.1 Greene Sustainability Index of Plastic Bags

The GSI can be calculated based on the data provided by Muthu et al. (2013). The GSI can provide an overall sustainability measurement of the plastic bags. The overall index for each of the materials can be found with the weighting factors of 50% for GWP, 25% for waste generation, and 25% for pollution factor. The pollution factor is an arithmetic average of eutrophication, acidification, and air pollution.

The GSI results reveal that paper bags have approximately 245% more negative environmental effects than HDPE plastic bags.

7.3.3 Reusable Plastic Bags

Plastic bags can be designed and manufactured for reusable use. The reuse of plastic bags can reduce the environmental effects by the number of reuses that occurs. The GHG emissions, waste generation, energy usage, water usage, pollution generation, and other environmental impacts can be divided by the number of uses for the bag. The water usage may increase as reusable bags should be washed if they are used to carry meats of dairy. Washing of reusable plastic bags can reduce the level of bacteria present in the bag.

7.3.3.1 Australian LCA of Reusable rPET Bags

An LCA report on plastic bags, from Consulting Pty Ltd of Victoria, Australia, compares the environmental impacts of shopping bag alternatives for carrying goods in Australia. The Australian report was funded by Sustainability Victoria, which was created from the Sustainability Victoria Act 2005. The LCA data in the report were updated from an earlier LCA report from an Australian University of Design for RMIT in 2002 with more accurate values of recycling rates, bag mass, and bag capacity. The HDPE plastic grocery bag was compared with bags made from paper, compostable plastics, cotton, and polypropylene. The cotton and polypropylene bags were reusable bags (Dili 2007).

The assumptions in the Australian LCA study are as follows:

Product category

- Equal carry capacity of the bags that can carry seven grocery items.
- The masses of the plastic bags were HDPE of 7 grams, Kraft paper of 43 grams, PP of 95 grams, and cotton of 85 grams.
- Each shopping trip would require 10 bags per week for 52 weeks.

Scope category

- End-of life included 75% of single-use HDPE plastic bags sent to landfill, 19% reused as trash liners then sent to landfill, 5% recycled, and 0.5% discarded as litter.
- End-of life included 99.5% of reusable PP plastic bags sent to landfill and 0.5% discarded as litter.
- Cradle-to-grave analysis was used.
- Eutrophication, acidification, and other pollution impacts were not considered.

TABLE 7.8
Environmental Impact of Grocery Bags in Australia

Bag material	Energy consumption	GHG (CO_2eq)	Water use	Disposal options
PP reusable bag	1	1	1	Recycle at major super markets
Cotton calico reusable bag	1	1	5	No recycling, sent to landfill
HDPE single-use bag	4	2	1	Recycle at major super markets
Kraft paper single-use bag	5	5	2	Reused as trash liner and sent to landfill

The Australian study used an LCA software called SimaPro 5.1 to assess the environmental impact of the carrier bags. The LCA analysis included production of raw materials, manufacturing of the bags, transportation of the bags to retailers, and disposal of the bags at the end-of-life. Australian data are used for energy production, material production, transportation, recycling, and waste disposal.

The Australian study found that the reusable polypropylene bags had the least amount of environmental impact. The cotton reusable bag had low environmental impact except for high water usage. The results of the study are listed in Table 7.8 with relative ratings of 1 (preferred) to 5 (unacceptable).

7.3.3.1.1 Sensitivity Analysis The Australian report was a good evaluation of the importance of reusable bags. The report did not provide enough information on the assumptions of the data for the LCA. The report though is limited by the different carrying capacities of the plastic and paper bags. The report does show the importance of using recycled plastics in the manufacture of single-use bags, but does not show the use of recycled plastics for reusable bags.

7.3.3.2 Scottish LCA of Reusable rPET Bags

An LCA report on reusable plastic bags from Scotland and the United Kingdom studied the environmental effects of taxes on several plastic bag scenarios. The Scottish report acknowledged the Scottish Waste Strategy Team, Carrier Bag Consortium, Convention of Scottish Local

Authorities, Friends of the Earth Scotland, Scottish Retail Consortium, and The Scottish Environment Protection Agency for direction and support during the project. The report used LCA to evaluate the environmental effects of grocery bag consumer choices. The report found that assessing a tax would reduce the use and prevalence of plastic in the environment and that consumption of non-renewable energy, solid waste, GHG emissions, and eutrophication of lakes and rivers would be significantly less (Cadman et al. 2005).

The assumptions of the Scottish LCA report are listed in the following:

Product category

- **a.** Two plastic bags had equal carrying capacity as one paper bag.
- **b.** Ten bags per week for 52 weeks were used.
- **c.** Volume of paper bag is 20.5 liters (paper/plastic bag ratio is 1.46:1).
- **d.** Single-use plastic bags were made from HDPE.
- **e.** Reusable plastic bags were made from LDPE.
- **f.** Recycling content of the paper bag was 40%.
- **g.** The mass of the single-use plastic bag is 6 grams and the paper bag is 52 grams.

Scope category

- **a.** Cradle-to-grave analysis was used.
- **b.** End-of-life impacts assume 45% of paper bags are recycled, 25% of paper bags are incinerated, and 26% of paper bags resent to landfill.
- **c.** Plastics bags were incinerated or sent to landfills.
- **d.** Eutrophication, acidification, and other pollution impacts are considered.

The Scottish report uses LCA data from a French study (Carrefour 2004). The Carrefour LCA study examined energy, fuel, water, and other resource requirements for production, manufacture, use, and disposal of several plastic bags. The study considered plastic grocery bags,

TABLE 7.9
Environmental Indicators for Plastic and Paper Bags in Scottish Report

Indicator of environmental impact	Single-use HDPE plastic bag	Reusable LDPE plastic bag (used 4×)	Reusable LDPE plastic bag (used 20×)	Single-use paper bag
Non-renewable energy	1.0	0.7	0.1	1.1
GHG emissions	1.0	0.6	0.1	3.3
Solid waste	1.0	0.7	0.1	2.7
Water use	1.0	0.6	0.1	4.0
Acid rain	1.0	0.7	0.1	1.9
Eutrophication	1.0	0.7	0.1	14.0
Ozone formation	1.0	0.3	0.1	1.3

reusable polyethylene bags, Kraft paper bags with recycled paper content, and compostable plastic bags. The Carrefour LCA study assessed the environmental impact of the energy use, fuel and other resource use, waste generation, GHG emissions, and pollutant emissions. The results are summarized in Table 7.9 for eight environmental indicators with relative ratings of 1 (preferred) to 5 (unacceptable).

The report found that reusing plastic bags created comparably low environmental impact. The reusable bags must be used more than four times to have equivalent environmental impacts as using single-use plastic bags four times. After reusable plastic bags are used more than 20 times, the environmental impacts of water use, GHG emissions, acid rain, ozone formation, eutrophication, and solid waste can be reduced more than 90% rather than using single-use plastic bags.

The report found that most negative environmental impacts come from the production of the plastic pellets and paper from the raw materials in the first stage of manufacturing. The second manufacturing stage of conversion of the pellets and paper into plastic and paper products that are sent to retailers has less environmental impact but not negligible. The end-of-life scenarios for grocery bags can have significant impact on the creation of solid waste in the environment.

Other environmental indicators include eutrophication and acid rain generation. The environmental effects on polyethylene and polypropylene reusable bags would be similar due to the similar plastic chemistry and process to manufacture the bags. The Scottish report found that reusable bags have significantly less eutrophication and acid rain generation than single-use plastic.

The results from the Scottish report demonstrate that synthetic reusable bags have lower environmental impacts than all other types of lightweight carrier bags, including paper, plastic, or degradable plastic. The report did not list environmental indicators of reusable polypropylene plastic bag. The report could go further by studying a reusable plastic bag made from recycled plastics.

7.3.3.3 New LCA Development for Reusable Plastic Bags: Step 1—Development of the Goal

The environmental impacts of reusable plastic bags can be compared with the environmental impacts of single-use plastic grocery bags. The environmental impacts of reusable and single-use plastic bags with equal carrying capacity can be evaluated with LCA. The reusable plastic bags are single-use HDPE, reusable LDPE with 40% post-consumer recycled content, recycled PP, and recycled PET. In our case, 1500 single-use plastic bags will be compared with 1000 reusable plastic bags for equal carrying capacity. The cradle-to-grave process steps for plastic bags manufacturing and use are shown in Table 7.10 (Greene 2011).

TABLE 7.10
Cradle-to-Grave Process Steps for Plastic Bags

	Steps	Grocery bag: HDPE	PE Reusable PCR	PP non-woven
1	Produce plastic pellets from oil and natural gas	X	X	X
2	Ship pellet to converter	X	X	X
3	Convert pellet to film	X	X	X
4	Convert film to non-woven			X
5	Ship product to retail stores	X	X	X
6	Consumer uses bag first time	X	X	X
7	Consumer uses bag multiple times per year		X	X
8	Consumer washes 20% of the reusable bag weekly.		X	X
9	Consumer recycles plastic bag	X	X	
10	Consumer throws plastic in trash for landfill			X

The consumer has the ability to recycle polyethylene bags because the recycling infrastructure is in place in the United States. Polyethylene plastic bags can be made from recycled LDPE from stretch wrap film recycling sources (Roplast Industries 2013). Reusable PP non-woven plastic bags are not readily recycled, due in part to the design of the PP non-woven plastic bag. rPET bags can be made from recycled PET plastic bottles (ChicoBag Company 2013).

7.3.3.4 New LCA Development for Reusable Plastic Bags: Step 2—LCI Development

The second step of the LCA process, LCI, tabulates the energy, fuel, water, and material inputs needed to produce and use plastic and paper bags and also lists solid waste that are created when the products are made, used, and thrown away for plastic and paper bags. Polyethylene can have three types of resins that are used for plastic bags, namely, Linear Low Density Polyethylene (LLDPE), LDPE, and HDPE. HDPE is commonly used for single-use grocery bags. LLDPE and LDPE are commonly used for trash bags and for thicker department store bags. Each of the three polyethylene plastics can be used for reusable plastic grocery bags. Each of the process steps from Table 7.10 has environmental aspects that affect energy usage, water usage, GHG emissions, pollution, and solid waste generation.

Table 7.11 lists the cradle-to-gate aggregate US-averaged values of energy required, solid waste, and GHGs produced during the production of polyethylene and polypropylene. Polyethylene and polypropylene are made from natural gas and petroleum. The amount of energy and water that are needed to make polyethylene and polypropylene plastic pellets well as the amount of solid waste, pollution, and GHG generated during production is provided in Table 7.11. The polyethylene pellets are

TABLE 7.11
LCA of Plastic Pellet Manufacturing of Four Plastic Materials per 1000 kg

Plastic	Energy (GJ)	Solid waste (kg)	GHG (tons CO_2)
HDPE	69	78	1480
LDPE	74	79	1480
PET	70.4	141	2733
PP	63	83	1340

extruded and then blown into plastic bags with a blown film extrusion line. Similarly, polypropylene pellets are extruded in a sheet extruder and pressed into non-woven film that is sewn into a bag.

Table 7.11 shows that PP requires less energy to produce pellets, and also then produces less GHG due to the lower energy use. PP though produces more solid waste than polyethylene during the manufacturing of plastic pellets. The solid waste and GHG information can be used to compare the environmental benefits of using recycled plastic as a source for plastic bags rather than virgin plastic. If recycled plastics are used for plastic bags, then the amount of energy needed to produce the virgin plastic can be saved when using recycled plastics because the plastic pellet is already available and does not need to be created from raw materials (Franklin and Associates 2011).

Figure 7.1 describes the energy and resource inputs during the production and use, and disposal of plastic bags as well as the waste, GHG, and pollution generation. The cradle-to-grave analysis calculates the environmental impacts of creating plastic pellets from raw materials, transporting them to the plastic bag converter, producing the plastic bags, and transporting the plastic bags to the retailers. The LCA is influenced by choices that consumers make on single-use versus reusable bags, and choices that consumers make on recycling, waste disposal, or waste-to-energy end-of-life options.

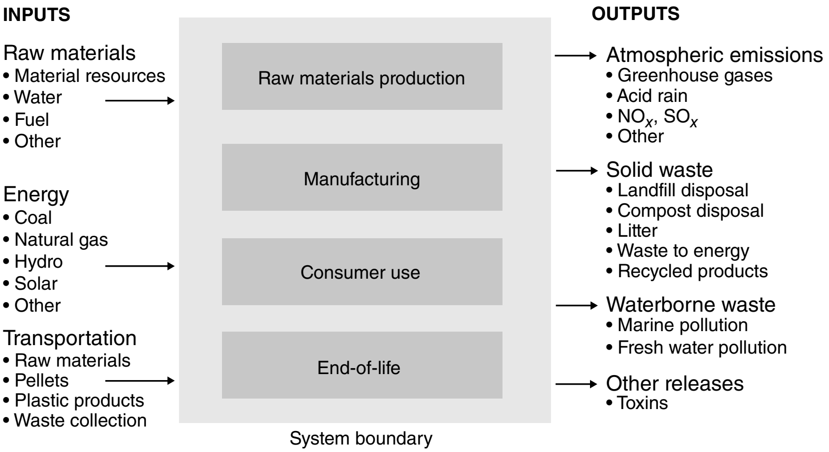

FIGURE 7.1 Process flow of inputs and outputs for plastic bag manufacturing, use, and end-of-life.

Life cycle inventory of the plastic bag manufacturing process can be determined based on the data from the Boustead report, the Australian report, and the Scottish report. The methodology used in this report combines the data from the Boustead report with the reusable bag data from the Australian and Scottish report.

The methodology for the new LCA normalizes the Boustead data energy use, GHG emissions, water usage, and waste generation for polyethylene plastic bags to the mass of the bag. The functional unit for the LCA analysis is a plastic bag of equal carrying capacity that would be used in 1-year timespan by consumers. The analysis assumes one trip per week that includes 10 bags.

The normalized Boustead data used in the LCA analysis include values of energy use, GHG emissions, water usage, and waste generation per kilogram of polyethylene. The reusable polyethylene and polypropylene bags will have the same dimensions without including handles. The reusable polyethylene thickness is 0.003 inches, whereas the reusable polypropylene bag is 80 grams per square meter (GSM) of bag. The LCA of polypropylene is calculated based on combining the Boustead data with the PP pellet manufacturing data from Table 8. The LCA of the PP per kilogram is calculated to include GHG emissions, energy usage, water usage, and waste generation per kilogram or PP. The LCA of reusable polyethylene and polypropylene bags is calculated by multiplying the per kilogram LCA by the mass of the reusable bags. Thus, we can determine the energy use, GHG emissions, water usage, and waste generation of three bags, that is, HDPE grocery bag (Boustead data), reusable polyethylene bag (modified Boustead data), and reusable non-woven polypropylene bag (modified Boustead data). Finally, the environmental credits for using recycled polyethylene in the reusable polyethylene bag are determined by subtracting the amount of energy use, GHG emissions, water usage, and waste generation from the virgin resin that was replaced by the recycled plastic, and adding the amount of energy and GHG produced by converting the recycled polyethylene to plastic pellets.

The assumptions of the new LCA are listed in the following:

Product category

a. One-and-a-half plastic bags had equal carrying capacity as one paper or reusable bag.

b. Ten bags per week for 52 weeks were used.

c. Single-use plastic bags were made from HDPE with a mass of 6 grams each.

d. Reusable plastic bags were made from LDPE with 40% recycle PCR, rPET with 90% recycled PCR, and PP.

e. The masses of the reusable plastic bags were 44 grams for LDPE, 42 for PP, and 45 grams for rPET.

f. Paper bags were made with 40% recycled content with a mass of 52 grams.

g. The Boustead data for single-use HDPE bag can be used to represent the manufacturing process of the thicker reusable polyethylene bag because it is made with the blown film extrusion process.

h. The Boustead data for single-use HDPE bag can be modified to represent the manufacturing process of the thicker reusable non-woven polypropylene bag because the non-woven PP bag is made with sheet extrusion process that requires similar energy use as blown film extrusion.

i. The production of PP non-woven bags has the same values for GHG, waste generation, energy usage, and water usage as HDPE blown film bags.

j. The non-woven PP bag is 80 GSM. The two options for polypropylene non-woven bags are 80 and 100 GSM based on industry standards.

k. Reusable polyethylene is manufactured in California and distributed throughout the United States.

l. Reusable rPET plastic bag is manufactured in California and distributed throughout the United States.

m. The rPET reusable plastic bag is made from 99% recycled PET.

n. The dimensions of the non-woven reusable bag are the same as the dimensions of the polyethylene reusable bag. The difference is the thickness of the bags.

o. For 40% recycled LLDPE and 99% recycled PET, the energy, GHG, waste, and water that are required from the pellet production are subtracted from the bag manufacturing minus the conversion costs of the recycled plastics to pellets.

p. Recycled PET bottles are converted into fiber and then into sheet for manufacturing into plastic bags.

q. 13 GJ of energy per ton is required to convert recycled PET bottles to fiber (Shen et al. 2011).

r. PET fiber to PET fabric assumes 131.7 MJ/kg PET fiber (Shen et al. 2011).

s. Energy usage conversion to GHG emissions was scaled from European data to USA LCA calculations with LCA information on plastic bags (Chaffe and Yaros 2007).

t. Eutrophication, acid rain, and ozone formulation values are created from the Scottish report (Cadman et al. 2005).

u. Eutrophication, acid rain, and ozone formulation values are equivalent for the reusable plastic bags.

Scope category

a. Cradle-to-grave analysis was used.

b. Plastics bags were incinerated or sent to landfills.

c. Eutrophication, acidification, and other pollution impacts are considered.

d. Transportation of non-woven polypropylene from China to Los Angeles has a distance of approximately 11,000 km. The GHG emissions from fuel consumptions are approximately 3% of the overall GHG emissions from the bag manufacturing based on data from the Australian report.

e. Recycled LDPE film into plastic bags does not include washing procedures in the recycling process.

f. Transportation of reusable non-woven polypropylene, rPET, and polyethylene bags throughout the United States accounts for 1% of the overall GHG emissions.

g. CO_2 emissions from the transportation of the rPET reusable bags from Vietnam/China to the United States account for 3% of the overall global warming potential of the bags.

h. The energy impacts of washing and drying reusable bags were not considered.

The LCI includes the manufacturing of plastic pellets and paper from raw materials, the conversion of plastic pellets into plastic bags, conversion of paper into paper bag, and transportation to the retail stores.

The "cradle-to-grave" analysis can illustrate the environmental benefits of reusing the plastic bag and the benefits of using recycled plastic.

7.3.3.5 New LCA Development for Reusable Plastic Bags Step 3: Life Cycle Assessment

The third step of the LCA process, life cycle impact assessment, takes the inventory of energy, fuel, water, materials, pollution, and waste and rearranges them in terms of the scope from the first step, to provide a comparison of environmental measures. In our case, the amount of energy, water, materials, and fuel needed to make 1500 plastic grocery bags can be compared with the amount of energy, water, materials, and fuel needed to make 1000 reusable plastic bags and 1000 paper bags. Likewise, the pollution, GHGs, and solid waste produced to make 1500 plastic grocery bags will be compared with the waste produced from 1000 reusable plastic bags and 1000 paper bags.

Table 7.12 lists the cradle-to-gate LCI of single-use plastic bags, single-use paper bags, reusable non-woven polypropylene plastic bags, and reusable polyethylene (LLDPE) plastic bags. The table lists grocery bags with equal amount of carrying capacity for up to 1 year or 52 weeks.

TABLE 7.12
Cradle-to-Gate LCA of Single-Use Plastic and Paper Bags, and Reusable Plastic Bags

Environmental impact indicator	1500 HDPE single-use bag	1000 Reusable LLDPE with 40% PCR bag used 52 times	1000 Reusable PP non-woven used 52 times	1000 Reusable rPET used 52 times	1000 Paper bag single-use
Non-renewable energy (GJ)	763	57	72	125	2620
GHG emissions (CO_2eq)	0.04	0.003	0.005	0.007	0.08
Solid waste (kg)	7	0.106	0.106	0.333	34
Freshwater consumption (liters)	99.6	18.9	18.9	11.16	1000
Mass (grams)	6	44	42	45	52

Single-use paper bags are presented as a comparison. The LCA data for paper bags are from the Boustead report. Recycling content is included in the reusable polyethylene bag. The reusable bags are washed at a rate of 20% of the bags over the time period in the table. The single-use plastic bag is smaller than the reusable and paper bags. Thus, 1500 single-use plastic bags have similar carrying capacity as 1000 reusable plastic and single-use paper bags. This is consistent with the Boustead report.

The data in Table 7.12 represent the environmental impacts of using equal carrying capacity bags for 1 year.

Table 7.12 illustrates that single-use reusable bags made from polypropylene or polyethylene have significantly worse environmental impacts than the single-use polyethylene bags. The reusable bags have a better environmental impact if they are used more than eight times, which is an environmental crossover point for reuse. The reusable plastic bags have significantly better environmental impact if they are used 52 times (once a week for 12 months) or more.

Table 7.12 also illustrates that the reusable polyethylene bag has the lowest environmental impact than the reusable polypropylene bag due to the use of recycled polyethylene plastic or PCR. Paper bags have a negative environmental impact compared to single-use plastic bags and reusable plastic bags.

The data in Table 7.12 can be normalized to evaluate the environmental impacts of reusable and single-use plastic bags if the data for each bag type is divided by the data from single-use plastic bags. Table 7.13 lists the normalized values for reusable and single-use plastic bags.

7.3.3.6 Greene Sustainability Index (GSI) of Reusable Plastic Bags

The GSI can be calculated based on the data listed in Table 7.13. The data can be rearranged with the LLDPE reusable plastic bag as the reference. Table 7.14 lists the environmental impacts of reusable and single-use plastic bags with the reusable plastic bag as the reference material.

The GSI can provide an overall sustainability measurement of the plastic bags. The overall index for each of the materials can be found with the weighting factors of 50% for GWP, 25% for waste generation, and 25% for pollution factor. The pollution factor is an arithmetic average of eutrophication, acidification, and air pollution. We can assume that the pollution impact would be equal for LDPE, rPET, and PP. The GSI can

TABLE 7.13

Normalized Cradle-to-Gate LCA of Single-Use Plastic and Paper Bags, and Reusable Plastic Bags

Environmental impact indicator	1500 HDPE single-use bag	1000 Reusable LLDPE with 40% PCR bag used 52 times	1000 Reusable PP non-woven used 52 times	1000 Reusable rPET used 52 times	1000 Paper bag single-use
Non-renewable energy (GJ)	1	0.07	0.09	0.16	3.43
GHG emissions (CO_2eq)	1	0.08	0.13	0.18	2.00
Solid waste (kg)	1	0.02	0.02	0.05	4.86
Freshwater consumption (liters)	1	0.19	0.19	0.11	10.04
Acid rain	1	0.1	0.1	0.1	1.9
Eutrophication	1	0.1	0.1	0.1	14
Ozone formation	1	0.1	0.1	0.1	1.3

TABLE 7.14

Normalized Cradle-to-Gate LCA with LLDPE as the Reference Material

Environmental impact indicator	1000 Reusable LLDPE with 40% PCR bag used 52 times	1000 Reusable PP non-woven used 52 times	1000 Reusable rPET used 52 times	1500 HDPE single-use bag	1000 Paper single-use bag
Non-renewable energy (GJ)	1	1.26	2.19	13.39	45.96
GHG emissions (CO_2eq)	1	1.67	2.33	13.33	26.67
Solid waste (kg)	1	1.00	3.14	66.04	320.75
Freshwater consumption (liters)	1	1.00	0.59	5.27	52.91
Acid rain	1	1.00	1.00	10	19
Eutrophication	1	1.00	1.00	10	140
Ozone formation	1	1.00	1.00	10	13
GSI	1	1.33	2.20	25.68	107.86

be calculated based on the data in the previous table. Table 7.14 lists the normalized environmental effects of single-use plastic and paper bags versus reusable plastic bags.

The GSI results reveal that after 52 uses, single-use plastic bags have approximately 25 times more negative environmental effects than reusable rLLDPE plastic bags with 40% PCR. Paper bags have approximately 108 times more negative environmental effects than a reusable rLDPE plastic bag made with 40% PCR. The PP reusable plastic bag has equivalent negative environmental effects as a reusable rLDPE plastic. The rPET reusable plastic bags have twice the negative environmental effects as a reusable LDPE plastic. Paper bags have approximately 12 times more negative environmental effects than a reusable rPET plastic bag.

7.4 LIFE CYCLE ASSESSMENT OF SUSTAINABLE PLASTIC BOTTLES

Sustainable plastic bottles can be made with biobased or recycled plastics, produced without regulated heavy metals or toxins, and made with clean manufacturing principles, and fair employment and safety practices. LCA can be used to provide a sustainable plastic bottle. The LCA process can include key elements of LCA, which features consistent functional units, energy, GHGs, waste, and pollution that include eutrophication, acidification, toxic chemical release, and end-of-life.

LCA can be used to compare the sustainability of bottles made from PLA, 100% recycled PET, and virgin PET. The sustainability will be evaluated with criteria defined in Chapter 3 as reductions in global warming potential, reductions in waste, and reductions in pollution.

7.4.1 LCAs Literature Review of Plastic Bottles

The first LCA from Franklin and Associates compares the environmental impacts of PET, rPET, and PLA (LCI Summary for PLA 2013). Franklin and Associates use SIM Pro LCA software with a database of LCI data. The LCA used the same methodology as in the report, “Life Cycle

Inventory of Five Products Produced from PLA and Petroleum-Based Resins" (Life Cycle Inventory of Five products 2013).

The assumptions in the LCA study are listed as follows:

Product category

- Ten thousand water bottles with capacity of 12-ounces each.
- Caps and labels for each bottle were ignored in the analysis because they are equivalent for all bottles.
- Higher heating values for PLA and PET are 19 and 26 MJ/kg, respectively.
- Ingeo PLA resin data were referenced with 16% reduction in energy usage and 35% reduction in CO_2eq per kilogram Ingeo PLA plastic (Vink et al. 2010).
- The mass of the PLA bottle was 21.0 grams and the mass of PET bottle was 20.3 grams.
- PET resin data were referenced from the US LCI database at http://www.nrel.gov/lci/.
- PLA resin data were referenced from "Life Cycle Inventory of Five Products Produced from PLA and Petroleum-Based Resins."

Scope category

- Composting of PLA is not considered.
- Cradle-to-grave analysis was used. End-of-life options include landfilling (80%), waste to energy (20%), and recycling of PET at a rate of 23.5%.
- Eutrophication, acidification, and other pollution impacts are considered.
- Transportation was included for the movement of plastic resins from resin producers to bottle converters, for example, PLA had 425 ton miles by combination truck, PET had 96 ton miles by combination truck.
- Water eutrophication data and acidification data were modified from the IFEU-Heidelberg data for 1000 clamshells. The data were interpolated to equivalent mass of water bottles in the current study (LCA NatureWorks LLC 2009).

TABLE 7.15
Environmental Impacts of PLA, PET, rPET Bottles

Environmental impact	PLA with 2005 data	Virgin PET	rPET (25% PCR)	[a]PLA data
Energy consumed (MJ)	19,000	16,600	15,200	16,568
Global warming potential (tons CO_2eq)	0.744	0.757	0.71	0.536
Solid waste generated (kg)	168	163	144	168
[a]Eutrophication, water (g PO_4eq)	99.26	38.87	34.79	80.79
[a]Acidification (kg SO_2eq)	5.30	3.47	3.11	4.59

[a] Data modified from LCA NatureWorks LLC (2009).

The LCA considers environmental impacts of the process, fuel, end-of-life, and energy material resource. The environmental categories considered are:

- **a.** Greenhouse gas emission (CO_2 equivalent)
- **b.** Energy usage (GJ)
- **c.** Waste generation (kg)
- **d.** Pollution (eutrophication and acidification)

Table 7.15 lists the environmental impacts of plastic bottles produced from PLA, PET, and rPET with 25% PCR recycled content.

7.4.2 Greene Sustainability Index of Sustainable Plastic Bottles

LCAs can compare the GHG generation, waste generation, and pollution generation for each scenario. The GSI can be used to compare the disposal options of plastic products. The weighting factors are 50% for generation, 25% for waste generation, and 25% for pollution generation. The weighting factors are factored with the most impact on cost for a plastics manufacturing operation. Reductions in GHG, waste generation, and pollution can be done with lowering energy costs, lower disposal costs, and lower cleanup costs.

The GSI can be calculated based on the data in Table 7.16. The GSI will provide an overall sustainability measurement of the four sustainable plastics.

TABLE 7.16

Normalized Environmental Impacts for Sustainable Bottles using Cradle-to-Grave Life Cycle Assessment

Environmental impact	PLA with 2010 data	PLA with 2005 data	Virgin PET	rPET (25% PCR)
Energy consumed (MJ)	1	1.15	1	0.92
Global warming potential (tons CO_2eq)	1	1.39	1.41	1.32
Solid waste generated (kg)	1	1	0.97	0.86
Eutrophication, water (g PO_4eq)	1	1.23	0.48	0.43
Acidification (kg SO_2eq)	1	1.16	0.76	0.68
GSI	1	1.24	1.1	1.02

Table 7.16 lists the environmental impacts of plastic bottles.

The GSI for each of the materials can be found with the weighting factors of 50% for GWP, 25% for waste generation, and 25% for pollution factor. The pollution factor is an arithmetic average of eutrophication and acidification.

The GSI results reveal that the new PLA resin bottles and recycled PET bottles have equivalent environmental impacts. The new PLA has 10% lower environmental impacts than virgin PET bottles and 24% lower environmental impacts as PLA from 2005 data.

7.4.3 Sensitivity Analysis

The LCA calculations on bottles provide an acceptable LCA analysis but failed to consider in-depth fuel data and the eutrophication data for PET were zero.

7.5 SUMMARY

Sustainable plastic products can be created with lower carbon footprint, lower waste, and lower pollution than conventional plastic products. Plastic products can be used for sustainable plastic packaging, bottles, and bags. Life cycle assessments can be used to compare the different options for plastic packaging, bottles, and bags.

Sustainable plastic packaging can be made from recycled plastics or biobased plastics, like PET, HDPE, PHA, PLA, starch, and others. Life cycle assessments show that containers made from PLA had lower global warming potential, lower pollution, and lower solid waste generation than containers made from recycled PET and virgin PET.

Containers made from recycled PET produce less GHG emission, less waste, and less pollution than containers made from virgin PET. Containers made from recycled PET produce equivalent chemicals that result in eutrophication, acidification, ozone depletion, and freshwater eco-toxicity than containers made from virgin PET.

Sustainable plastic bags can be made from recycled plastics or made to be used multiple times. After 52 uses, reusable plastic bags can result in significantly lower GHGs, waste, and pollution. After 52 uses, single-use plastic bags have approximately 25 times more negative environmental effects than reusable LLDPE plastic bags with 40% PCR. Paper bags have approximately 108 times more negative environmental effects than a reusable rLDPE plastic bag made with 40% PCR.

Sustainable plastic bottles can be made with biobased PLA and recycle PET plastics. Plastics bottles made with PLA resin and recycled PET have equivalent environmental impacts. PLA and recycled PET bottles have 10% lower environmental impacts than virgin PET bottles.

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REVIEW QUESTIONS

Q.7.1 Sustainable plastic products can be defined as products that are created with lower GHGs, lower waste generation, and lower pollution. T or F?

Q.7.2 Sustainable plastic containers can be made with PLA or recycled PET. T or F?

Q.7.3 Plastics bags made with 40% recycled content are made with lower carbon footprint than plastics bags made with virgin plastic. T or F?

Q.7.4 Reusable plastic bags result in lower GHG emissions, waste generation, and pollution than single-use plastic or paper bags. T or F?

Q.7.5 Plastic bottles made from recycled PET or PLA result in lower GHG emissions, waste generation, and pollution than bottles made with virgin PET. T or F?

Q.7.6 According to Case 2 LCA, PLA clamshells containers had lower carbon footprint than clamshells made from PET. T or F?

Q.7.7 According to Table 7.11, HDPE generated less GHGs than LDPE, PET, and PP during the production of the plastic pellets. T or F?

Q.7.8 According to Case 3 LCA, PLA clamshells containers had higher carbon footprint than clamshells made from PET. T or F?

Q.7.9 According to Table 7.11, PET generated more solid waste than LDPE, HDPE, and PP during the production of the plastic pellets. T or F?

Q.7.10 The Greene Sustainability Index can be used to provide an overall sustainability score for materials that include GHG emission, waste generation, and pollution. T or F?

REVIEW PROBLEMS

P.7.1 According to Case 2 LCA, which of the following clamshell container materials generated the most tons of CO_2eq?

a. PLA
b. PET
c. PP
d. OPS

P.7.2 According to Case 2 LCA, which of the following clamshell container materials generated the most solid waste?

a. PLA
b. PET
c. PP
d. OPS

P.7.3 According to Case 2 LCA, which of the following clamshell container materials generated the most eutrophication in water?

a. PLA
b. PET
c. PP
d. OPS

P.7.4 According to Table 7.11, which of the following plastics generated the most solid waste during the production of the plastic pellets?

a. HDPE
b. LDPE

c. PET

d. PP

P.7.5 According to Case 3 LCA, which of the following clamshell container materials generated the most tons of CO_2eq?

a. PLA

b. PET

c. GPPS

d. PP

P.7.6 According to the LCA in Table 7.4, which of the following plastic container materials generated the most tons of CO_2eq?

a. PLA

b. PET

c. rPET

d. rPLA

P.7.7 According to the LCA in Table 7.4, which of the following plastic container materials generated the most solid waste?

a. PLA

b. PET

c. rPET

d. rPLA

P.7.8 According to the LCA in Table 7.4, which of the following plastic container materials generated the most eutrophication in water?

a. PLA

b. PET

c. rPET with 40% recycled content

d. PLA with 40% recycled content

P.7.9 According to the LCA in Table 7.5, which of the following plastic container materials had the highest overall sustainability index?

a. PLA with 5% composting

b. virgin PET

c. rPET with 40% recycled content

d. virgin PLA

P.7.10 After 52 uses, which of the following plastic bag generates the least amount of CO_2eq?

a. single-use HDPE bag

b. single-use paper bag with 30% recycled content
c. reusable plastic bag made from PP
d. reusable plastic bag made from LDPE with 40% recycled content

REVIEW EXERCISES

E.7.1 Determine the plastic used in a yogurt container. Calculate an LCA with the methodology in the chapter for the plastic material, PLA, and recycled plastic.

E.7.2 Determine the availability of reusable plastic bags in your community. Determine the plastic materials that are used in the reusable plastic bag. Conduct an LCA with the methodology in the chapter for the reusable plastic bag as compared to single-use plastic and paper bag.

E.7.3 Determine the plastic materials that are used in the production of a shampoo bottle. Calculate an LCA with the methodology in the chapter for plastic shampoo bottles made from the plastic material, PHA, PLA, and recycled plastic.

E.7.4 Calculate your personal LCA for plastic bags based on your usage rate. Consider the number of single-use plastic bags and single-use paper bags used at the grocery store for 1 week. Consider replacing the single-use bags with a reusable plastic bag made from PP. How much will the GHG emissions and waste be reduced? Then, extrapolate the results for 1 year.

E.7.5 Calculate an LCA for an aluminum reusable water bottle and compare the results to the LCA for PLA and PET water bottles. How many times would you have to reuse an aluminum water bottle to equal the GHG emission and waste generation of PET plastic water bottles.

CHAPTER 8

Biobased and Biodegradation Standards for Polymeric Materials

8.1 INTRODUCTION

Biodegradable plastics are available throughout the world. Biodegradable plastics can be made with reduced carbon emissions, reduced waste, and reduced toxic pollution compared to traditional petroleum-based plastics. Typically, plastics account for 10% by weight or 20% of the volume of the landfill. Organic food waste can account for 20–30% of the landfill weight and 30–40% of the volume. Biodegradable plastics can reduce the amount of food waste and plastic waste if they are used to wrap or package the food items and then sent to industrial composting facilities rather than to landfills.

Biodegradation is an important feature of biodegradable plastics. Two essential components of the biodegradation process are that the material must be a food source for the bacteria in the disposal environment and that the biodegradation must take place within a short time period, typically 6 months. Therefore, biodegradation can occur in an industrial compost environment for biodegradable plastics if they are used as food source for the bacteria in the compost and that they are

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Sustainable Plastics: Environmental Assessments of Biobased, Biodegradable, and Recycled Plastics, First Edition. Joseph P. Greene.

consumed within a short timespan. Likewise, biodegradation can occur in the marine environment if the bacteria in the seawater consume a major portion of the plastic within a short timespan.

Biodegradation standards are created to capture these essential components. These standards define the environment of biodegradation and time of biodegradation. Thus, plastic materials can be defined as biodegradable in compost environment if they biodegrades in one growing season, or 6 months. Alternatively, materials can be properly defined as biodegradable in marine environment if they partially biodegrade within 6 months.

This chapter describes the worldwide biodegradation standards for biodegradable plastics, including starch-based plastics, in common disposal environments, including compost, marine, anaerobic digestion, soil, and landfill. Compost environments include aerobic conditions within hot industrial compost environments. Marine environments include cold aerobic conditions. Landfill disposal environments include aerobic and anaerobic conditions. Anaerobic-digestion environments include hot anaerobic conditions.

8.1.1 Biodegradation Standards

Biodegradation standards for plastic materials are established based on two necessary categories for biodegradation: biodegradation testing method and biodegradation performance specifications. The first standard is a test method that accurately simulates the intended environment and specifies a method for measuring biodegradation. The second standard is a specification standard that assigns a minimum value to establish biodegradation. Both types of standards are necessary and sufficient to adequately establish the biodegradation performance of plastic materials.

Solid waste disposal environments for plastic materials can include industrial compost, home compost, anaerobic digestion, landfill, litter, and ocean water. Only two disposal environments have both biodegradation standards for test methods and biodegradation performance standards, for example, industrial compost and marine biodegradation environments. Test method standards are available for anaerobic digestion, home compost, and landfill environments. The second necessary performance specification standard for biodegradation performance is not available for anaerobic digestion, home compost, or landfill environments. Therefore, plastic materials can claim meeting biodegradation performance standards for industrial compost and marine environments, but not for anaerobic-digestion, home compost, or landfill environments.

8.1.2 Worldwide Biodegradation Standards Agencies

Several worldwide organizations as listed in Table 8.1 are involved in setting standards for biodegradable and compostable plastics, including American Society for Testing and Materials (ASTM), International Committee for Standardization (CEN), International Standards Organization (ISO), German Institute for Standardization (DIN), Japanese Institute for Standardization (JIS), and British Plastics Federation. The standards from these organizations have helped the industry create biodegradable and compostable products that meet the increasing worldwide demand for more environmentally friendly plastics (Narayan and Pettigrew 1999). International, American, and Japanese certification schemes are cooperating to enable international cross-certification of products so that a product certified in one of these countries would automatically be eligible for certification in other countries.

Biodegradation standards are provided in the following sections. The standards are organized based on disposal environment. Thus, the biodegradation standards from different worldwide standards organizations are presented in an industrial compost section, marine environment section, an anaerobic-digestion section, landfill section, and home compost section.

TABLE 8.1
Biodegradation Standards Agencies

Standards agency	Country	Web address	Certification agency
ASTM	USA	http://www.astm.org	http://www.bpiworld.org/BPI-certification-requirements
CEN	International Union	http://www.cen.eu	http://www.din.de/cmd
ISO	Worldwide	http://www.iso.org	http://www.din.de/cmd
JIS	Japan	http://www.jsa.or.jp	http://www.jbpaweb.net/english/english.htm

Standards for biobased materials are, also, presented in the following to establish the parameters of claims that plastic materials are biobased. Biodegradable plastics can be produced from organic materials or petroleum-based materials.

8.1.3 Certification

Certification is needed for biodegradable plastics to ensure that they meet the performance specification requirements in the biodegradation standards. Several certification companies, listed in Table 8.1, are available to certify the biodegradation performance of compostable plastics. In the United States, Biodegradable Products Institute (BPI) and the US Composting Council established the Compostable Plastics certification program in the United States to certify compostable plastics as meeting the ASTM D6400 or ASTM D6868 compostability standards.

In Europe, the DIN certification organization was created to certify that biodegradable plastics (BPI Certified Compostable 2013) meet the International standard EN 13432 for compostability. Vinçotte is also a certification company for certification of compostable plastics in Europe. Vinçotte OK Biodegradable mark ensures that the plastic material will pass the performance biodegradable specification in a specific natural environment (soil, fresh water, seawater, etc.), and also ensures that the plastic material meets the performance specification of compostable plastics in EN 13432.

In Japan, the BioPlastics Association (JBPA) was created to certify biodegradable plastics meet the International Standard EN 13432 for compostability. JBPA in Japan established GreenPla certification and labeling system based on international biodegradation standards.

8.2 BIOBASED STANDARD TEST METHOD

Many biodegradable plastics are made with biobased materials. These are derived from organic carbon sources such as cereal, corn, potato, rice, soy, sugar cane, wheat, vegetable oil, etc. Biobased plastics are made with a renewable resource that can have lower environmental impacts than petroleum-based plastics. Replacing petroleum-based carbon with organic carbon from today can reduce the carbon footprint of the plastic material (Narayan 2011a). Biological carbon content analysis can establish the carbon footprint of bioplastics with life cycle assessment methods (Narayan 2011b). Biobased content of the plastic material can be established by tests that measure carbon isotopes of the material.

8.2.1 US Biobased Standard

8.2.1.1 ASTM D6866-10 Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis

8.2.1.1.1 Summary This American test method establishes the procedures, equipment, materials, and conditions to measure the ^{14}carbon content of the plastic sample through radiocarbon analysis. This test method is applicable to carbon-based plastic products that can undergo combustion in the presence of oxygen to produce carbon dioxide gas (CO_2). This test method can be useful for companies and US federal agencies to promote the use of biobased products in commercial, non-food products. The test method directly discriminates between 14C/12C content of plastic samples made from contemporary carbon and those plastic samples made from petroleum sources that do not have 14C. Measurement of a plastic product's 14C/12C content is determined relative to the modern carbon-based oxalic acid radiocarbon Standard Reference Material 4990c.

8.2.1.1.2 Procedures The radiocarbon analysis can be performed with three methods, as listed in the following:

1. *Method B:* Accelerator mass spectrometry (AMS) and isotope ratio mass spectrometry (IRMS) techniques to quantify the biobased content of a given product. Sample preparation methods are identical to Method A. Stored CO_2 is sent to an AMS facility for final processing and analysis. The maximum error is 1–2% for AMS and 0.1–0.5% for IRMS.
2. *Method C:* Liquid scintillation counting (LSC) radiocarbon techniques to quantify the biobased content of a product. Method C uses LSC analysis of sample carbon that has been converted to benzene rather than CO_2 solutions of Method A. The maximum error is ±3%.

8.2.1.1.3 Equipment

1. Liquid scintillation counting
2. Accelerator mass spectrometry
3. Isotope ratio mass spectrometry

8.2.2 International Biobased Standards

Currently, there are no ISO test methods that are equivalent to biobased standard test method.

8.3 INDUSTRIAL COMPOST ENVIRONMENT

Biodegradation standards for industrial compost environment require a biodegradation specification standard and a biodegradation test method standard. The specification standards in the United States are for compostable plastics and for coatings that can be used for packaging and containers. Both specification standards require the use of the same test method. Table 8.2 lists the biodegradation standards for industrial compost in several countries. The standards listed are the performance specification standard and the test method standards in the industrial compost environment. The standards are discussed in more detail in the following section. For complete information on the standards, consult the documentation from the standards agency.

TABLE 8.2
Biodegradation Standards for Industrial Composting Environment

Region	Performance specification	Test method	Measurement method	Disintegration test method
Australia	ISO 17088	ISO 14855-2	CO_2 measurement	ISO 16929, ISO 20200
Europe	ISO 17088/ EN13432	ISO 14855-2	CO_2 measurement	ISO 16929, ISO 20200
Japan	ISO 17088	ISO 14855-2	CO_2 measurement	ISO 16929, ISO 20200
USA	ASTM D6400, D6868	ASTM D5338	CO_2 measurement	ISO 16929

8.3.1 US Biodegradation Standards for Industrial Compost Environment

8.3.1.1 Biodegradation Performance Specification Standard: ASTM D6400-04. Standard Specification for Compostable Plastics

8.3.1.1.1 Summary This American specification standard establishes the performance requirements for biodegradation of compostable plastic materials that are designed to biodegrade into CO_2, water, and biomass in an industrial compost environment. The industrial compost environment is one that maintains a temperature above 40°C and results in thermophilic conditions. The performance specification standard requires the use of ASTM D5338-05 test method to measure the amount of CO_2 that is emitted from the degrading plastic sample.

ASTM D6400-04 performance specification standard requires the product must demonstrate each of the three characteristics as follows:

1. Sufficient disintegration during composting;
2. Adequate level of inherent biodegradation; and
3. No adverse impacts on the ability of compost to support plant growth.

8.3.1.1.2 Procedures Three test characteristics for the ASTM D6400-04 standard specify that three types of tests are performed on the plastic samples. The first characteristic measures the percentage of disintegration of the plastic samples while under hot and moist compost conditions. The plastic samples are weighed prior to exposure to test conditions. The samples are placed in compost soil with the use of a sack, bag, or screened container. The plastic samples are exposed to industrial composting conditions of at least 58°C and 50% moisture for 12 weeks. The mass of the plastic sample is measured after 12 weeks by passing the plastic sample and compost through a 2.0-mm sieve. ASTM D-6400 specifies the test specimen must disintegrate at least 90% of the dry weight within 12 weeks.

The second characteristic for ASTM D6400-04 standard specifies that a satisfactory rate of *biodegradation* of the plastic material is under industrial composting conditions of at least 58°C and 50% moisture for 180 days, that is, more than 90% of the carbon in the original plastic sample is converted into CO_2 as measured by a CO_2 respirometer or wet chemistry methods. The details of the test procedure are listed in ASTM D5338-11 test method.

The third characteristic for ASTM D6400-04 standard specifies a satisfactory ability of the compost soil at the end of the biodegradation testing to *support plant growth* through phytotoxicity testing and very low regulated heavy metal concentrations. Phytotoxicity testing is achieved through planting of tomato, cucumber, radish, rye, barley, or cress grass seeds in the tested compost soil. The growth of the plants after 10 days indicates positive soil conditions for plant growth. Plant biomass tests can reveal quality differences between composts and can indicate potential plant stress induced by the compost at the given level used in the test.

Regulated heavy metal testing measures the concentrations of regulated heavy metals in the compost soil at the end of the biodegradation testing. The level of regulated heavy metals can be measured with Flame Atomic Absorption Spectrophotometer using an air-acetylene flame and equipped with a Pb hollow-cathode lamp. The compost samples must have regulated metal concentrations less than 50% of the acceptable levels of regulated heavy metals as prescribed in 40 CFR Part 503.13, that is, lead (75 mg/kg), cadmium (8.5 mg/kg), chromium (not specified), copper (375 mg/kg), nickel (105 mg/kg), zinc (700 mg/kg), and mercury (4.25 mg/kg) (Title 40: Protection of the Environment 2013).

8.3.1.1.3 Specification ASTM D6400-04 standard specifies that a plastic material is compostable if it meets the following specifications:

1. *Disintegration:* Greater than 90% disintegration of the original dry weight of the plastic material after 12 weeks of exposure to industrial composting conditions specified in ISO 16929 test method standard for disintegration.
2. *Biodegradation:* Greater than 90% of the carbon in the original plastic sample is converted into CO_2 after 180 days of exposure to industrial composting conditions specified in ASTM D5338 test method standard.
3. *Nontoxic to plants:* No measureable phytotoxicity or regulated heavy metals greater than allowable levels as described in 40 CFR Part 503.13.

8.3.1.2 Biodegradation Performance Specification Standard: ASTM D6868–03. Standard Specification for Biodegradable Plastics Used as Coatings on Paper and Other Compostable Substrates

8.3.1.2.1 Summary This American specification standard establishes the performance requirements for biodegradation of materials and products (including packaging, films, and coatings) that are attached (either through lamination or extrusion directly onto the paper) to compostable substrates plastic materials. The compostable plastics are designed to biodegrade in an industrial compost environment. The industrial compost environment is one that maintains a temperature above 40°C and results in thermophilic conditions. The performance specification standard requires the use of ASTM D-5338-05 test method to measure the amount of CO_2 that is emitted from the degrading plastic sample.

ASTM D-6868-03 performance specification standard requires the product must demonstrate each of the three characteristics as follows:

1. Sufficient disintegration during composting;
2. Adequate level of inherent biodegradation; and
3. No adverse impacts on the ability of compost to support plant growth.

8.3.1.2.2 Procedures The test procedures for ASTM D6868-03 standard specify that three types of tests are performed on the plastic samples. The first characteristic measures the percentage of disintegration of the plastic samples while under hot and moist compost conditions. The plastic samples are weighed prior to exposure to test conditions. The samples are placed in compost soil with the use of a sack, bag, or screened container. The plastic samples are exposed to industrial composting conditions of at least 58°C and 50% moisture for 12 weeks. The mass of the plastic sample is measured after 12 weeks by passing the plastic sample and compost through a 2.0-mm sieve. ASTM D-6868 specifies that no more than 10% of the original dry weight of the plastic material remains.

The second characteristic for ASTM D6868-03 standard specifies that a satisfactory rate of *biodegradation* of the plastic material is under industrial composting conditions of at least 58°C and 50% moisture for 180 days, that is, more than 90% of the carbon in the original plastic sample is converted into CO_2 as measured by a CO_2 respirometer or wet chemistry methods. If the packaging or paper product is a combination of several materials, then each of the materials must individually pass the respirometry test. The details of the test procedure are listed in ASTM D5338-11 test method.

The third characteristic for ASTM D6868-03 standard specifies a satisfactory ability of the compost soil at the end of the biodegradation testing to *support plant growth* through phytotoxicity testing and very low regulated heavy metal concentrations. Phytotoxicity testing is achieved through planting of tomato, cucumber, radish, rye, barley, or cress grass seeds in the tested compost soil. The growth of the plants after 10 days indicates positive soil conditions for plant growth.

Regulated heavy metal testing measures the concentrations of regulated metals in the compost soil at the end of the biodegradation testing.

8.3.1.2.3 Specification ASTM D6868-03 standard specifies that a plastic coating material is compostable if it meets the following specifications:

1. *Disintegration:* Less than 10% of the original dry weight of the plastic material remains after 12 weeks of exposure to industrial composting conditions.
2. *Biodegradation:* Greater than 90% of the carbon in the original plastic sample is converted into CO_2 as measured by a CO_2 respirometer after 180 days of exposure to industrial composting conditions.
3. *Nontoxic to plants:* No measureable phytotoxicity or regulated heavy metals greater than allowable levels as prescribed in 40 CFR Part 503.13.

8.3.1.3 Biodegradation Test Method Standard: ASTM D5338-11. Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials under Controlled Composting Conditions

8.3.1.3.1 Summary This test method establishes the procedures, equipment, materials, and conditions to measure the degree and rate of biodegradation of plastic materials under aerobic thermophilic composting conditions. This test method is designed to produce repeatable and reproducible test results under controlled composting conditions that simulate industrial compost conditions. The plastic test samples are exposed to an inoculum that is derived from industrial compost. The aerobic thermophilic conditions of the test are provided in an environment where temperature, aeration, and humidity are closely monitored and controlled. The plastic samples are cut into small pieces and placed in a vessel with warm and moist compost soil. The test containers are at 58°C (±2°C) for 180 days. The biogas from the container is measured for CO_2 and O_2 over the testing period.

8.3.1.3.2 Procedures The test procedures for ASTM D-5338-11 involve placing 500 grams of industrial compost soil that has maturity level of 2–3 months into a container vessel greater than 2 liters and less than 5 liters. The ASTM test procedure for industrial compost is explained in more detail in Appendix D.

A minimum of 12 composting vessels are required for the test. The containers are provided for the test specimens that include plastics, blank, positive control, and negative control samples. The testing is completed in triplicate. The plastic samples are added to the container in quantities of 100 grams. The container must have 25% free air space above the samples. The pH, moisture content, C/N ratio, and percentage solids are measured for the compost soil. The sample containers must have moist air supplied to the container that is free of CO_2. The biogas from the sample containers is measured periodically for CO_2 and O_2. The O_2 level must be greater than 6% during the duration of the test. The test containers should be rotated every 2 or 3 days to reduce the packing of the soil and to mix fresh air to the compost soil. An example of a test apparatus is provided in Figure 8.1.

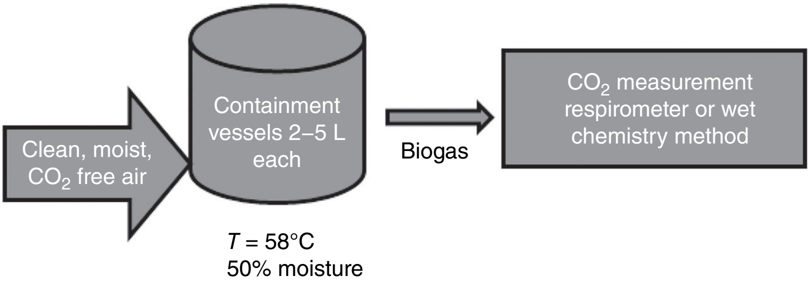

FIGURE 8.1 Experimental setup for laboratory environment.

8.3.1.3.3 Materials

- Plastic samples
- Blank compost soil
- Positive control: cellulose powder or cellulose paper
- Negative control: polyethylene film
- Barium hydroxide solution

8.3.1.3.4 Equipment

- Composting vessels with size greater than 2 liters and less than 5 liters
- Water bath or other temperature control device
- Pressurized air system with CO_2 free and H_2O saturated air
- Carbon dioxide trapping apparatus with $Ba(OH)_2$ solution
- Flexible tubing non-permeable to CO_2
- Stoppers equipped with sampling ports
- Analytical balance (±0.1 mg)
- 100-mL Burette
- 0.05 N HCL
- pH meter
- Respirometer devices for measuring CO_2 and O_2 periodically (optional)
- CO_2 trapping equipment with gas flow meter, gas chromatograph, or other suitable equipment

8.3.2 International Biodegradation Standards for Industrial Compost Environment

The ISO is the world's largest developer of standards. ISO is a network of the national standards institutes of 157 countries who agree on specifications and criteria to be applied consistently in the classification of materials, in the manufacture and supply of products, in testing and analysis, in terminology, and in the provision of services. The test method is designed to yield the percentage conversion of the carbon in the test material to evolve carbon dioxide as well as the rate of conversion.

In Europe, compostable plastics are being used in several applications. Compostable plastics must comply with the International Norm

EN13432 that is the criteria for compostability. The EN13432 specifications standard is very similar to ASTM D-6400 specifications standard. Certification with ISO compostability standard is compatible with certification for ASTM D6400 standard. EN13432 requires a compostable plastic material to break down to the extent of at least 90% to H_2O and CO_2 and biomass within a period of 6 months. ISO14855 standard specifies a testing method to evaluate the ultimate aerobic biodegradability of plastics, based on organic compounds, under controlled composting conditions by the measurement of the amount of carbon dioxide evolved and the degree of plastic disintegration at the end of test. ISO 14852 is the determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium. The test method measures the evolved carbon dioxide and is similar to ASTM D-5338 test method standard.

DIN-Certco is a very well-known and utilized certification system in Europe (Bastioli 2005). Sample materials are tested for regulated metals, organic contaminants, complete biodegradation, disintegration under compost conditions, and phytotoxicity (plant toxicity). The regulated metals and organic chemical tests ensure that neither organic contaminants nor heavy metals such as lead, mercury, and cadmium can enter the soil via the biodegradable materials. The procedures for testing complete biodegradation in the laboratory and disintegration under compost conditions ensure that materials are completely degraded during one process cycle of a standard composting plant. The DIN compostability certification is very similar to BPI certification, which meets ASTM D-6400 standards.

Table 8.3 illustrates the heavy metal limits in the International standard and the US standards (Rudnik 2008). Heavy metal concentrations in the EN13432 standard allows a limited amount of metal, that is, lead (30 mg/kg), cadmium (0.3 mg/kg), chromium (30 mg/kg), copper (22.5 mg/kg), nickel 15 mg/kg), zinc (100 mg/kg), and mercury (0.3 mg/kg). The US standard allows the following amounts: lead (150 mg/kg), cadmium (17 mg/kg), chromium (not specified), copper (750 mg/kg), nickel 210 mg/kg), zinc (1400 mg/kg), and mercury (8.5 mg/kg) (Rudnik 2008). Acceptable levels of heavy metals in sewer sludge are provided as per US EPA Subpart 503-13.

Biodegradation standards for industrial compost environment require a biodegradation specification standard and a biodegradation test method standard. The specification standards in Europe are for plastics and for packaging. Both specification standards require the use of the same test method.

TABLE 8.3
Regulated Heavy Metal Allowable Concentrations

Element	ASTM D-6400-USA (mg/kg)	ASTM D-6400-Canada (mg/kg)	EN 13432 (mg/kg)	Japan (mg/kg)
Zn	1400	463	150	180
Cu	750	189	50	60
Ni	210	45	25	30
Cd	17	5	0.5	0.5
Pb	150	125	50	10
Hg	8.5	1	0.5	0.2
Cr	–	265	50	50
Mo	–	5	1	–
Se	50	4	0.75	–
As	20.5	19	5	5
F	–	–	100	–
Co	–	38	–	–

8.3.2.1 Biodegradation Performance Specification Standard: EN 13432-2000. Packaging Requirements for Packaging Recoverable through Composting and Biodegradation Test Scheme and Evaluation Criteria for the Final Acceptance of Packaging

8.3.2.1.1 Summary This international specification establishes the performance requirements for biodegradation of plastic materials and products (including packaging, films, and other products). The compostable plastics are designed to biodegrade in an industrial compost environment. The industrial compost environment is one that maintains a temperature above 40°C and results in thermophilic conditions. The performance specification standard requires the use of EN 14995 (ISO 17088) test method to measure the amount of CO_2 that is emitted from the degrading plastic sample. EN 13432-2000 performance specification standard requires the product must demonstrate each of the following characteristics:

1. biodegradability;
2. disintegration during biological treatment;
3. minimal effect on the biological treatment process; and
4. minimal effect on the quality of the resulting compost.

8.3.2.1.2 Procedures The test procedures for EN 13432 standard specifies that three types of tests are performed on the plastic samples. The first test measures the percentage of disintegration of the plastic samples while under hot and moist compost conditions. The plastic samples are weighed prior to exposure to test conditions. The samples are placed in compost soil with the use of a sack, bag, or screened container. The plastic samples are exposed to industrial composting conditions of at least 58°C and 50% moisture for 12 weeks. The mass of the plastic sample is measured after 3 months by passing the plastic sample and compost through a 2.0-mm sieve. EN 13432 specifies that no more than 10% of the original dry weight of the plastic material remains.

The second test procedure for EN 13432 standard specifies that a satisfactory rate of *biodegradation* of the plastic material is under industrial composting conditions of at least 58°C and 50% moisture for 26 weeks, that is, more than 90% of the carbon in the original plastic sample is converted into CO_2 as measured by a CO_2 respirometer or wet chemistry methods. The details of the test procedures are listed in EN 14046 or ISO 14855 test method.

The third test procedure for EN 13432 standard specifies a satisfactory ability of the compost soil at the end of the biodegradation testing to *support plant growth* through phytotoxicity testing and very low regulated heavy metal concentrations. Phytotoxicity testing is achieved through planting of two seed crops in the tested compost soil. The growth of the plants after 10 days indicates positive soil conditions for plant growth. Plant biomass tests can reveal quality differences between composts and can indicate potential plant stress induced by the compost at the given level used in the test.

Regulated heavy metal testing measures the concentrations of regulated metals in the compost soil at the end of the biodegradation testing.

The test procedures for EN 13432 standard specifies that three types of tests are performed on the plastic samples. The first test measures the percentage of disintegration of the plastic samples while under hot and moist compost conditions. The plastic samples are weighed prior to exposure to test conditions. The samples are placed in compost soil with the use of a sack, bag, or screened container. The plastic samples are exposed to industrial composting conditions of at least 58°C and 50% moisture for 12 weeks. The mass of the plastic sample is measured after 3 months by passing the plastic sample and compost through a 2.0-mm sieve. EN 13432 specifies that no more than 10% of the original dry weight of the plastic material remains.

The second test procedure for EN 13432 standard specifies that a satisfactory rate of *biodegradation* of the plastic material is under industrial composting conditions of at least 58°C and 50% moisture for 26 weeks, that is, more than 90% of the carbon in the original plastic sample is converted into CO_2 as measured by a CO_2 respirometer or wet chemistry methods. The details of the test procedures are listed in EN 14046 or ISO 14855 test method.

The third test procedure for EN 13432 standard specifies a satisfactory ability of the compost soil at the end of the biodegradation testing to *support plant growth* through phytotoxicity testing and very low regulated heavy metal concentrations. Phytotoxicity testing is achieved through planting of two seed crops in the tested compost soil. The growth of the plants after 10 days indicates positive soil conditions for plant growth. Plant biomass tests can reveal quality differences between composts and can indicate potential plant stress induced by the compost at the given level used in the test.

Regulated heavy metal testing measures the concentrations of regulated metals in the compost soil at the end of the biodegradation testing.

8.3.2.1.3 Specifications EN 13432 standard specifies that a plastic material is compostable if it meets the following specifications:

1. Satisfactory *disintegration* of the plastic material that is under pilot-scale composting test of at least 58°C and 50% moisture for 84 days that no more than 10% of the original dry weight of the plastic material remains after passing through a 2.0-mm sieve. Also, the biodegradation testing shall not have any adverse effects on the composting process. The standard requires the use of ISO 16929 or ISO 2020 test method standard.
2. Satisfactory rate of *biodegradation* of the plastic material that is under industrial composting conditions of at least 58°C and 50% moisture in 6 months, that is, more than 90% of the carbon in the original plastic sample is converted into CO_2 as measured by measuring the amount of release of CO_2 through wet chemistry methods. The standard requires the use of ISO 148455 or ASTM D5338 test method standard.
3. Satisfactory ability of the compost soil at the end of the biodegradation testing to support plant growth through phytotoxicity testing with seedling emergence and seedling growth test (OECD 208).

8.3.2.2 Biodegradation Performance Specification Standard: ISO 17088 (EN 13432). Plastics—Evaluation of compostability—Test Scheme and Specification

This international standard is very similar to EN 13432-2000 and establishes the performance requirements for biodegradation of plastic materials and products (including packaging, films, and other products). The compostable plastics are designed to biodegrade in an industrial compost environment. The industrial compost environment is one that maintains a temperature above 40°C and results in thermophilic conditions. The performance specification standard requires the use of EN 14995 (ISO 17088) test method to measure the amount of CO_2 that is emitted from the degrading plastic sample. EN 13432-2000 performance specification standard requires the product must demonstrate each of the four following characteristics:

1. biodegradability,
2. disintegration during biological treatment,
3. minimal effect on the biological treatment process, and
4. minimal effect on the quality of the resulting compost.

ISO 17088 standard specification establishes the performance requirements for biodegradation of compostable plastic materials that are designed to biodegrade into CO_2, water, and biomass in an industrial compost environment according to test methods described in EN 14046 and ISO 14855. The industrial compost environment is one that maintains thermophilic temperatures. The performance specification standard requires the use of EN 14046 or ISO 14855 test method to measure the amount of CO_2 that is emitted from the degrading plastic sample.

8.3.2.2.1 Procedures The test procedures for ISO 17088 standard specifies that three types of tests are performed on the plastic samples. The first test measures the percentage of disintegration of the plastic samples while under hot and moist compost conditions. The plastic samples are weighed prior to exposure to test conditions. The samples are placed in compost soil with the use of a sack, bag, or screened container. The plastic samples are exposed to industrial composting conditions of at least 58°C and 50% moisture for 84 days. The mass of the plastic sample is measured after 3 months by passing the plastic sample and compost through a 2.0-mm sieve. EN 13432 specifies that no more than 10% of the original dry weight of the plastic material remains.

The second test procedure for ISO 17088 standard specifies that a satisfactory rate of *biodegradation* of the plastic material is under industrial composting conditions of at least 58°C and 50% moisture for 26 weeks, that is, more than 90% of the carbon in the original plastic sample is converted into CO_2 as measured by a CO_2 respirometer. The details of the test procedures are listed in ISO 14855 or ASTM D5338 test method.

The third test procedure for ISO 17088 standard specifies a satisfactory ability of the compost soil at the end of the biodegradation testing to *support plant growth* through phytotoxicity testing and very low regulated heavy metal concentrations. Phytotoxicity testing is achieved through planting of tomato, cucumber, radish, rye, barley, or cress grass seeds in the tested compost soil. The growth of the plants after 10 days indicates positive soil conditions for plant growth.

Regulated heavy metal testing measures the concentrations of regulated metals in the compost soil at the end of the biodegradation testing. The compost samples must have regulated metal concentrations less than prescribed levels, listed in Table 8.3.

8.3.2.2.2 Specifications ISO 17088 standard specifies that a plastic material is compostable if it meets the following specifications:

1. Satisfactory *disintegration* of the plastic material that is under pilot-scale composting test of at least 58°C and 50% moisture for 3 months that no more than10% of the original dry weight of the plastic material remains after passing through a 2.0-mm sieve. Also, the biodegradation testing shall not have any adverse effects on the composting process.
2. Satisfactory rate of *biodegradation* of the plastic material that is under industrial composting conditions of at least 58°C and 50% moisture for 6 months, that is, more than 90% of the carbon in the original plastic sample is converted into CO_2 as measured by a CO_2 respirometer or wet chemistry methods.
3. Satisfactory ability of the compost soil at the end of the biodegradation testing to *support plant growth* through phytotoxicity testing and very low regulated heavy metal concentrations. Plant growth test (OECD 208).

8.3.2.3 Biodegradation Test Method Standard: ISO 14855-2 (EN 14046) Packaging. Evaluation of the Ultimate Aerobic Biodegradability and Disintegration of Packaging Materials under Controlled Composting Conditions. Method by Analysis of Released Carbon Dioxide

8.3.2.3.1 Summary This international standard specifies a test method for the evaluation of the ultimate aerobic biodegradability of packaging materials based on organic compounds under controlled composting conditions by measurement of released carbon dioxide at the end of the test. This method is designed to resemble typical aerobic composting conditions for the organic fraction of mixed municipal solid waste. The packaging material is exposed in a laboratory test to an inoculum which is derived from compost. The aerobic composting takes place in an environment where especially temperature, aeration, and humidity are closely monitored and controlled. The test method is designed to yield a percentage and rate of conversion of carbon of the test material to released carbon dioxide. The conditions described in this standard do not necessarily always correspond to the optimal conditions allowing the maximum degree of biodegradation to occur.

This test method establishes the procedures, equipment, materials, and conditions to measure the degree and rate of biodegradation of plastic materials under aerobic thermophilic composting conditions. This test method is designed to produce repeatable and reproducible test results under controlled composting conditions that simulate industrial compost conditions. The testing is completed in duplicate. The plastic test samples are exposed to an inoculum that is derived from industrial compost. The aerobic thermophilic conditions of the test are provided in an environment where temperature, aeration, and humidity are closely monitored and controlled. The plastic samples are cut into small pieces and placed in a vessel with warm and moist compost soil. The test containers are at 58°C (±2°C) for 180 days. The biogas from the container is measured for CO_2 and O_2 over the testing period.

8.3.2.3.2 Procedures The test procedure for ISO 14855 involves placing 120 grams of moist (~50% moisture) industrial compost soil that has maturity level of 6 months and 50% total solids into a container vessel of approximately 500 mL. The containers will be provided for the plastic sample and the following samples, blank, positive control, and negative control. The testing is done in duplicate. The plastic samples are added to the container in quantities of 10 grams. The pH, moisture content, C/N ratio, and percentage solids are measured for the compost soil. The sample containers must have moist air supplied to the container that is free of CO_2. The biogas from the sample containers is measured periodically for CO_2 and O_2. The test containers should be rotated every 2 or 3 days to reduce the packing of the soil and to mix fresh air to the compost soil. The tests are run in duplicate.

8.3.2.3.3 Materials

- Plastic sample
- Blank compost soil
- Positive control reference: cellulose powder
- Negative control: polyethylene film

8.3.2.3.4 Equipment

- Composting vessels with size approximately 500 mL
- Water bath or other temperature control device
- Pressurized air system with CO_2 free and H_2O saturated air
- Carbon dioxide trapping apparatus
- Flexible tubing non-permeable to CO_2
- Stoppers equipped with sampling ports
- Analytical balance (±0.1 mg)
- 100-mL Burette
- pH meter
- Respirometer devices for measuring CO_2 and O_2 periodically (optional)
- CO_2 trapping equipment with gas flow meter, gas chromatograph, or other suitable equipment

8.3.2.4 ISO 16929 (EN14045:2003) Plastics—Determination of the Degree of Disintegration of Plastic Materials under Simulated Composting Conditions in a Pilot-Scale Test

8.3.2.4.1 Summary This international standard specifies a method for the evaluation of the disintegration of plastic materials while under industrial composting conditions. The testing environment is pilot scale at an industrial compost facility. The mass of plastic sample is measured prior to the test. The samples are placed in a sack or aerated bag with compost soil. The sack is placed in an aerated pile of at least 1 meter deep at an industrial compost facility. The compost vessel should be a minimum of 140 liters and a maximum of 250 liters. The concentration is 1% by weight plastic sample and 99% compost. The temperature of the compost pile should be between 40°C and 75°C. The aerated compost pile should be turned twice per week.

8.3.2.4.2 Procedures The test procedure for ISO 16929:

1. Measure the mass of plastic samples.
2. Place in sack or aerated container between 140 and 250 liters.
3. Add samples and compost to sack or container.
4. Bury container in compost pile at least 1 meter from the surface.
5. Rotate the compost soil around container at least twice per week.
6. Measure the temperature of the compost.
7. After 12 weeks, remove compost and plastic.
8. Sieve in 2-mm screen.
9. Wash and dry plastic to remove compost soil.
10. Measure the mass of the plastic samples.
11. Measure the quality of the compost soil for maturity, percentage of solid, pH, moisture content, carbon/nitrogen ratio, temperature.

8.3.2.4.3 Materials

- Plastic
- Mature compost
- Container minimum 140 liters

8.3.2.4.4 Equipment

- Industrial compost facility.

8.3.2.5 ISO 20200 (EN14806:2005) Plastics—Determination of the Degree of Disintegration of Plastic Materials under Simulated Composting Conditions in a Laboratory-Scale Test

8.3.2.5.1 Summary This international standard specifies a method for the evaluation of the disintegration of plastic materials while under industrial composting conditions. The testing environment is pilot scale at an industrial compost facility. The mass of plastic sample is measured prior to the test. The samples are placed in a sack or aerated bag with compost soil. The sack is placed in an aerated pile at least 1 meter deep at an industrial compost facility. The compost vessel should be a minimum of 5 liters and a maximum of 20 liters. The concentration is 1% by weight plastic sample and 99% compost. The temperature of the compost pile should be between 40°C and 75°C. The aerated compost pile should be turned twice per week.

8.3.2.5.2 Procedures The test procedure for ISO 20200:

1. Measure the mass of plastic samples.
2. Place in sack or aerated container between 5 and 20 liters.
3. Add samples and compost to sack or container at concentrations of 1% (weight) plastic and 99% compost.
4. Bury container in compost pile at least 1 meter from the surface.
5. Rotate the compost soil twice per week.
6. Measure the temperature of the compost.
7. After 12 weeks, remove compost and plastic.
8. Sieve in 2-mm screen.
9. Wash and dry plastic to remove compost soil.
10. Measure the mass of the plastic samples.
11. Measure the quality of the compost soil for maturity, percentage of solid, pH, moisture content, carbon/nitrogen ratio, temperature.

8.3.2.5.3 Materials

- Plastic
- Mature compost
- Container minimum 5 liters

8.3.2.5.4 Equipment

- Industrial compost facility.

8.3.2.6 Australian Biodegradation Standards for Industrial Compost

The Australian standard for degradable plastics includes test methods that enable validation of biodegradation of degradable plastics and designation as "compostable" in Australia. The Australian standard for industrial compost is AS4736-2006 (AS4736-2013 2013). The AS4736 standard is based on EN 13432-2000 standard for the determination of the ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions. AS4736-2006 requires that plastic materials meet the following requirements:

1. A minimum of 90% biodegradation of plastic material within 180 days while under industrial composting conditions of 58°C and 50% moisture.
2. A minimum of 90% disintegration of plastic material within 12 weeks while under industrial composting conditions of 58°C and 50% moisture.
3. No toxic effects on the resulting compost for plants and earthworms.
4. Toxic levels of regulated metals are less than the maximum allowable levels.
5. Minimum of 50% organic material in the plastic.

8.3.2.7 Japanese Biodegradation Standards for Industrial Compost

The Japanese JIS standards are met with a GreenPLA certification system. The GreenPLA system has very similar testing requirements as per the US and International certification methods. In particular, the GreenPLA certification assures biodegradability by measuring carbon dioxide evolution after microbial biodegradation, mineralization by the ability to disintegrate and not have visible fragments after composting, and organic compatibility by the ability of the compost to support plant growth. The same amount of carbon dioxide evolution (60%) in 45 days is required for certification. The same 11 regulated metals are monitored in GreenPLA as EN 13432. However, several aspects of the certification are different than the US BPI and International Din-Certco certifications.

8.4 MARINE ENVIRONMENT

Plastic debris is accumulating in the oceans around the world endangering animal life, releasing toxic chemicals, and collecting floating toxins that can enter the food stream through fish. The fate of plastics in the oceans can lead to fragmentation and result in slurry of plastic particles floating or suspended in the water column. The plastic fragments can degrade and release toxic chemicals into the ocean waters.

Biodegradation of biodegradable plastics in marine environment is based upon two levels of standards: the first for a test method standard and the second for a performance specification standard. Biodegradation standards for the marine environment are listed in Table 8.4. The marine biodegradation standards cover non-floating products made from plastics that are designed to biodegrade in the aerobic marine environment. The standard applies to deep seawater, shallow seawater, and brackish inland waters. In the standards, plastic materials must demonstrate disintegration and inherent biodegradation during marine water exposure and not exhibit any adverse environmental impacts on the survival of marine organisms while in the marine environment.

The plastic sample also must pass several marine toxicity tests, including Polytox (microbial oxygen absorption), Microtox (microbial bioluminescence) test, fish Acute Toxicity (static conditions) OPPTS 850.1075, Daphnia Acute Toxicity (static conditions) OPPTS 850.1010, or Static Algal Toxicity Test OPPTS 850.5400. The plastic samples must also have less than 25% of maximum allowable concentrations of regulated heavy metals.

TABLE 8.4
Biodegradation Standards for Marine Environment

Region	Performance specification	Test method	Measurement method	Other requirements
Australia	None	ISO 14851, ISO 14852	CO_2 measurement	None
Europe	None	ISO 14851, ISO 14852	CO_2 measurement	None
Japan	None	ISO 14851, ISO 14852	CO_2 measurement	None
USA	ASTM D7081	ASTM D6691	CO_2 measurement	ASTM D6400

Marine biodegradation standards require that the plastic samples should also pass the ASTM D-6400 standard for biodegradation under industrial aerobic compost conditions. The ASTM D-6400 standard requires plastic samples to convert 90% of the carbon in the plastic sample to CO_2 after 180 days while at 58°C.

8.4.1 US Biodegradation Standards for Marine Environment

8.4.1.1 Biodegradation Performance Specification Standard: ASTM D-7081-05. Non-floating Biodegradable Plastic in the Marine Environment

8.4.1.1.1 Summary This American specification establishes the performance requirements for biodegradation of plastic materials and products, including packaging, films, and coatings. The marine environment includes conditions of aerobic marine waters or anaerobic marine sediments, or both. This specification establishes the requirements for biodegradation of plastic materials that have rates that are similar to known compostable materials. The specification also specifies that the degradation of the plastic materials will not cause any harm to sea life or habitat.

The performance specification standard requires the use of ASTM D6691-08 test method to measure the amount of CO_2 that is emitted from the degrading plastic sample while in the cool marine water.

ASTM D-7081-05 performance specification standard requires the product must demonstrate each of the three characteristics as follows:

1. Disintegration during marine biodegradation.
2. Inherent biodegradation of the plastic material.
3. Minimal adverse effect on the marine environment.

8.4.1.1.2 Procedures The test procedures for ASTM D-7081-05 standard specify that three types of tests are performed on the plastic samples. The first test measures the percentage of disintegration of the plastic samples while exposed to cool marine water conditions, described in ASTM D-6691-08 test conditions. The plastic samples are weighed prior to exposure to test conditions. The samples are placed in containers with ocean water. The plastic samples are exposed to aerobic marine water conditions of 30°C for 12 weeks. The mass of the plastic sample is measured after 12 weeks by passing the plastic sample and marine water through a 2.0-mm sieve. ASTM D-7081-05 specifies that no more than 30% of the original dry weight of the plastic material remains.

The second test procedure for ASTM D-7081-05 standard specifies that a satisfactory rate of *biodegradation* of the plastic material is under marine conditions of 30°C for 180 days, that is, more than 30% of the carbon in the original plastic sample is converted into CO_2 as measured by a CO_2 respirometer or other measurement device. The details of the test procedures are listed in ASTM D6691-08 test method.

The third test procedure for ASTM D-7081-05 standard specifies that the plastic product shall undergo toxicity testing with one of the following tests: Polytox, Microtox, fish acute toxicity, Daphnia acute toxicity, or Static Algal toxicity.

The fourth test procedure for ASTM D-7081-05 standard specifies that the plastic sample shall have less than 25% of the regulated heavy metal concentrations that is specified in the country where the product is sold.

8.4.1.1.3 Specifications ASTM D-7081-05 standard specifies that a plastic coating material is compostable if it meets the following specifications:

1. Satisfactory *disintegration* of the plastic material that is under aerobic marine water test of 30°C for 12 weeks that no more than 30% of the original dry weight of the plastic material remains after passing through a 2.0-mm sieve.
2. Satisfactory rate of *biodegradation* of the plastic material that is under aerobic marine water test of 30°C in 6 months, that is, more than 30% of the carbon in the original plastic sample is converted into CO_2 as measured by measuring the amount of release CO_2.
3. Satisfactory passing of one of the several marine toxicity tests.
4. Less that 25% of the regulated heavy metal concentrations that is specified in the country where the product is sold.
5. Satisfactory rate of *biodegradation* specified in ASTM D6400 standard for compostability is a necessary but not sufficient prerequisite.

8.4.1.2 Biodegradation Test Method Standard: ASTM D6691-09. Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in the Marine Environment by a Defined Microbial Consortium or Natural Seawater Inoculum

8.4.1.2.1 Summary ASTM D6691-09 test method provides a description of the testing procedures that best simulate the marine environment and a method by which to measure biodegradation. ASTM D6691-09 test method is used to determine the degree and rate of aerobic biodegradation of plastic materials exposed to the indigenous population of existing seawater or synthesized seawater with pre-grown population of at least 10 aerobic marine microorganisms of known genera. The ASTM test procedure for marine biodegradation is explained in more detail in Appendix E.

The test method consists of preparing a uniform inoculum of marine water, exposing the plastic samples to the marine water, measuring biodegradation with a carbon dioxide respirometer or equivalent measurement method, and assessing the percentage of carbon conversion in the plastic to carbon dioxide. The testing is carried out at 30 ± 2°C under controlled laboratory conditions for 180 days. The standard recommends the use of 125-mL autoclave bottles, a recipe of marine organisms and nutrients, and seawater. The standard recommends adding 20 mg of plastic sample with 75 mL of marine water inoculum in a constant temperature environment of 30 ± 2°C. The amount of biodegradation of the plastic sample is compared to the biodegradation of a positive control, for example, cellulose powder.

This test method establishes the procedures, equipment, materials, and conditions to measure the degree and rate of biodegradation of plastic materials under aerobic mesophilic marine water conditions. This test method is designed to produce repeatable and reproducible test results under controlled test conditions that simulate the marine environment.

8.4.1.2.2 Procedures The test procedures for ASTM D6691-08 involve placing 20 mg of plastic sample with 75 mL of marine stock solution or natural seawater with inorganic nutrients are placed in 125-mL bottles in a sterile environment as shown in Figure 8.2. A minimum of 12 composting vessels are required for the test. The

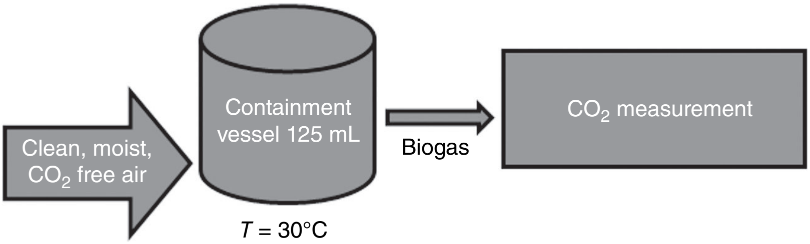

FIGURE 8.2 Experimental setup for laboratory environment of marine biodegradation test.

containers will be provided for the plastic sample and the following samples, blank, positive control, and negative control. The testing is completed in triplicate. The marine inoculum is tested for marine ingredients.

8.4.1.2.3 Materials

- Plastic samples
- Blank marine water
- Positive control: cellulose powder or paper
- Negative control: polyethylene film

8.4.1.2.4 Equipment

- Sterile jar with volume of 125 mL
- Water bath or other temperature control device
- Carbon dioxide trapping apparatus with $Ba(OH)_2$ solution
- Flexible tubing non-permeable to CO_2
- Stoppers equipped with sampling ports
- Analytical balance (±0.1 mg)
- pH meter
- Respirometer devices for measuring CO_2 and O_2 periodically (optional)
- CO_2 trapping equipment with gas flow meter, gas chromatograph, or other suitable equipment

8.4.2 International Aqueous Biodegradation Standards

8.4.2.1 Biodegradation Test Method Standard: ISO 14852-1999 (EN14047). Determination of Ultimate Aerobic Biodegradability of Plastic Materials in an Aqueous Medium—Method by Analysis of Evolved Carbon

8.4.2.1.1 Summary This international standard specifies a method for the evaluation of the biodegradation of plastic materials while exposed to aqueous mineral medium. Biodegradation is determined by measuring the evolved carbon dioxide from the biodegrading sample. The test is used to measure the degree and rate of aerobic biodegradation of plastic materials on exposure to activated-sludge biomass or a suspension of active soil under laboratory conditions at solid concentrations between 100 and 2000 mg/L. The temperature of the test environment should be between 20°C and 25°C. The tests are run in duplicate.

8.4.2.1.2 Procedures The test procedure for ISO 14852 is:

1. Measure the mass of plastic samples.
2. Measure the quality of the inoculum soil for percentage of solid, pH, moisture content, carbon/nitrogen ratio, temperature. Carbon/nitrogen ratio should be approximately 40:1.
3. Add the plastic sample in the form of powder or small pieces to a concentration of 100–2000 mg/L of TOC with activated sludge or active soil in a test flask.
4. Connect the sample flasks to CO_2 free air production.
5. Maintain the test flasks at temperature between 20°C and 25°C.
6. Bubble CO_2 free air through flasks at a rate of 50–100 mL/min.
7. Measure CO_2 from the sample flasks.

8.4.2.1.3 Materials

- Plastic samples
- Blank activated sludge or active soil
- Positive control: cellulose powder or cellulose paper

- Negative control: polyethylene film
- Barium hydroxide solution

8.4.2.1.4 Equipment

- Flasks
- Water bath or other temperature control device
- Pressurized air system with CO_2 free and H_2O saturated air
- Carbon dioxide trapping apparatus
- Flexible tubing non-permeable to CO_2
- Stoppers equipped with sampling ports
- Analytical balance (±0.1 mg)
- 100-mL Burette
- 0.05 N HCL
- pH meter
- CO_2 trapping equipment with gas flow meter, gas chromatograph, or other suitable equipment

8.4.2.2 Biodegradation Test Method Standard: ISO 14851 (EN14048). Determination of Ultimate Aerobic Biodegradability of Plastic Materials in an Aqueous Medium—Method by Measuring the Oxygen Demand in a Closed Respirometer

8.4.2.2.1 Summary This International standard specifies a method for the evaluation of the biodegradation of plastic materials while exposed to aqueous mineral medium. Biodegradation is determined by measuring oxygen demand produced from the biodegrading sample. The percentage of biodegradation is calculated by comparing the biological oxygen demand to the chemical oxygen demand, determine by chemical oxidation of the test item or by stoichiometric formula. The principle and test procedures are very similar to ISO 14852 (Bastioli 2005).

The test is used to measure the degree and rate of aerobic biodegradation of plastic materials on exposure to activated-sludge biomass or a suspension of active soil under laboratory conditions at solid concentrations between 100 and 2000 mg/L. The temperature of the test environment should be between 20°C and 25°C. The tests are run in duplicate.

8.4.2.2.2 Procedures The test procedure for ISO 14852 is:

1. Measure the mass of plastic samples.
2. Add the plastic sample in the form of powder or small pieces to a concentration of 100–2000 mg/L of TOC with activated sludge or active soil in a test flask.
3. Connect the sample flasks to CO_2 free air production.
4. Maintain the test flasks at temperature between 20°C and 25°C.
5. Bubble CO_2 free air through flasks at a rate of 50–100 mL/min.
6. Measure CO_2 from the sample flasks.

8.4.2.2.3 Materials

- Plastic samples
- Blank activated sludge or active soil
- Positive control: cellulose powder or cellulose paper
- Negative control: polyethylene film

8.4.2.2.4 Equipment

- Flasks
- Water bath or other temperature control device
- Pressurized air system with CO_2 free and H_2O saturated air
- Flexible tubing non-permeable to CO_2
- Stoppers equipped with sampling ports
- Analytical balance (±0.1 mg)
- 100-mL Burette
- pH meter
- O_2 trapping equipment with gas flow meter, gas chromatograph, or other suitable equipment

8.5 ANAEROBIC DIGESTION

Anaerobic digestion is a process where food and agricultural waste can be converted to methane and carbon dioxide in a thermophilic reactor. Anaerobic digestion is a series of processes in which microorganisms break down biodegradable material in the absence of oxygen (NNFCC

Renewable Fuels and Energy Factsheet: Anaerobic Digestion 2013). It is used for industrial or domestic purposes to manage waste and/or to release energy.

The digestion process begins with bacterial hydrolysis of the input materials to break down insoluble organic polymers, such as carbohydrates, and make them available for other bacteria. Acidogenic bacteria then convert the sugars and amino acids into carbon dioxide, hydrogen, ammonia, and organic acids. Acetogenic bacteria then convert these resulting organic acids into acetic acid, along with additional ammonia, hydrogen, and carbon dioxide. Finally, methanogens convert these products to methane and carbon dioxide.

Anaerobic digestion is used as part of the process to treat organic and agricultural waste and sewage sludge. Anaerobic digestion can also be used to remove organic waste at waste water treatment operations. Biodegradable plastics can hold organic and agricultural waste with the use of biodegradable plastic bags. The biodegradable plastic can be a food source for the anaerobes in the digester. The biodegradable plastic and organic waste can be converted in to carbon dioxide, methane, and other trace gases.

Standards are necessary to monitor the performance of biodegradable plastics in an aerobic digestion reactor. The anaerobic decomposition takes place under high solids (more than 30% total solids) and static non-mixed conditions. The biodegradation process usually requires 1–2 weeks of dwell time. Table 8.5 lists the biodegradation standards for anaerobic digestion.

8.5.1 US Biodegradation Standards for Anaerobic Digestion

8.5.1.1 Biodegradation Test Method Standard: ASTM D5511-02. Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials under High Solids Anaerobic-Digestion Conditions

8.5.1.1.1 Summary This test method establishes the procedures, equipment, materials, and conditions to measure the degree and rate of biodegradation of plastic materials under anaerobic thermophilic conditions in an aqueous environment. This test method is designed

TABLE 8.5
Biodegradation Standards for Anaerobic-Digestion Environment

Region	Performance specification	Test method	Measurement method
Australia	None	ISO 14853	CO_2 measurement
Europe	None	ISO 14853	CO_2 measurement
Japan	None	ISO 14853	None
USA	None	ASTM D5511	CO_2 measurement

to produce repeatable and reproducible test results under controlled anaerobic-digestion conditions that simulate industrial conditions. The plastic test samples are exposed to an inoculum that is derived from an aerobic digester or waste water treatment operation. The anaerobic thermophilic conditions of the test are provided in an environment where temperature, methane, carbon dioxide, and oxygen levels are closely monitored and controlled. The plastic samples can be in the form of films, powders, pellets, or molded pieces and are placed in a vessel with warm inoculum with proper anaerobic bacteria. The test containers are at 50°C (±2°C) for 30 days. The biogas from the container is measured for CH_4, CO_2, and O_2 over the testing period. The standard for anaerobic digestion comprises a biodegradation test method and not a biodegradation specification.

8.5.1.1.2 Procedures The test procedures for ASTM D-5511-02 involve placing 1000 grams of inoculum derived from properly operating anaerobic digester that is made from pretreated household waste. The inoculum should be derived from a digester operating under greater than 20% total solids conditions. A minimum of 12 test vessels are required for the test. The containers will be provided for the plastic sample and the following plastic samples, blank, positive control, and negative control. The testing is completed in triplicate. The plastic samples are added to each test container in quantities up to 100 grams. The positive control must obtain greater than 70% biodegradation in 30 days. The inoculum is tested for pH, volatile fatty acids, and NH_4^+-N ratio.

The test apparatus can include an inverted graduated cylinder or plastic column. The graduated cylinder or plastic column is inverted in a low pH fluid to avoid CO_2 loss through the dissolution in the fluid. The biogas is calculated through a pressure measurement of the inverted tubes. The biogas can also be measured with a gas chromatograph to determine the percentage of CH_4 and CO_2 in the biogas. An example

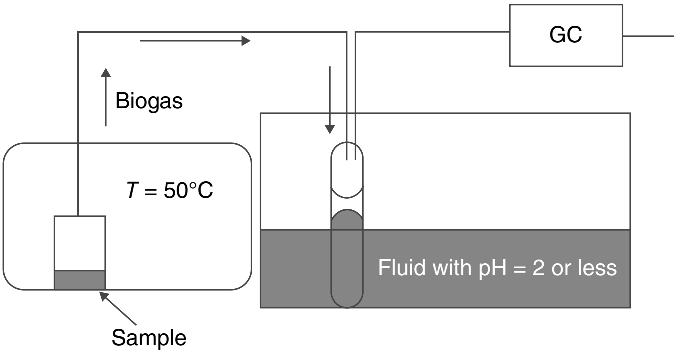

FIGURE 8.3 Experimental setup for laboratory environment for anaerobic digester test per ASTM standards.

of a test apparatus is provided in Figure 8.3. The testing apparatus will provide measurements of pressure over 30 days. Through ideal gas law, the pressure can be converted to grams of biogas. The concentration of biogas can be converted to concentrations of CO_2 and CH_4. The conversion of carbon from the plastic sample to CO_2 and CH_4 can be determined. This will result in the carbon biodegradation percentage over 30 days in a high solids anaerobic digester.

8.5.1.1.3 Materials

- Plastic samples
- Blank anaerobic digester inoculum
- Positive control: cellulose powder or cellulose paper
- Negative control: polyethylene film

8.5.1.1.4 Equipment

- Test jars
- Low pH fluid bath or other temperature control device
- Flexible tubing non-permeable to $CH_{4,}$ $CO_{2,}$ O_2
- Stoppers equipped with sampling ports
- Graduated cylinder or plastic tube
- Analytical balance (±0.1 mg)
- pH meter
- Gas chromatograph

8.5.2 International Biodegradation Standards for Anaerobic Digestion

8.5.2.1 Biodegradation Test Method Standard: ISO 14853:2005 Plastics. Determination of Ultimate Anaerobic Biodegradation of Plastic Materials in an Aqueous System. Method of Biogas Production

8.5.2.1.1 Summary This test method specifies a method for determining the ultimate biodegradability of plastics by anaerobic microorganisms. The conditions described in this test method simulate the conditions of some anaerobic digesters. The plastic test samples are exposed to an inoculum that is derived from digested sludge from waste water treatment operations. The anaerobic thermophilic conditions of the test are provided in an environment where temperature, methane, carbon dioxide, and oxygen levels are closely monitored and controlled. The plastic samples can be in the form of films, powders, pellets, or molded pieces and are placed in a vessel with warm inoculum with proper anaerobic bacteria. The test containers are at 35°C (±2°C) for 60 days. The biogas from the container is measured for CH_4, CO_2, and O_2 over the testing period. The standard for anaerobic digestion comprises a biodegradation test method and not a biodegradation specification.

8.5.2.1.2 Procedures The test procedures for ISO 14853:2005 involve placing 1000 mL of inoculum derived from properly operating anaerobic digester that is made from digested sludge. The concentration of test materials is 20–200 mg/L of organic carbon. Approximately, 350 mL of inoculum is added to the test sample. A head space of 20% is recommended. A reference material or positive control can be cellulose, poly (hydroxybutyrate), or poly (ethylene glycol). The glass vessels have sizes of 0.1–1 liters with gas tight septum rated for 2000 kPa. Plastic samples are added to glass containers that include plastic samples, blank, positive control, and negative control. The testing is completed in triplicate. The positive control must obtain greater than 70% biodegradation in 60 days. The inoculum is tested for pH, volatile fatty acids, and NH_4^+-N ratio.

Biogas measurement is achieved with a monometer or volumetric device. An example of a test apparatus is provided in Figure 8.4. The testing apparatus will provide measurements of pressure over 60 days. Through ideal gas law, the pressure can be converted to grams of biogas. The concentration of biogas can be converted to concentrations of CO_2

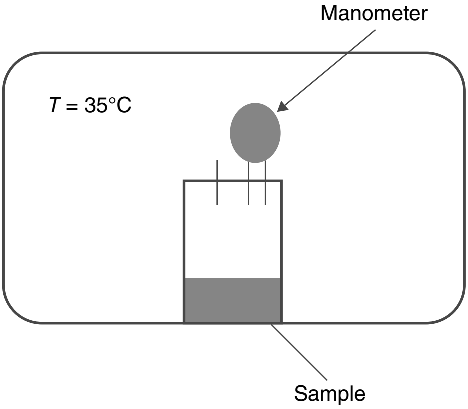

FIGURE 8.4 Experimental setup for laboratory environment for anaerobic digester test per ISO standards.

and CH_4. The conversion of carbon from the plastic sample to CO_2 and CH_4 is determined. This will result in the carbon biodegradation percentage over 30 days in a high solids anaerobic digester.

8.5.2.1.3 Materials

- Plastic samples
- Blank anaerobic digested sludge inoculum
- Positive control: cellulose powder or poly(hydroxybutyrate), or poly(ethylene glycol)
- Negative control: polyethylene film

8.5.2.1.4 Equipment

- Test jars: 0.1–1 liters
- Low pH fluid bath or other temperature control device
- Flexible tubing non-permeable to CH_4, CO_2, O_2
- Stoppers equipped with sampling ports
- Graduated cylinder or plastic tube
- Manometer
- Analytical balance (±0.1 mg)
- pH meter
- Gas chromatograph

TABLE 8.6
Biodegradation Standards for Active Landfill Environment

Region	Performance specification	Test method	Measurement method
Australia	None	None	–
Europe	None	None	–
Japan	None	None	–
USA	None	D5526, D7575	CO_2 measurement

8.6 ACTIVE LANDFILL

Landfills in the United States are typically built with the EPA guidelines with the use of clay linings and a landfill cap (Criteria for Solid Waste Disposal Facilities 2013). The most common material for landfill caps is made from asphalt or concrete (Remediation Technologies Screening Matrix and Reference Guide 2013). Landfills can operate with creation of biogas that is composed of methane, carbon dioxide, and other trace gases. Methane gas can be vented and burned or can be captured and stored for energy purposes. The carbon dioxide and other gases must be scrubbed to provide a clean methane gas without carbon dioxide or other gases. Some landfills are considered active and provide clean methane gas for energy consumption. Biodegradable plastics can hold the waste as trash bags for disposal and provide food source for the aerobic and anaerobic bacteria that are in the landfill. Standards are needed to evaluate the biodegradation of biodegradable plastics in landfills. Table 8.6 lists the biodegradation standards for an active landfill environment. The standard for active landfill comprises a biodegradation test method and not a biodegradation specification.

8.6.1 US Biodegradation Standards for Active Landfill

8.6.1.1 Biodegradation Test Method Standard: ASTM D5526-11. Determining Anaerobic Biodegradation of Plastic Materials under Accelerated Landfill Conditions

8.6.1.1.1 Summary This test method establishes the degree and rate of anaerobic biodegradation of plastic materials under anaerobic mesophilic conditions in an accelerated landfill test environment. This test method is designed to yield percentage of carbon conversion from the plastic sample to methane or carbon dioxide biogas. This test method is designed to provide repeatable and reproducible test results under controlled anaerobic conditions that simulate high solids (>30%) active landfill conditions. The plastic test samples are exposed to an inoculum that is derived from an aerobic digester or waste water treatment operation. The anaerobic mesophilic conditions of the test are provided in an environment where temperature, methane, carbon dioxide, and oxygen levels are closely monitored and controlled. The plastic samples can be in the form of films, powders, pellets, or molded pieces and are placed in a vessel with cool inoculum with proper anaerobic bacteria. The test containers are at 35°C (±2°C) for up to 365 days. The biogas from the container is measured for CH_4, CO_2, and O_2 over the testing period.

8.6.1.1.2 Procedures The test procedures for ASTM D5526 involve placing 600 grams of household waste with 100 grams of inoculum derived from properly operating anaerobic digester that is made from pretreated household waste. The inoculum should be derived from a digester operating under greater than 30% total solids conditions. A minimum of 27 test vessels are required for the test with a volume between 4 and 6 liters. The containers will be provided for the plastic sample and the following plastic samples, blank, positive control, and negative control. The testing is completed in triplicate. The plastic samples are added to each test container in quantities between 60 and 100 grams of dry weight. The mixture should contain approximately 60% dry weight of solids. The positive control must obtain greater than 70% biodegradation at the end of the test. The inoculum is tested for pH, volatile fatty acids, and NH_4^+-N ratio.

The test apparatus can include a pressure-resistant glass vessel. The vessel should withstand a pressure of two atmospheres. The graduated cylinder or plastic column is inverted in a low pH fluid to avoid CO_2 loss through the dissolution in the fluid. The biogas is calculated through a pressure measurement of the inverted tubes. The biogas can also be measured with a gas chromatograph to determine the percentage of CH_4 and CO_2 in the biogas. An example of a test apparatus is provided in Figure 8.5. The testing apparatus will provide measurements of pressure over 30 days. Through ideal gas law, the pressure can be converted to grams of biogas. The concentration of biogas can be converted to

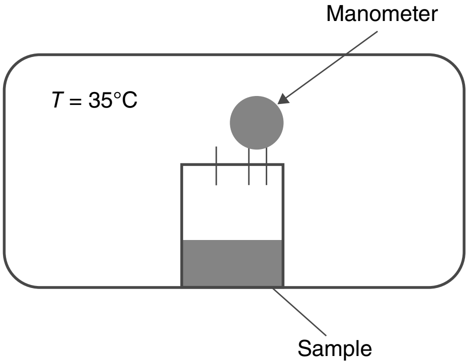

FIGURE 8.5 Experimental setup for laboratory environment for active landfill test.

concentrations of CO_2 and CH_4. The conversion of carbon from the plastic sample to CO_2 and CH_4 can be determined. This will result in the carbon biodegradation percentage over 30 days in a high solids anaerobic digester.

8.6.1.1.3 Materials

- Plastic samples
- Anaerobic digester inoculum
- Pretreated household solid organic waste
- Positive control: cellulose powder or cellulose paper
- Negative control: polyethylene film

8.6.1.1.4 Equipment

- Test jars
- Flexible tubing non-permeable to CH_4, CO_2, O_2
- Stoppers equipped with sampling ports
- Incubator
- Pressure transducer
- Analytical balance (±0.1 mg)
- pH meter
- Gas chromatograph

8.6.1.2 Biodegradation Test Method Standard: ASTM D7475-11. Determining Aerobic Degradation and Anaerobic Biodegradation of Plastic Materials under Accelerated Landfill Conditions

8.6.1.2.1 Summary This two-tiered test method modifies ASTM D5526 by adding an aerobic degradation test method to the anaerobic biodegradation test method. ASTM D7475 establishes the degree of aerobic degradation and rate of anaerobic biodegradation of plastic materials under anaerobic mesophilic conditions in an accelerated landfill test environment. This test method is designed to establish mechanical tests or materials tests in addition to percentage of carbon conversion from the plastic sample to methane or carbon dioxide biogas. This test method is designed to provide repeatable and reproducible test results under controlled aerobic and anaerobic conditions that simulate high solids (>30%) active landfill conditions. The plastic test samples are exposed to an inoculum that is derived from an aerobic digester or waste water treatment operation. The first tier of the test method is designed to estimate aerobic biodegradation through the measurement of loss of mechanical properties, for example, tensile strength or modulus, molecular weight, or other characteristics. In the second tier of the test method, anaerobic is designed to provide mesophilic conditions of the test in an environment where temperature, methane, carbon dioxide, and oxygen levels are closely monitored and controlled. The plastic samples can be in the form of films, powders, pellets, or molded pieces and are placed in a vessel with cool inoculum with proper anaerobic bacteria. The test containers are at 35°C (±2°C) for up to 365 days. The biogas from the container is measured for CH_4, CO_2, and O_2 over the testing period.

8.6.1.2.2 Procedures The test procedures for the first tier of ASTM D7475-11 involve measuring baseline mechanical or chemical properties and then placing test specimens in an aerobic degradation environment. The mechanical or chemical properties are measured after a specified time. Differences in mechanical or chemical properties are recorded.

The test procedures for the second tier of ASTM D7475-11 involve placing 600 grams of household waste with 100 grams of inoculum derived from properly operating anaerobic digester that is made from pretreated household waste. The inoculum should be derived from a digester operating under greater than 30% total solids conditions. A minimum of 27 test vessels are required for the test with a volume between 4 and 6 liters. The containers will be provided for the plastic sample and the following plastic samples, blank, positive control, and negative control. The testing is completed in triplicate. The plastic samples are added to each test container in quantities between 60 and 100 grams of dry weight. The mixture should contain approximately 60% dry weight of solids. The positive control must obtain greater than 70% biodegradation at the end of the test. The inoculum is tested for pH, volatile fatty acids, and NH_4^+-N ratio.

The test apparatus can include a pressure-resistant glass vessel. The vessel should withstand a pressure of two atmospheres. The graduated cylinder or plastic column is inverted in a low pH fluid to avoid CO_2 loss through the dissolution in the fluid. The biogas is calculated through a pressure measurement of the inverted tubes. The biogas can also be measured with a gas chromatograph to determine the percentage of CH_4 and CO_2 in the biogas. An example of a test apparatus is provided in Figure 8.5. The testing apparatus will provide measurements of pressure over 30 days. Through ideal gas law, the pressure can be converted to grams of biogas. The concentration of biogas can be converted to concentrations of CO_2 and CH_4. The conversion of carbon from the plastic sample to CO_2 and CH_4 can be determined. This will result in the carbon biodegradation percentage over 30 days in a high solids anaerobic digester.

8.6.1.2.3 Materials

- Plastic samples
- Anaerobic digester inoculum
- Pretreated household solid organic waste
- Positive control: cellulose powder or cellulose paper
- Negative control: polyethylene film

8.6.1.2.4 Equipment

- Test jars
- Flexible tubing non-permeable to $CH_{4,}$ $CO_{2,}$ O_2
- Stoppers equipped with sampling ports

- Incubator
- Pressure transducer
- Analytical balance (±0.1 mg)
- pH meter
- Gas chromatograph
- Mechanical tests, for example, tensile, impact, etc.
- Chemical tests, for example, FTIR, DSC, GC/MS, molecular weight

8.6.2 International Biodegradation Standards for Active Landfill

Currently, there are no ISO test methods that are equivalent active landfill standard test method.

8.7 HOME COMPOST

8.7.1 European Home Compost Certification

AIB-Vinçotte International has a biodegradable home compost test certification for plastic products that references EN 13432 performance specification and other ISO biodegradable test methods. Biodegradation in soil environments is based on International OK Biodegradable Soil standards. Table 8.7 lists the biodegradation standards for home composing.

TABLE 8.7
Biodegradation Standards for Home Composting Environment

Region	Performance specification	Test method	Measurement method
Australia	None	None	–
Europe	EN13432 modified for longer times	ISO 14855-2 modified for lower temperatures	CO_2 measurement
Japan	None	None	–
USA	None	None	–

8.7.1.1 Summary

This European certification establishes the performance requirements for biodegradation of plastic materials and products (including packaging, films, and other products) while under cool home composting conditions. The certification specifies modifications to EN 13432. The home compost environment is one that maintains a temperature below 30°C and results in mesophilic conditions. The certification requires the use of EN 14855 (ISO 17088) test method to measure the amount of CO_2 that is emitted from the degrading plastic sample. Vinçotte home compost certification requires the product must demonstrate each of the four characteristics as follows:

1. biodegradability;
2. disintegration during biological treatment;
3. minimal effect on the organic matter with limit on heavy metals and other hazardous substances; and
4. minimal effect on the quality of the resulting compost.

8.7.1.2 Procedures

The Vinçotte home compost certification specifies that three types of tests are performed on the plastic samples. The first test measures the percentage of disintegration of the plastic samples while under cool home compost conditions. The plastic samples are weighed prior to exposure to test conditions. The samples are placed in home compost soil with the use of a sack, bag, or screened container. The plastic samples are exposed to home composting conditions between 20°C and 30°C for 12 months. The mass of the plastic sample is measured after 6 months by passing the plastic sample and compost through a 2.0-mm sieve. EN 13432 standard specifies that no more than 10% of the original dry weight of the plastic material remains.

The second test procedure for EN 13432 standard specifies that a satisfactory rate of *biodegradation* of the plastic material that is cool home composting conditions between 20°C and 30°C for 12 months, that is, more than 90% of the carbon in the original plastic sample is converted into CO_2 as measured by a CO_2 respirometer or wet chemistry methods. The details of the test procedures are listed in ISO 14855, ISO 14851, ISO 14852, or ISO 17566 test methods.

The third test procedure for the EN 13432 standard specifies a satisfactory ability of the compost soil at the end of the biodegradation testing to *support plant growth* through phytotoxicity testing and very low regulated heavy metal concentrations. Phytotoxicity testing is achieved through planting of two seed crops in the tested compost soil. The growth of the plants after 10 days indicates positive soil conditions for plant growth. Plant biomass tests can reveal quality differences between composts and can indicate potential plant stress induced by the compost at the given level used in the test.

Regulated heavy metal testing measures the concentrations of regulated heavy metals or other toxic and hazardous substances in the compost soil at the end of the biodegradation testing. The concentrations of regulated heavy metals or other toxic and hazardous substances must be less than 0.1% of the dry weight of the plastic material.

8.7.1.3 Specifications

Home compost specification specifies that a plastic material is compostable if it meets the following specifications:

1. Satisfactory *disintegration* of the plastic material that is under home composting conditions between 20°C and 30°C for 12 months that no more than 10% of the original dry weight of the plastic material remains after passing through a 2.0-mm sieve. Also, the biodegradation testing shall not have any adverse effects on the composting process.
2. Satisfactory rate of *biodegradation* of the plastic material that is under industrial composting conditions between 20°C and 30°C for 12 months, that is, more than 90% of the carbon in the original plastic sample is converted into CO_2 as measured by measuring the amount of release CO_2 through wet chemistry methods.
3. Satisfactory ability of the compost soil at the end of the biodegradation testing to *support plant growth* through phytotoxicity testing and less than 0.1% of dry weight of regulated heavy metals, toxic, or hazardous substances.

8.7.2 US Home Composting Standards

Currently, ASTM does not have a test method or specification for home compost biodegradation.

TABLE 8.8
Biodegradation Standards for Soil Biodegradation Environment

Country	Performance specification	Test method	Measurement method
Australia	None	None	–
Europe	EN13432 modified for longer times	ISO 14855-2 modified for lower temperatures	CO_2 measurement
Japan	None	None	–
USA	None	None	–

8.8 SOIL BIODEGRADATION

8.8.1 European Soil Biodegradation Certification

AIB-Vinçotte International has a certification for biodegrade in soil environments based on International OK Biodegradable Soil standards. The certification for plastic products references EN 13432 performance specification and other ISO biodegradable test methods. Table 8.8 lists the biodegradation standards for soil biodegradation.

8.8.1.1 Summary

This European certification establishes the performance requirements for biodegradation of plastic materials and products (including packaging, films, and other products) while under cool soil burial conditions. The certification specifies modifications to EN 13432. The soil biodegradation environment is one that maintains a temperature below 30°C and results in mesophilic conditions. The certification requires the use of EN 14855 (ISO 17088) test method to measure the amount of CO_2 that is emitted from the degrading plastic sample. Vinçotte soil biodegradation certification requires the product must demonstrate each of the following characteristics:

1. biodegradability and
2. minimal ecotoxicity on the organic matter with limit on heavy metals and other hazardous substances.

8.8.1.2 Procedures

The Vinçotte soil biodegradation certification specifies that two types of tests are performed on the plastic samples. The first test procedure for modified EN 13432 standard specifies that a satisfactory rate of *biodegradation* of the plastic material is under soil burial conditions between 20°C and 30°C for 24 months, that is, more than 90% of the carbon in the original plastic sample is converted into CO_2 as measured by a CO_2 respirometer or wet chemistry methods. The details of the test procedures are listed in ISO 14855, ISO 14851, ISO 14852, or ISO 17566 test methods.

The third test procedure for the modified EN 13432 standard specifies a satisfactory ability of the soil at the end of the biodegradation testing to *support plant growth* through ecotoxicity testing to identify detrimental environmental effects. Testing is conducted according to methods listed in EN 13432 on ecotoxicity.

8.8.1.3 Specifications

Soil biodegradation specification specifies that a plastic material is compostable if it meets the following specifications:

- Satisfactory rate of *biodegradation* of the plastic material that is under industrial composting conditions between 20°C and 30°C for 24 months, that is, more than 90% of the carbon in the original plastic sample is converted into CO_2 as measured by measuring the amount of release CO_2 through wet chemistry methods.
- Satisfactory ability of the compost soil at the end of the biodegradation testing to *support plant growth* through ecotoxicity testing.

8.8.2 US Soil Biodegradation Standards

Currently, ASTM does not have a test method or specification for soil biodegradation.

8.9 SUMMARY

Biodegradation standards of plastic materials require that plastic materials must convert to CO_2, water, and biomass in a disposal environment in a defined timespan. Biodegradation standards are established from several worldwide standards organizations for disposal environments, including industrial compost, marine environment, anaerobic digestion, landfill, and home compost. Biodegradation standards for plastic materials in industrial compost and marine environments are established based on two necessary categories for biodegradation: biodegradation testing method and biodegradation performance specifications.

For industrial compost, ISO and ASTM composting standards require that plastic materials under prescribed testing conditions, disintegrate sufficiently after 12 weeks during composting, biodegrade sufficiently after 180 days, and result in no adverse impacts on the ability of compost to support plant growth. Certification is available for meeting ISO or ASTM standards for biodegradation under industrial compost.

For home compost, Vinçotte has a certification for biodegrade in soil environments based on International OK Biodegradable Soil standards. The home composting certificate requires that plastic materials under prescribed testing conditions, biodegrade sufficiently after 24 months, and result in no adverse impacts on the ability of compost to support plant growth. ASTM does not, currently, provide standards for home composting.

For marine environment, ISO and ASTM composting standards require that plastic materials under prescribed testing conditions, disintegrate sufficiently after 12 weeks during composting, biodegrade sufficiently after 180 days, and result in no adverse effect on the marine environment. Certification is available for meeting ISO or ASTM standards for marine biodegradation.

Anaerobic digestion has ISO and ASTM standards for testing methods but not for biodegradation performance. Anaerobic-digestion test method establishes the procedures, equipment, materials, and conditions to measure the degree and rate of biodegradation of plastic materials under anaerobic thermophilic conditions. Certification is not available for meeting performance standards for biodegradation under anaerobic-digestion conditions.

Test method standards for plastic materials in active landfill conditions are available with ASTM standards but not with ISO standards. This test method establishes the degree and rate of anaerobic biodegradation of plastic materials under anaerobic mesophilic conditions in an accelerated landfill test environment. Certification is not available for meeting performance standards for biodegradation under active landfill conditions.

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REVIEW QUESTIONS

Q.8.1 ASTM D6400 and EN14432 require that plastic materials biodegrade into CO_2 at a rate greater than 90% conversion within 180 days. T or F?

Q.8.2 ASTM D5333 and EN14432 require that cellulose positive control biodegrade into CO_2 at a rate of 40% within 45 days.

Q.8.3 ASTM 7081 requires that plastic materials biodegrade into CO_2 at a rate greater than 50% conversion within 180 days. T or F?

Q.8.4 Plastics can be certified as biodegradable in landfill if they meet the requirements of ASTM D5526? T or F?

Q.8.5 Vinçotte LLC provides certification for soil biodegradation for plastics based on a modified EN 13432. T or F?

Q.8.6 ASTM D5338 is the test method for industrial compost biodegradation and requires that 100 grams of plastic pieces be added to 600 grams of compost soil. T or F?

Q.8.7 ASTM D5338 is the test method for industrial compost biodegradation and requires that the sample pieces and compost be held at 58°C with 50% moisture for 180 days. T or F?

Q.8.8 ASTM D6691 is the test method for marine biodegradation and requires that the samples pieces and marine water be held at 30°C for 180 days. T or F?

Q.8.9 Plastic samples can claim biodegradation in landfill environment based on ASTM D5511 biodegradation standards. T or F?

Q.8.10 Plastic pellets can be tested for biodegradation under industrial composting conditions. T or F?

REVIEW PROBLEMS

P.8.1 Which of the following are not biodegradation standard agencies?

a. ASTM
b. ISO
c. EPA
d. JIS

P.8.2 Which of the following ASTM standards establishes biobased content in materials?

a. ASTM D5338

- **b.** ASTM D6400
- **c.** ASTM D6996
- **d.** ASTM D7880

P.8.3 What standards are required for a plastic to establish biodegradation?

- **a.** Test method standard alone
- **b.** Performance standard alone
- **c.** Test method and performance standard
- **d.** Certification by ASTM

P.8.4 ASTM D6400 biodegradation standard requires which of the following tests?

- **a.** Biodegradation and disintegration tests
- **b.** Biodegradation test, disintegration test, and regulated heavy metals test
- **c.** Biodegradation test and phytotoxicity test
- **d.** Biodegradation test, disintegration test, phytotoxicity test, and regulated heavy metals test

P.8.5 ASTM D7081 biodegradation standard requires which of the following tests?

- **a.** Biodegradation and disintegration tests
- **b.** Marine biodegradation test, marine animal toxicity test, and regulated heavy metals test
- **c.** Biodegradation test and marine animal toxicity test
- **d.** Marine biodegradation test, industrial compost test, and regulated heavy metals test

P.8.6 How much plastic sample and marine water are combined under ASTM D6691 conditions?

- **a.** 100 grams sample and 600 mL of ocean water
- **b.** 10 grams sample and 150 mL of ocean water
- **c.** 20 mg sample and 75 mL of ocean water
- **d.** 30 mg sample and 125 mL of ocean water

P.8.7 What test methods are used to measure biodegradation in anaerobic digesters?

- **a.** ISO 14853
- **b.** ISO 14855
- **c.** ASTM 6400
- **d.** ASTM 7081

P.8.8 How is biodegradation measured in ASTM D5511?

a. Through mass loss of the plastic sample after 12 months.

b. Through biogas measurement from a CO_2 detector after 2 years.

c. Through biogas measurement from pressure measurement of inverted tubes after 12 months.

d. Through disintegration of the plastic samples after 60 days.

P.8.9 How is biodegradation measured for home compost biodegradation environment?

a. Through disintegration of the plastic samples after 12 weeks.

b. Through biogas measurement from a CO_2 detector after 12 months.

c. Through mass loss of the plastic sample after 24 months.

d. Through biogas measurement from a CO_2 detector after 18 months.

P.8.10 What are the temperature and test duration test requirements for plastic samples under soil biodegradation certification from Vinçotte?

a. 20–30°C for 180 days

b. 30–40°C for 360 days

c. 20–30°C for 720 days

d. 30–40°C for 720 days

REVIEW EXERCISES

E.8.1 Compare the biodegradation testing standards for ASTM D6400 and ISO 17088. What are testing methods used for each? What are the biodegradation requirements for each?

E.8.2 Compare the biodegradation test method standards for ASTM D5338 and ISO 14855-2? What are the conditions for each test method? What are the positive and negative controls for each?

E.8.3 Compare the biodegradation standards for anaerobic digestion and active landfill? What are the conditions for each test method? Can a plastic material claim to be biodegradable in landfill conditions? Why or why not?

E.8.4 Compare the certification for soil biodegradation in the United States and Europe? What are the conditions for each test method? Can a plastic material claim to be biodegradable in soil conditions? Why or why not?

E.8.5 Compare the biodegradation test method standards for ASTM D7081 and ISO 14852-1999? What are the test conditions for each test method? What are the positive and negative controls for each?

CHAPTER 9

Sustainable Strategies for Plastics Companies

9.1 SUSTAINABLE PLASTICS MANUFACTURING AND BEST PRACTICES

Sustainable plastics manufacturing is an operational management of the supply chain of the manufacturing process to reduce carbon footprint, waste, and pollution generation. Sustainable plastic manufacturing incorporates Operation Clean Sweep (OCS 2013) practices to reduce pellet loss. Waste oils, inks, and concentrates are recycled, regulated heavy metals are not used as paints, and water-based paints are used. Commercial examples of sustainable plastics manufacturing are the Ingeo PLA from NatureWorks LLC that increased the production output of PLA with lower energy and lower carbon footprint (NatureWorks LLC$^{\text{TM}}$ Ingeo Story 2013).

The new Ingeo production system implemented new fermentation technology to reduce environmental impacts. The 2009 version of Ingeo was an improvement to the 2005 version of PLA. As shown in Table 7.16, the 2009 Ingeo PLA is produced with 15% less energy, 39% less global warming potential, 23% less eutrophication pollution, and 16% less acidification pollution. Overall, the 2009 Ingeo PLA has 24% less environmental impacts than the 2005 version of PLA as defined by the Greene sustainability index from Table 7.16.

Sustainable Plastics: Environmental Assessments of Biobased, Biodegradable, and Recycled Plastics, First Edition. Joseph P. Greene.

9.2 MANUAL CREATION OF LIFE CYCLE ASSESSMENT CALCULATIONS

Life cycle assessments (LCAs) can be completed at plastics manufacturing operations to understand the effects that manufacturing changes have on the carbon footprint, waste generation, and pollution. LCA can be used to design sustainability into products and processes. LCA can be calculated with the use of an LCA tool provided online (LCA Tool 2013).

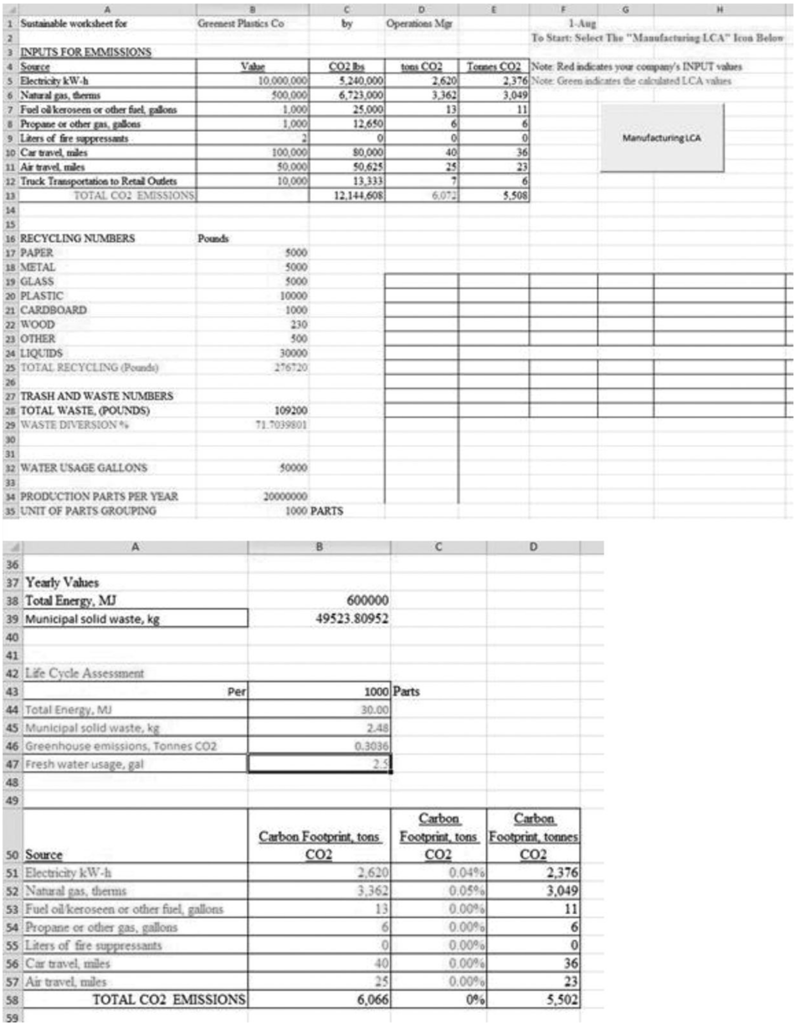
The LCA tool enables users to input energy consumption, transportation mileage, and recycling quantities for a company during the production of a manufactured product. The LCA tool calculates the carbon footprint and diversion rate of a company. The input sheet for the LCA tool is listed in Figure 9.1.

LCA calculations use a 10-step process. The LCA process requires input from unit operations to calculate carbon footprint, waste generation, and pollution. The carbon footprint of the plastic manufacturing operations depends upon the electricity, natural gas, fuels, car travel, air travel, fire suppression releases, and the amount of plastic products manufactured during the year.

The worksheet accepts inputs for manufacturing production data and provides an LCA for the production operation. The input for carbon footprint calculations is as follows:

a. Utilities and fuel sources
   i. Electricity usage at plant: annual kWh
   ii. Natural gas usage at plant: annual therms
   iii. Petroleum fuels usage at plant: gallons or equivalent
   iv. Other fuel usage at plant: gallons or equivalent
   v. Number of fire suppression releases
b. Travel for company business
   i. Car travel for company business
   ii. Air travel miles total for company business

The waste generated during the year depends upon the amount of solid and liquid waste produced at the manufacturing location and the amount of oil, ink concentrates, glass, paper, metal, plastic, cardboard, and other recyclables that were recycled during the year. The worksheet can



Sustainable worksheet for Greenest Plastics Co by Operations Mgr 1-Aug

To Start: Select The "Manufacturing LCA" Icon Below

Note: Red indicates your company's INPUT values

Note: Green indicates the calculated LCA values

INPUTS FOR EMMISSIONS

Source	Value	CO2 lbs	tons CO2	Tonnes CO2
Electricity kW-h	10,000,000	5,240,000	2,620	2,376
Natural gas, therms	500,000	6,723,000	3,362	3,049
Fuel oil kerosene or other fuel, gallons	1,000	25,000	13	11
Propane or other gas, gallons	1,000	12,650	6	6
Liters of fire suppressants	2	0	0	0
Car travel, miles	100,000	80,000	40	36
Air travel, miles	50,000	50,625	25	23
Truck Transportation to Retail Outlets	10,000	13,333	7	6
TOTAL CO2 EMISSIONS		12,144,608	6,072	5,508

RECYCLING NUMBERS	Pounds
PAPER	5000
METAL	5000
GLASS	5000
PLASTIC	10000
CARDBOARD	1000
WOOD	230
OTHER	500
LIQUIDS	30000
TOTAL RECYCLING (Pounds)	276720

TRASH AND WASTE NUMBERS

TOTAL WASTE, (POUNDS)	109200
WASTE DIVERSION %	71.7039801
WATER USAGE GALLONS	50000
PRODUCTION PARTS PER YEAR	20000000
UNIT OF PARTS GROUPING	1000 PARTS

Yearly Values

Total Energy, MJ	600000
Municipal solid waste, kg	49523.80952

Life Cycle Assessment

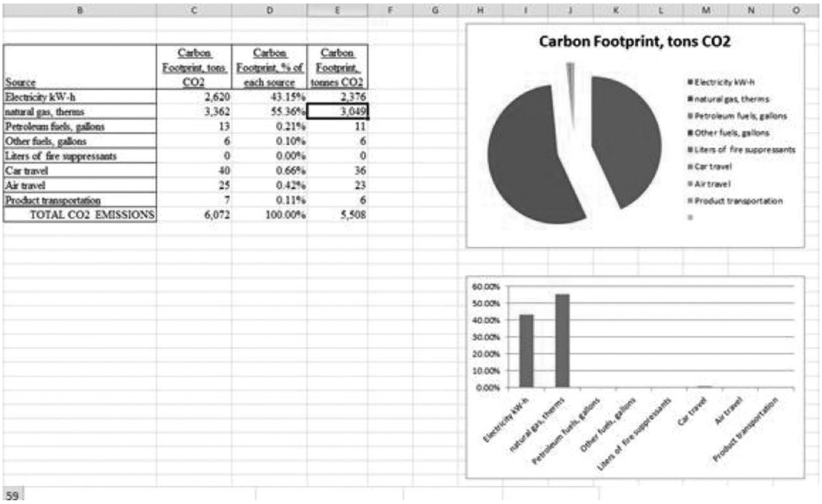
Per	1000 Parts
Total Energy, MJ	30.00
Municipal solid waste, kg	2.48
Greenhouse emissions, Tonnes CO2	0.3036
Fresh water usage, gal	2.5

Source	Carbon Footprint, tons CO2	Carbon Footprint, tons CO2	Carbon Footprint, tonnes CO2
Electricity kW-h	2,620	0.04%	2,376
Natural gas, therms	3,362	0.05%	3,049
Fuel oil/kerosene or other fuel, gallons	13	0.00%	11
Propane or other gas, gallons	6	0.00%	6
Liters of fire suppressants	0	0.00%	0
Car travel, miles	40	0.00%	36
Air travel, miles	25	0.00%	23
TOTAL CO2 EMISSIONS	6,066	0%	5,502

FIGURE 9.1 LCA tool input sheet.

calculate the diversion rate of the production operation. The input for waste diversion is as follows:

- **a.** Recycling rate
  - **i.** Plastic, paper, metal, glass, wood recycled per year
- **b.** Solid waste disposal per year at plant
  - **i.** Liquid waste
  - **ii.** Solid waste



Source	Carbon Footprint, tons CO2	Carbon Footprint, % of each source	Carbon Footprint, tonnes CO2
Electricity kW-h	2,620	43.15%	2,376
natural gas, therms	3,362	55.36%	3,049
Petroleum fuels, gallons	13	0.21%	11
Other fuels, gallons	6	0.10%	6
Liters of fire suppressants	0	0.00%	0
Car travel	40	0.66%	36
Air travel	25	0.42%	23
Product transportation	7	0.11%	6
TOTAL CO2 EMISSIONS	6,072	100.00%	5,508

FIGURE 9.2 LCA output from LCA tool.

Finally, the input necessary for LCA of the production operation requires information from the production operation and the functional unit for the LCA. The input for LCA calculations is as follows:

- **a.** Yearly plastic production numbers for plant
  - **i.** Number of plastic products produced
  - **ii.** Mass or weight of plastic used at the plant per year
  - **iii.** LCA functional unit, for example, 1000 parts

The information can be used to calculate the graphs of the LCA for the plant, recycling rate and diversion rate. Carbon credits can be calculated based on the recycling rates.

Figure 9.2 provides an example of the results from the LCA tool.

9.2.1 LCA Example CO_2 Emission Calculation

The steps to calculate the CO_2 emissions and LCA for the manufacturing operation from the information listed previously are as follows:

1. Calculate CO_2 generated from the plastic pellet production. Multiply the kilogram of plastic used at the plant by the CO_2 factor

provided by the utility company. Calculate CO_2 generated from the plastic product manufacturing.

   a. Multiply the electrical energy usage per year, kWh, by the CO_2 conversion rate from the utility. For PG&E utility, the rate is 0.237642 kg of CO_2 emission per kWh.

   b. Multiply the natural gas energy usage per year, therms, by the CO_2 conversion rate from the utility. For PG&E utility, the rate 6.097959 kg of CO_2 emission per therm.

   c. Multiply the other fuels energy usage per year by the CO_2 emission factor provided by the fuel utility.

2. Calculate CO_2 generated from car and air travel for sales force and management team.

   a. Divide the miles driven by the average fuel economy of the vehicles and the multiply by the gasoline emission factor. The gasoline emission factor for gasoline is 0.524 lbs CO_2 per gallon of gasoline and for diesel is 13.446 lbs CO_2 per gallon of diesel (EPA Fuel Emissions 2013).

   b. Multiply the miles flown by company personnel by 1.12 pounds of CO_2 per passenger mile flown (BlueSkyModel.org 2013).

3. Calculate CO_2 generated from fire extinguishers that release CO_2.

4. Add up steps 1, 2, and 3 for total CO_2 emissions for the plant.

5. Divide the total emissions for the plant by the number of products produced per year to get a CO_2 emission factor per unit.

6. Multiply the CO_2 emission factor from Step 6 by the number of functional units, for example, 1000 plastic bags, 10,000 plastic bottles, or 10,000 containers. This will provide the CO_2 emission per functional unit.

The steps to calculate the waste diversion and recycling rates for the manufacturing operation from the information listed previously are as follows:

1. Multiply the number of bins of trash by an MSW weight factor per cubic yard of solid waste. According to the EPA, the weight of a cubic yard of MSW is between 150 and 300 lbs (EPA Waste 2013).

2. Add the mass of liquid waste to the mass of a cubic yard to calculate the total mass of waste.
3. Sum the total mass (kg) of recycled plastic, paper, metal, glass, cardboard, oil, paint, ink concentrates, and other recyclables.
4. Calculate a diversion rate by dividing the total mass of recycled materials by the total mass of solid and liquid wastes.

The carbon footprint output can display the results of the calculations as shown in Figure 9.3. The figure shows that 81% of the carbon footprint is produced from electricity sources in the plant, 17% of the carbon footprint is produced from burning natural gas, and 2% of the carbon footprint can be attributed to car and air travel of employees. The company also produced 2252 tons of CO_2. The carbon footprint can be evaluated every year with these calculations and provide a means to reduce overall carbon footprint by improving the manufacturing operations.

The diversion rate can be calculated based on the amount of waste generated and the amount of recycled materials. As an example, the amount of waste generated at the plastic manufacturing operation was 125,000 kg per year and the total amount of recycled materials was 18,000 kg per year. The diversion rate would then be 14.4%.

LCA can be used to measure the sustainability of the plastic products. As an example, the production of plastic bottles can be evaluated with LCA tools. The amount of energy consumed, fossil fuel used, CO_2

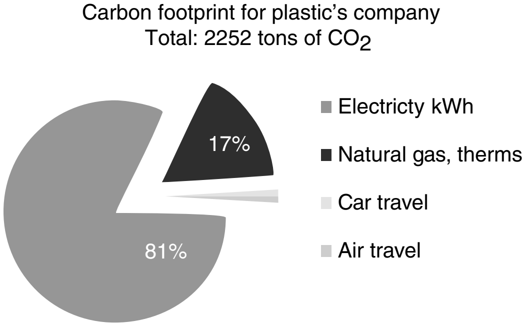


FIGURE 9.3 Carbon footprint example of a typical plastic manufacturing operation.

TABLE 9.1
LCA of Plastics Manufacturing for 10,000 Plastic Bottles

Environmental impact	LCA results
Total energy (MJ)	1898.73
Fossil fuel used (kg)	70.54
Greenhouse emissions (tons, CO_2)	0.0563
Municipal solid waste (kg)	2.69

emitted, and waste generated per functional unit are found by dividing the total energy consumed, fossil fuel used, CO_2 emitted, and waste generated by the number of parts produced per year and then multiplying by the functional unit. For example, for 10,000 bottles produced per year, the energy consumed, CO_2eq emitted, and waste generated are listed in Table 9.1.

LCA tools can help companies monitor their environmental performance and develop ways to reduce their environmental impacts. An LCA tool is available for manufacturing companies to compute LCA on their plastic products.

9.3 CARBON CREDITS AND CARBON TAXES

Several countries are using carbon credits and taxes to reduce the carbon emissions for the environment. A carbon tax can be thought of as a tax on the carbon content of fuels. Typically, fuels are burned for electricity and other uses for manufacturing operations.

Recently, Australia implemented a carbon tax on companies based on their production of CO_2eq emissions. Australian businesses and individuals pay $23 AUD per ton of CO_2eq emissions. Five hundred of the top CO_2 polluters in Australia must pay the carbon tax (Carbon Tax Facts 2013).

In the United States, California introduced California's Global Warming Solutions Act of 2006 AB32 (Assembly Bill 32) to set an absolute statewide limit on greenhouse gas (GHG) emissions. AB 32 requires the state of California to lower GHGs to 1990 levels by 2020 through a series of programs and industrial incentives (California Cap and Trade 2013).

California Assembly Bill 32 (AB32) includes the following:

- Expand and strengthen energy efficiency programs with building and appliance standards.
- Achieve statewide renewable energy sources of 33% by the year 2020.
- Develop a statewide cap-and-trade program with links to other western states to create a regional market system.
- Establish targets for transportation-related GHG emissions for California regions.
- Implement measures to reduce GHG emissions through automotive emission standards, retail transportation measures, and a low carbon fuel standard.

AB 32 legislation was passed to reduce emissions of GHGs associated with the burning of fossil fuels. California's law applied a Greenhouse Gas Cap-and-Trade Program for industrial producers allowance cap and a trading mechanism for compliance. California Air Resource Board provided an auction of GHG credits at a value of $14 per ton. The Air Resource Board raised $280 million in the third carbon auction (California Carbon Auction 2013). In California, 400 large industrial polluters are required to cap their emissions. Companies can trade for carbon credits to offset their emissions.

9.4 SUMMARY

Plastics can be made with lower environmental impacts of lower GHGs, lower waste generation, and lower pollution. NatureWorks LLC provides a sustainable plastic example by producing the Ingeo PLA with lower energy and lower carbon footprint than previous versions of PLA.

LCA can be used to track the production of GHGs, waste generation, and pollution. An Excel worksheet program is available for manufacturing companies to calculate GHGs, waste generation, recycling and diversion rates, and pollution. The worksheet can help provide LCA graphs and tracking for companies to reduce their carbon footprint and increase their recycling rates and lower pollution.

Carbon tax has been issued in Australia for companies and for the public. Carbon credits are traded in California. Carbon credits can be calculated based on the use of recycled materials in the production process and with using lower energy manufacturing processes.

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REVIEW QUESTIONS

Q.9.1 Sustainable plastics manufacturing includes producing plastic pellets with minimum pellet loss, without the use of regulated metals in inks and concentrates, and with the practice of recycling waste oils, inks, and other products. T or F?

Q.9.2 CO_2 emissions can be calculated based on electricity, natural gas, fuels, and transportation usage at a manufacturing facility. T or F?

Q.9.3 Diversion rate can be calculated based mainly on recycling rates of plastics, metals, glass, and paper at a manufacturing site. T or F?

Q.9.4 Manufacturing companies in Australia pay \$50 per ton of CO_2eq that they produce per year. T or F?

Q.9.5 Using recycled PET in the production of plastic strapping materials can reduce CO_2 emissions versus using virgin PET. T or F?

Q.9.6 The 2009 version of Ingeo PLA can be manufactured with less energy, less global warming potential, and less eutrophication potential than earlier versions of PLA. T or F?

Q.9.7 A web-based LCA tool is available that can calculate the carbon footprint for manufacturing companies. T or F?

Q.9.8 Australia assesses a carbon tax on some manufacturing companies and some individuals. T or F?

Q.9.9 The state of California assesses a carbon tax on some manufacturing companies and some individuals. T or F?

Q.9.10 The Australia carbon tax is approximately $23 AUD per ton of CO_2eq emissions. T or F?

REVIEW PROBLEMS

P.9.1 What should an LCA tool calculate for a manufacturing company?

- **a.** Total carbon footprint for the year
- **b.** Total recycling rate for the year
- **c.** Total waste generation for the year
- **d.** All of the above

P.9.2 How many tons of CO_2eq emissions are generated for a CA company that uses 1 million kWh of electricity?

- **a.** 155 tons of CO_2eq
- **b.** 238 tons of CO_2eq
- **c.** 259 tons of CO_2eq
- **d.** 301 tons of CO_2eq

P.9.3 How many tons of CO_2eq emissions are generated for a CA company that uses 10,000 therms of natural gas?

- **a.** 61 tons of CO_2eq
- **b.** 77 tons of CO_2eq
- **c.** 81 tons of CO_2eq
- **d.** 86 tons of CO_2eq

P.9.4 If a company produces two million plastic bags at the CA manufacturing plant with utilities from questions P.9.2 and P.9.3, what is the carbon footprint per 1000 plastic bags?

- **a.** 0.101 tons of CO_2eq per 1000 plastic bags
- **b.** 0.119 tons of CO_2eq per 1000 plastic bags
- **c.** 0.150 tons of CO_2eq per 1000 plastic bags
- **d.** 0.179 tons of CO_2eq per 1000 plastic bags

P.9.5 If CA imposes the same carbon tax as Australia of $23 per ton of CO_2eq emissions, how much will the company from questions P.9.2 and P.9.3 pay in carbon taxes?

- **a.** $3542
- **b.** $4783
- **c.** $5491
- **d.** $6877

REVIEW EXERCISES

E.9.1 How much CO_2eq can be saved by using 100,000 kg of recycled LDPE in the manufacturing of plastic bags versus virgin LDPE?

E.9.2 What is the carbon footprint for the company, with annual usage of nine million kWh of electricity and 1,000,000 therms of natural gas? What is the percentage of electricity use on the carbon footprint?

E.9.3 What is the diversion rate of a company with the following recycling and waste numbers? Recycled glass of 2000 kg, recycled plastic of 4000 kg, recycled metal of 1000 kg, recycled cardboard of 500 kg, and recycled oils of 10,000 kg. The waste bin size is 12 yd^3 that is picked up weekly for 50 weeks.

CHAPTER 10

Future of Sustainable Plastics

The future of sustainable plastics can be described as excellent growth, especially for biobased plastics. In 2010, bioplastics comprise less than 1% of the 181 million metric tons of synthetic plastics (Nampoothiri et al. 2010). Biobased polymer production capacity is expected to triple from 3.5 million tons in 2011 to 12 million tons in 2020. Bioplastics are expected to comprise of 3% of the global polymer production in 2020 (Nova 2013).

North America is expected to have modest gains from 159,000 tons in 2011 to 202,000 tons in 2016 (Environmental Leader Calculations 2012). The largest gains are expected for South America and Asia due to better access to agricultural feedstock and favorable political framework (Nova 2013).

The growth in bioplastics can be supported by the development of biobased plastics from non-food-based agricultural sources, the development of durable products in addition to biodegradable products, and the development of new biobased chemicals for thermoplastic and thermoset polymers.

Sustainable Plastics: Environmental Assessments of Biobased, Biodegradable, and Recycled Plastics, First Edition. Joseph P. Greene.

10.1 SUSTAINABLE BIOBASED PLASTICS MADE FROM RENEWABLE SOURCES

Global production of PHA and PLA is expected to quadruple in capacity from 2011 to 2020. PHA is expected to be produced in 14 companies at 16 locations in 2020. PLA is expected to be produced in 27 companies at 32 locations in 2020 (Nova 2013).

PHA and PLA are both produced from sugars that are generated from starchy agricultural sources, or biomass. Currently, corn starch or sugarcane can be used to produce the biopolymers through bacterial synthesis. In 2009, approximately, 190 billion bushels of corn was produced in the United States. Of that as shown in Figure 10.1, approximately 44% of the corn is used as livestock feed, approximately 22% of the corn is used for effective ethanol production, approximately 13% of the corn is exported, approximately 11% of the corn is used for other purposes, and approximately 9% of the corn is used for human food, seed, and industrial use (National Corn Growers 2013). In the world, approximately, 60% of the harvested agricultural biomass is used for animal feed, 32% for human food, 4% for material use, and 4% for energy use (Carus and Dammer 2013).

Future sources of sugars can come from plant oils, lignocellulose, and agricultural waste products. In 2008, 10 billion tons of biomass was

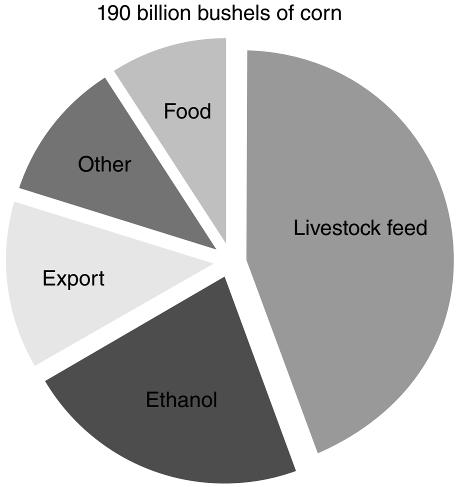

FIGURE 10.1 Corn utilization in the United States for 2009.

TABLE 10.1
Production Yields and Products from the Fermentation of Sugars from Agricultural Sources

Biobased material	Yield dry matter (ton/ha per year)	Sugar content percentage of dry matter	Sugar yield (ton/ha per year)	Agricultural residues yield (ton/ha per year)	GHG emission (kg CO_2eq/ha)	NO_2 emission (NO_2eq/ha)
Corn (maize)	7.44	75	5.58	16.3	3120	1910
Sugar beet	17.0	73.5	12.05	40	1120	1220
Sugarcane	20.0	52	11.00	30	1400	700
Wheat	7.14	75	5.00	4.30	900	1740

harvested worldwide. In 2008, 60% of the worldwide agricultural land was used to produce animal feed, 32% of the agricultural land was used to produce agricultural products for food, 4% was used for creation of materials, and 4% was used for creation of energy. The materials use included raw materials for the production of biobased plastics and chemicals (Nova Food 2013).

Table 10.1 lists the production yields and products from the fermentation of sugars from agricultural sources. Combustion of bagasse fibers can provide sufficient power and heat requirements for a typical sugar mill (Bos et al. 2012).

Table 10.1 shows that sugarcane and beets produce the most amounts of annual sugar and agricultural residues per hectare. Corn produces the most GHG emission and NO_2 emission per hectare.

PLA can be made with starchy biomass and other natural waste products. The production of PLA from starchy substrates can yield a range of lactic acid production. Table 10.2 provides a list of starch and lignocellulosic substrates for the production of lactic acid (John et al. 2008).

Table 10.2 illustrates that cassava bagasse and whole wheat produce equivalent sugars and lactic acid as corn starch. Cellulose produces less sugars and lactic acid than corn starch.

Table 10.2 shows that cellulosic materials are a viable carbon source for bioplastic production. Sugarcane bagasse can be used to produce lactic acid (John et al. 2005). A PLA bio-refinery system is economically viable with reduced GHG emissions with the use of agricultural residues.

TABLE 10.2
Starchy and Cellulosic Substrate Materials for Production of Lactic Acid

Substrate material	Lactic acid production percentage versus 1 gram of corn starch
Corn starch	100
Barley	98.93
Cassava bagasse	100.53
Cellulose	95.19
Potato starch	98.40
Wheat starch	94.65
Whole wheat	100.53

The costs of the bio-refinery depend greatly on the production levels of the manufacturing operation. PLA production from short rotation wood leads to a positive gain of land use per year in Europe (Dornburg et al. 2006).

PHA can be produced with sugarcane bagasse, waste cheese whey, starchy waste water, and from renewable oil-palm biomass (Yu 2001; Albuquerque et al. 2007; Obruca et al. 2010; Hassan et al. 2013).

A review of the PHA production method with carbon-rich wastes provides promising economic promise for reduced environmental impacts with less land use and food crop use (Nikodinovic-Runic et al. 2013).

10.2 SUSTAINABLE TRADITIONAL PLASTICS MADE FROM RENEWABLE SOURCES

Traditional plastics can be made from agricultural products, including PET, PBT, nylon 6, nylon 10, and acrylics. The largest interest has occurred with the biobased PET bottle. Currently, Coca-Cola introduced a biobased PET bottle, for example, Plant Bottle, with 30% biobased and 70% petroleum based (After Dasani Test 2009). PET bottles are made typically from 30% mono-ethylene glycol (MEG) and 70% terephthalic acid. The MEG can be made with biobased sources and the terephthalic acid is made from petroleum sources. The production capacity of the 30% bio-PET bottle is 452,000 tons. Coca-Cola plans to launch a 100% PET bottle in the future (Race to 100% bio-PET).

TABLE 10.3
Non-Renewable Energy Use for the Production of One Ton of Biobased Polyethylene

Biobased material	Energy (GJ per ton)	Land use (ha per ton)
Corn (maize)	29	0.6
Sugar beet	27	0.3
Sugarcane	−18	0.35
Wheat	25	0.68
Fossil fuel (as a reference)	78	–

Cradle-to-gate non-renewable energy use from producing traditional polymers with agricultural product sources is listed in Table 10.3. The energy to produce polyethylene is lowest for sugarcane than for corn, sugar beet, or wheat. The residues from sugarcane processing into sugar are converted into energy resulting in a negative energy use for the production of polyethylene from sugarcane. In all cases, the production of polyethylene from agricultural sources requires 60–70% less energy than from fossil fuel sources (Bos et al. 2012).

Production of polyethylene from sugarcane or sugar beets requires half of the land use than from corn (Bos et al. 2012).

10.3 GROWTH IN BIOBASED PLASTICS WITH DEVELOPMENT OF DURABLE GOODS

Biobased plastics can be made into durable goods to complement the biodegradable plastic products. In 2009, durable biopolymers accounted for 7% of the estimated global production capacity of 318,000 tons. In 2010, durable biobased plastics accounted for 40% of the global capacity of 724,000 tons. The significant contributor to the growth of durable biobased plastics was Braskem Company, Brazil, that produces sugarcane-based HDPE. In 2015, the projected global biobased plastic production capacity is expected to reach 1,700,000 tons with durable biopolymers accounting for 60% of the market (Market Update Bioplastics 2012).

In 2015, the growth in biobased plastics is expected to be led by biopolyethylene and bio-PET. Table 10.4 lists the anticipated production volumes of biobased polymers (Market Update Bioplastics 2012).

Traditional plastics can be produced with starch, lignocellulose, plant oils, and sugars. Glucose can be produced from the starch,

TABLE 10.4
Biobased Polymer Production Capacity for 2015

Biobased polymer	Capacity (tons)	Percentage of market
Bio-PE	450,000	26
Bio-PET	290,000	17
PLA	216,000	13
PHA	147,100	9
Bio-polyesters	143,500	8
Starch blends	124,800	7
Bio-PVC	120,000	7
Bio-PA	75,000	5
Regenerated cellulose	36,000	2
PLA blends	35,000	2
Bio-PP	30,000	2
Bio-PC	20,000	1
Others	22,300	1
Total	1,709,700	100

lignocellulose, and sugars. Glucose can be fermented to produce thermoplastic polymers. Glycerol and fatty acids can be produced from plant oils and then produce thermoset polymers. Table 10.5 lists the renewable source, and intermediates in the production of traditional thermoplastics and thermosets (Nova 2013).

Polyurethane polymer can be made with agricultural sources for the polyol and isocyanates (More et al. 2013). Epoxy polymer can be made from grapeseed oil and epoxidized linseed oil (Stemmelen et al. 2011).

10.4 GROWTH IN BIOBASED PLASTICS FOR PHARMACEUTICALS AND MEDICAL DEVICES

Biobased plastics can be used for coatings for drug delivery, bio-absorbable, and other medical devices. Biopolymers are made from non-toxic materials that are compatible with human tissues. PLA, PGA, and PCL are commonly used in biomedical devices (Cheng et al. 2009). The biopolymers are degraded with simple hydrolysis of the ester bonds without the use of enzymes that prevent inflammation. The biodegraded bio-products are eliminated from the body through normal cellular activity and urine. PLA can be used as a bio-absorbable polymer for resorbable plates and screws (Lasprilla et al. 2012). PLA can provide a

TABLE 10.5
Biobased Polymer Production from Renewable Sources and Intermediates

Biobased polymer	Intermediate	Intermediate
Bio-PET and bio-PBT	Ethanol, isobutanol	Ethylene, MEG, *p*-Xylene, terephthalic acid
Bio-HDPE and bio-LDPE	Ethanol	Ethylene
Bio-PVC	Ethanol	Ethylene, vinyl chloride
Bio-PP	Ethanol	Ethylene, propylene
Bio-PMMA	Ethanol	Methyl methacrylate
Bio-nylon	Adipic acid	Hexamethylene diamine (HMDA)
Bio-PBS	Succinate	1,4-Butanediol
Bio-PC	Sorbitol	Isosorbide
Bio-SBR	isobutanol	
Bio-epoxy (thermoset)	Glycerol	Epichlorohydrin
Bio-nylon (thermoset)	Glycerol	Diacids
Bio-polyesters (thermoset)	Glycerol	Polyols, diacids
Bio-PU (thermoset)	Glycerol, triglycerides	Polyol, isocyanates

biocompatible alternative to titanium plates or other metallic implants that do not erode the bone structures (Dearnaley et al. 2005).

PHA biopolymers are promising materials for biomedical applications because they are biodegradable, biocompatible, and made from non-toxic materials. The physical and material properties of PHA can be modified with different functional groups formed on the side of the polymer chain. PHAs can be used in applications for tissue engineering, drug delivery, and scaffolding for arteries (Hazer et al. 2012; Chen 2010; Zinn et al. 2001).

10.5 SUMMARY

The future of sustainable plastics is expected to have as excellent growth, especially for biobased plastics. The growth in bioplastics can be supported by the development of biobased plastics from non-food-based agricultural sources, the development of durable products in addition to biodegradable products, and the development of new biobased chemicals for thermoplastic and thermoset polymers.

Bioplastics in the future can be produced from plant oils, lignocellulose, and agricultural waste products. Sugarcane and beets produce the most amounts of annual sugar and agricultural residues per hectare. Corn produces the most GHG emission and NO_2 emission per hectare.

For PLA production, cassava bagasse and whole wheat produce equivalent sugars and lactic acid as corn starch. Cellulose produces less sugars and lactic acid than corn starch. In a PLA bio-refinery system, agricultural residues can be used to produce PLA with economic viability and reduced GHG emissions.

Traditional plastics can be made from agricultural products. PET can be made currently with up to 30% from biobased sources. PET in the near future can be made with 100% plant-based materials. Polyethylene is currently made from sugarcane. Polypropylene will soon be made from sugarcane.

Biobased plastics can be used for coatings for drug delivery, bioabsorbable, and other medical devices. Biopolymers are made from non-toxic materials that are compatible with human tissues. PLA, PGA, and PCL are commonly used in biomedical devices.

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REVIEW QUESTIONS

Q.10.1 Polyethylene and polypropylene can be made from sugarcane materials. T or F?

Q.10.2 PLA that is made with sugarcane or sugar beets can have twice the yield of PLA production per hectare of land use. T or F?

Q.10.3 PHA can be produced with sugarcane bagasse, waste cheese whey, starchy waste water, and from renewable oil-palm biomass. T or F?

Q.10.4 PET is made from 100% plant materials. T or F?

Q.10.5 PLA and PGA do not make suitable biomedical products because they are biodegradable. T or F?

REVIEW PROBLEMS

P.10.1 What are the future non-food-based sources for bioplastics?

a. Plant oils

b. Lignocellulose biomass

c. Agricultural waste products

d. All of the above

P.10.2 What percentage of the US corn production is used for animal feed and human food, seed, and industrial use?

a. animal feed = 63% and human food = 14%

b. animal feed = 60% and human food = 30%

c. animal feed = 55% and human food = 22%

d. animal feed = 44% and human food = 9%

P.10.3 Which of the following agricultural sources has the highest sugar yields in ton per hectare per year?

a. corn

b. sugar beet

c. sugarcane

d. wheat

P.10.4 Which of the following agricultural sources has the highest GHG emissions in kilogram CO_2eq per hectare?

a. corn

b. sugar beet

c. sugarcane

d. wheat

P.10.5 Which of the following plastics will have the greatest projected production in 2015?

a. bio-PET

b. bio-polypropylene

c. bio-PLA

d. bio-polyethylene

REVIEW EXERCISES

E.10.1 How much sugarcane would be necessary to produce 1 ton of polyethylene?

E.10.2 If 99.9% of the sugars are converted to PLA, how much sugar beets are required to produce 1 ton of PLA?

E.10.3 What is the chemical method to produce bio-PET form starting chemicals?

APPENDIX A

Injection Molding

A.1 INTRODUCTION

Injection molding is a process where solid plastic is melted, injected into a mold, and then cooled back to a solid as shown in Figure A.1.

Plastic injection molding equipment, typically, comprises an extruder and a compression press. The plastic pellets are placed in the hopper and fed through the extruder in three main heated zones. The temperature profile in the three zones is dependent on the plastic type. The first zone is called the feed zone. The second zone is called the compaction zone. The third zone is called the metering zone. The first zone has the largest opening between the rotating screw and the barrel. The metering zone has the largest screw diameter and the smallest flight depth or gap between the screw and the barrel.

The feed zone has the lowest temperature of the three zones. The feed zone is typically 50% of the length of the screw for injection molding (BASF Screw Designs 2013). Special low-shear screws are needed for PVC and nylon materials.

The compaction zone has an increasing screw diameter from the small diameter in the feed zone to the larger diameter in the metering zone. The gaps between the screw and the barrel are reduced in the compaction zone. The plastic is melted in the compaction zone due to increased temperature and shear heating from the small clearance between the screw and the barrel.

Sustainable Plastics: Environmental Assessments of Biobased, Biodegradable, and Recycled Plastics, First Edition. Joseph P. Greene.

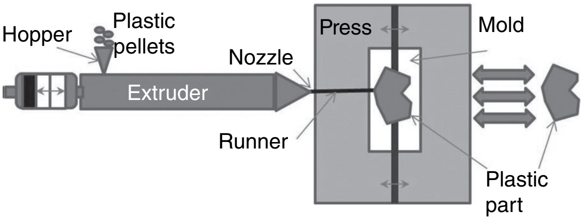

FIGURE A.1 Injection molding process.

The metering zone has a constant diameter and gap between the screw and barrel. Plastic is transported with the rotating screw at a rate specified in the machine process parameters.

The length and diameter of the screw and flight depth are important parameters for injection molding. The *L*/*D* ratio is typically 20–30 for injection molding. The flight depth is the gap between the screw and the barrel. The flight depth ratio is the ratio of the flight depth in the feed section and the flight depth in the metering section (Screw Designs BASF). The flight depth ratio is typically between 2 and 3 for injection molding.

The nozzle is at the end of the metering zone. The melted plastic accumulates at the end of the metering zone with the rotation of the screw. The screw is pushed forward as the plastic is injected through the nozzle and then into the runner of the mold, and finally into the part mold.

The hot plastic is cooled in the mold that is located in the press. After sufficient cooling time, that part is ejected from the mold and inspected for quality.

A.2 PROCESS CONTROL DURING INJECTION MOLDING

The process of injection molding can be controlled by monitoring four areas of the molding process, namely temperature, pressure, time, and distance. The four parameters are shown in Figure A.2.

A.2.1 Temperature Control

Temperature must be controlled throughout the injection molding process. The temperature of the plastic is increased in the barrel to melt the plastic. The melting temperature and glass transition temperature of

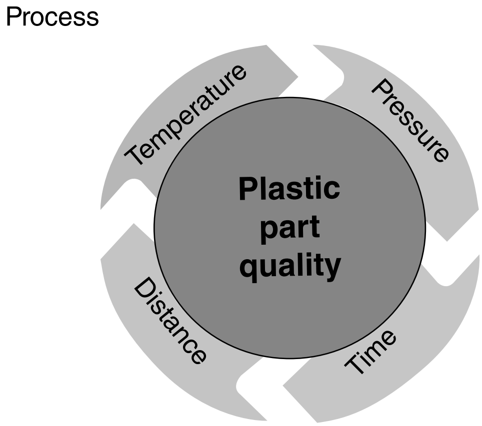

FIGURE A.2 Process control variables for injection molding.

common plastics are listed in Table A.1 (Belofsky 1995a). The temperature is increased in the three zones of the extruder. The temperature is lowest at the feed section of the barrel. The feed section is the area where plastic pellets are fed from the hopper to the feed throat of the injection molder. The feed section is usually kept at a low temperature so as to prevent the plastic from bridging the screw. If bridging occurs from the plastic melting and coating the screw, the feed zone must be cooled down to freeze the plastic around the screw.

The temperature is increased in the compaction zone where the solid plastic is melted from shear heating and from the increased temperature. The temperature is increased in the metering zone and the nozzle.

A.2.1.1 Glass Transition Temperature

As shown in Figure A.3, the glass transition temperature is the temperature at which the plastic changes from a glassy state to a rubbery state. As the temperature is increased above the melting temperature, the plastic material is in a liquid state with amorphous structure. As the temperature is reduced below the melting temperature, crystallization begins at various nuclei throughout the polymer. The polymer molecules form a mixture of crystals and amorphous regions. Crystallization continues as the temperature drops until maximum crystallinity is achieved. As the temperature drops below the glass transition temperature, the amorphous regions are rubbery and do not contribute to the stiffness of

TABLE A.1
Plastic Material Melting and Glass Transition Temperatures

Plastic material	Melt temperature range, °C (°F)	Glass transition temperature, T_g, °C (°F)
Acrylonitrile butadiene styrene (ABS)	215–220 (419–428)	102 (215)
Polyacetal (POM)	170–175 (338–347)	−80 (−112)
Polymethyl methacrylate (PMMA)	155–160 (311–320)	45 (113)
Nylon 6	215–220 (419–428)	50 (122)
PHA	170–175 (338–347)	–
Polybutylene terephthalate (PBT)	220–225 (428–437)	110 (230)
Polycarbonate	215–220 (419–428)	150 (300)
Polyethylene (LDPE)	130–135 (266–275)	−78 (−108)
Polyethylene (HDPE)	135–140 (275–284)	−110 (−166)
Polyethylene terephthalate (PET)	195–200 (383–392)	69 (156)
Polypropylene (PP)	165–170 (329–338)	−35 (−31)
Polystyrene (PS)	235–240 (455–464)	90 (194)
Polyvinyl chloride (PVC)	210–215 (410–419)	90 (194)

Source: From Belofsky (1995a).

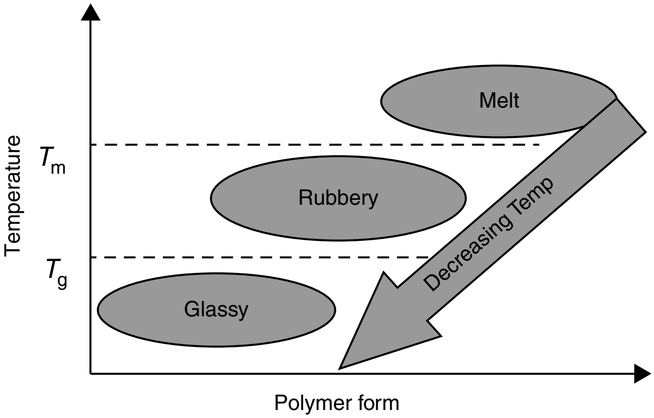

FIGURE A.3 Thermal transitions of plastics.

TABLE A.2
Amorphous and Crystalline Polymers

Amorphous polymers	Crystalline polymers
Acrylonitrile butadiene styrene (ABS)	Polyacetal (POM)
Acrylic (PMMA)	Polybutylene terephthalate (PBT)
Polycarbonate	Polyethylene (HDPE, LDPE)
Polystyrene (PS)	Polyethylene terephthalate (PET)
Polyvinyl chloride (PVC)	Polypropylene (PP)
Phenoxy	Polyether ether ketone (PEEK)
Styrene acrylonitrile (SAN)	Polyphenylene sulfide (PPS)
Polyphenylene oxide (PPO)	Polytetrafluoroethylene (PTFE)
Polylactide (PLA)	Polyhydroxyalkanoate (PHA)

Source: From Belofsky (1995a).

the polymer. The crystalline regions are unaffected by temperature and are glassy and rigid.

Plastics can be either amorphous or crystalline. Pure crystallinity is rare among polymers. Most polymers have crystalline and amorphous regions and are considered semi-crystalline. Amorphous polymers have low crystallinity or irregular crystalline regions. A listing of amorphous and crystalline polymers is found in Table A.2 (Belofsky 1995a).

A.2.1.2 Mold Temperature

Control of the mold temperature is a key component for plastics quality. Table A.3 lists the typical mold temperatures for common plastics during injection molding (http://www.matweb.com/). The mold temperature can influence the quality of the plastic part. Warmer mold temperatures can help relieve stresses imposed on the plastic part during injection molding process and aid material flow of thin wall sections. The stresses imposed on the plastic part can cause warpage in the plastic part after it is removed from the mold. Cooler mold temperatures can help cool the plastic part faster and cause a reduction in cycle time.

A.2.2 Pressure Control

Pressure control in the injection molding process is a very important aspect to achieve excellent part quality. The injection pressure is a very important pressure control. During the plastic filling of the mold during

TABLE A.3
Plastic Material Mold Temperatures

Plastic material	Mold temperature, °C (°F)
Acrylonitrile butadiene styrene (ABS)	10–85 (50–185)
Polyacetal (POM)	60–100 (140–212)
Nylon 6	2–120 (70–248)
Polyhydroxyalkanoate (PHA)	55–65 (130–149)
Polybutylene terephthalate (PBT)	10–260 (50–500)
Polycarbonate	71–93 (160–200)
Polyethylene (LDPE)	10–65 (50–150)
Polyethylene (HDPE)	10–65 (50–150)
Polyethylene terephthalate (PET)	10–163 (50–325)
Polypropylene (PP)	10–65 (50–150)
Polystyrene (PS)	10–65 (50–150)

Source: http://www.matweb.com/

injection molding, the pressure in the part die increases dramatically as shown in Figure A.4. The injection pressure for plastics can range between 4 and 170 MPa (500 and 25,000 psi). Table A.4 lists the typical injection pressures for plastic materials (http://www.matweb.com/). The injection pressure varies depending upon the plastic material.

The pack or hold pressure follows the injection process and is needed to improve the stability of the polymer and to minimize warpage. The pack or hold pressure enables the plastic to maintain its dimensional

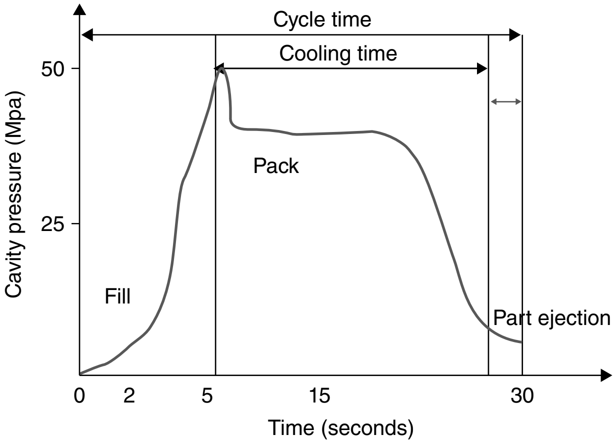

FIGURE A.4 Pressure distribution during injection molding process (http://www.matweb.com/).

TABLE A.4
Plastic Material Injection Pressures

Plastic material	Injection pressure, MPa (Psi)	Hold pressure, MPa (Psi)	Back pressure, MPa (Psi)
Acrylonitrile butadiene styrene (ABS)	4–130 (500–19,000)	30–90 (4000–13,000)	0.172–60 (24.9–8500)
Nylon 6	4–170 (500–25,000)	30–100 (4000–14,500)	0.172–60 (24.9–8500)
Polyhydroxyalkanoate (PHA)	2.76–103 (400–15,000)	2.02–8.27 (300–1200)	3.45 (500)
Polybutylene terephthalate (PBT)	30–120 (4000–17,500)	5–80 (725–11,600)	0.172–18 (24.9–2610)
Polycarbonate	75–124 (11,000–18,000)	5–70 (725–10,150)	0.172–1.38 (24.9–200)
Polyethylene (LDPE)	68.9–103 (10,000–15,000)	2.02–8.27 (300–1200)	0.172–1.03 (24.9–150)
Polyethylene (HDPE)	2.76–103 (400–15,000)	2.02–8.27 (300–1200)	0.172–1.03 (24.9–150)
Polyethylene terephthalate (PET)	68.9–120 (10,000–17,400)	2.02–8.27 (300–1200)	8–18 (1160–2610)
Polypropylene (PP)	2.76–103 (400–15,000)	2.02–8.27 (300–1200)	0.172–1.03 (24.9–150)
Polystyrene (PS)	2.76–103 (400–15,000)	2.02–8.27 (300–1200)	0.34–58.8 (49.3–8530)

control while the plastic cools below the glass transition temperature. The pack or hold pressure is applied at the end of the initial injection stroke, and is intended to complete the final filling of the mold and hold pressure to solidify the plastic and until the gate solidifies. The pack or hold pressure is applied against a cushion or pad of material at the nozzle. The pack or hold pressure is needed to insure dimensional tolerances on plastic parts as they cool and shrink in the mold. The shrinkage values for common plastics are listed in Table A.5 (http://www.matweb.com/). The pack or hold pressure is typically 50–80% of injection pressure (Belofsky 1995a, 1995b).

The back pressure is applied to keep the screw secure with the nozzle during the packing stage. During this time, the screw is rotated to accumulate the next shot.

Clamping pressure is the pressure needed to hold the clamp closed during injection and packing stages of injection molding. The clamping pressure times the projected area of the part must not exceed the tonnage

TABLE A.5
Shrinkage of Common Plastics

Plastic material	Linear mold shrinkage cm/cm (in/in)
Acrylonitrile butadiene styrene (ABS)	0.0015–0.0080
Nylon 6	0.00330–0.0200
Polyhydroxyalkanoate (PHA)	0.01250–0.0155
Polybutylene terephthalate (PBT)	0.00100–0.0650
Polycarbonate	0.0060
Polyethylene (LDPE)	0.01000–0.0500
Polyethylene (HDPE)	0.01000–0.0300
Polyethylene terephthalate (PET)	0.00100–0.0200
Polypropylene (PP)	0.00150–0.0200
Polystyrene (PS)	0.00500–0.01143

Source: http://www.matweb.com/

of the injection molding clamp. The force exerted during the injection molding process is described in Equation A.1.

$$F = P \times A_{\mathrm{p}} \tag{A.1}$$

where F is the clamping force, P is the mold pressure from injection or packing, and A_{p} is the projected area of the part.

A.2.3 Time Control

Time is an important parameter to control during injection molding. The time of many parameters is adjusted during injection molding. The injection molding process includes times for gate close, mold close, injection speed, pack and hold, cooling, mold open, and ejection. The total time to produce a part is referred to a cycle time. A typical cycle time for plastic injection molding is listed in Figure A.5. The 30-second cycle time is an arbitrary value for illustration purposes.

The fill time is the time necessary to fill the mold. The fill time is dependent upon the shot size or dosage stroke and the injection rate. Plastic materials have different injection rates associated with them. The pack or hold time is needed to control the part warpage. Likewise, cool time is needed to minimize part warpage due to shrinkage of the plastic material. The time for filling the mold, packing the part, and cooling the part can be optimized to improve the quality of the plastic part and to minimize cycle time.

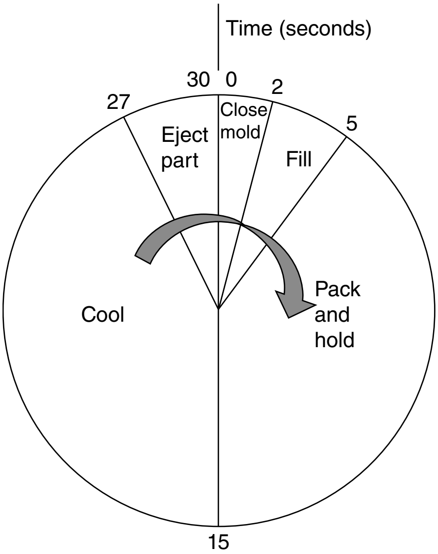

FIGURE A.5 Cycle time during injection molding process.

A.2.4 Distance Control

Distances can be controlled during injection molding. Control of distances is critical to producing high quality products at a low cost because longer distances result in longer cycle times. The most common distances are used for mold close, dosage or shot size, cushion or pad, screw return, mold open, and ejection.

Mold close distance can be set to provide a fast initial close speed followed by a slow close speed. The slow close speed is needed to accurately close the mold halves. Injection hold distance is set to switch at a cross-over point from constant injection rate to constant holding pressure. This cross-over point is an adjustable molding parameter. During the packing or hold stage of injection pressure, plastic material is pushed against a cushion or pad of plastic material. The cushion or pad distance, set with a small amount of material, should be left in barrel for the hold pressure to be applied against. The cushion is created by creating a total shot size that is slightly larger than that required to fill the mold. The thickness of cushion is critical. The minimum cushion is 3mm. This amount can provide proper control with the injection process. The cushion is set to less than 6mm to prevent freezing of the cushion that could block the nozzle.

The screw return distance prepares for the next shot. The return distance is determined to provide slightly more material in the barrel after the shot is taken. The RPM should fall within 30–160. The mold open distance allows the mold to open slowly to break the vacuum created from filling. The ejection distance is the amount of ejection required to push the part freely. Typically, 3–6 mm distance is added for ejection travel to maximum part depth.

A.3 MOLDS FOR INJECTION MOLDING

Molds are used with injection molding to form plastic resin into a shape that is depicted in the mold. Molds for injection molding are typically made from tool steel, for example, P-20, H13, S-4. The part features are produced with the cavity (A-side) and core (B-side). Figure A.6 provides a schematic representation of common items in an injection mold.

The locator ring helps fit the injection mold into a press clamp. The sprue bushing is a channel by which the plastic flows from the injection

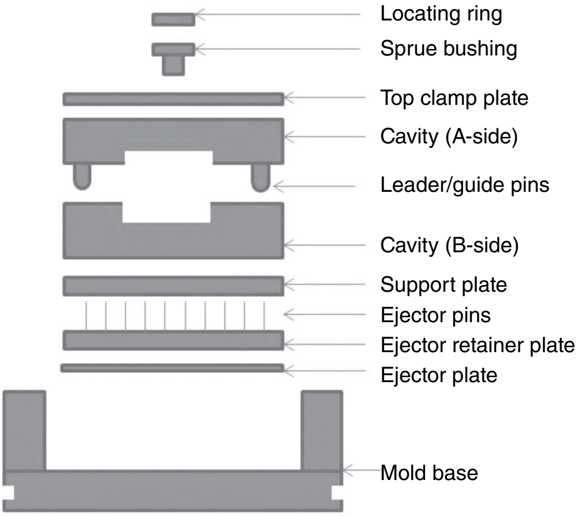

FIGURE A.6 Typical mold components for injection molding (not to scale).

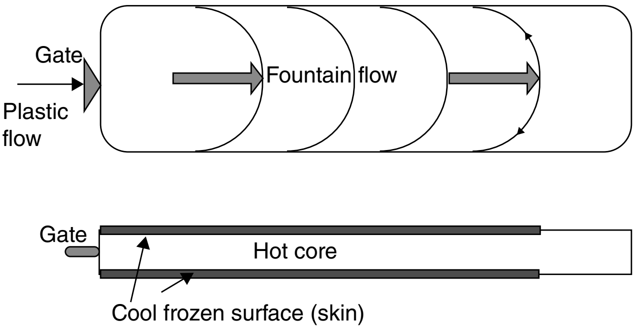

FIGURE A.7 Plastic fountain flow inside cavity of injection molds.

unit into the mold. The cavity is the section of the tooling that has the shape of the plastic part. The top cavity is the A-side and the bottom cavity is the B-side of the injection mold. The ejector pins are placed in an ejector plate and is moved to push out the part from the B-side cavity.

The plastic flows inside the cavities to form the part. The flow of a plastic materials inside the mold is characterized by fountain flow as described in Figure A.7. The hot plastic flows through a gate and then into runners in the mold and finally into the cavity of the injection mold. The hot plastic flows at the center of the gap until it reaches the edge of flow and then flows to the walls of the cavity and cools. This results in a thin frozen layer of plastic on the mold walls and forms a skin layer of plastic. The hot plastic in the middle of the gap is called the core of plastic. The thickness of the core can be adjusted with processing conditions of pressure, injection speed, mold temperature, and melt temperature.

Key design guidelines for building injection molding molds are listed below.

- Runner size and length should be minimized to the cycle time in the production process.
- Gate location should be near the thickest section of the part.
- Inject plastic in the thickest section and make it to flow into thinner sections.
- Keep the uniform thickness in part.

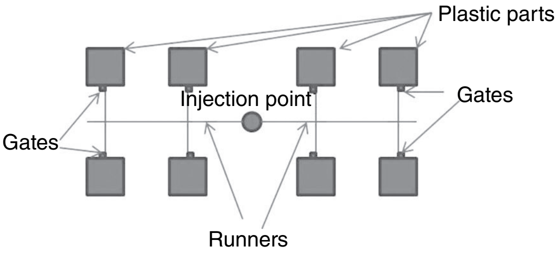

FIGURE A.8 Standard Herringbone runner design.

- Venting is needed at the end of flow of the plastic in the mold to allow for air to escape the mold during filling of plastic.
- Draft angles in the cavity and core should be between 0.5° and 2°.
- Parting lines should be flat and in a single plane, if possible.

A.3.1 Runners and Gates

Runners and gates help provide a balanced flow in the injection molded part. Runners allow the plastic to flow from the hot nozzle to the gate. The runner design is especially important when multi-cavity or family tools are used to produce the plastic part. Figures A.7, A.8, A.9, and A.10 list the common runner designs. Figure A.11 lists a standard gate design. Designs of runners and gates should take into account balancing of the plastic flow in the mold, cycle time, and balancing of pressures in the mold, runners, and gate. More detailed information is available in other sources (Malloy 1994; Rosato and Rosato 2000; Rosato et al. 2001; Osswald et al. 2007).

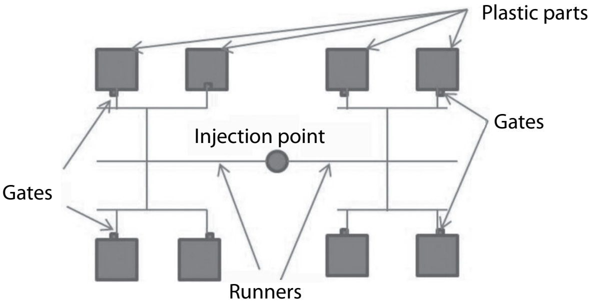

FIGURE A.9 “H” branching runner design.

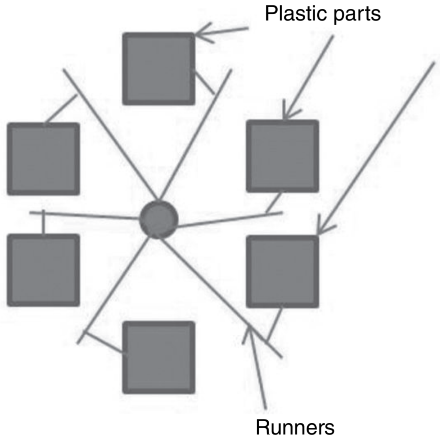

FIGURE A.10 Radial pattern runner design.

A.4 MOLDING DEFECTS

Molding defects can occur during the injection molding of plastic parts. Some common molding defects and possible causes are listed in Table A.6 (Belofsky 1995b).

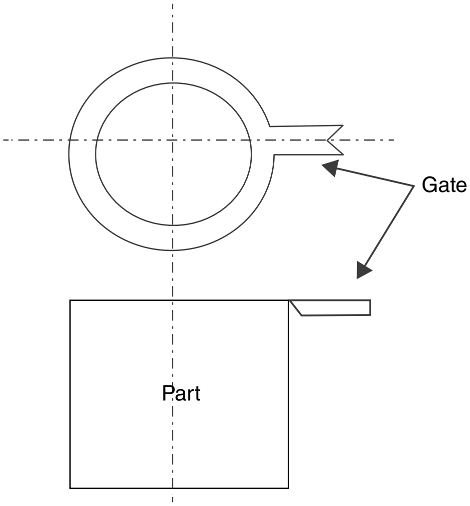

FIGURE A.11 Standard gate design.

TABLE A.6
Molding Defects in Plastic Parts

Molding defect	Description	Causes
Blister	Raised or layered zone on surface of the part	Tool or material is too hot, often caused by a lack of cooling around the tool or a faulty heater
Burn marks	Black or brown burnt areas on the part located at furthest	Air entrapment in mold due to lack of venting
Color streaks	Localized change of color in plastic part	Masterbatch was not mixed properly or the *L*/*D* of the screw is not high enough
Delamination	Thin mica-like layers formed in part wall	Contamination of plastic resin
Flash or burrs	Excess material in thin layer exceeding normal part geometry	Tool damage in parting line, injection speed too high, clamping force too low, or dirt in plastic
Flow marks	Directionally wavy patterns in part	Injection speeds too low, mold temperature too low
Jetting	Part deformed by turbulent flow of material	Poor tool design, gate position or runner, injection speed set too high, poor gate design causing small die swell in part
Knit lines	Small lines	Plastic flow front flowing around an hole, boss, or other feature in the part
Polymer degradation	Plastic breaks down from hydrolysis or degradation	Excess water in the plastic pellets, excessive temperatures in barrel, excessive screw speeds, long residence time of plastic in barrel
Sink marks	Localized depression in part	Holding time or pressure too low, cooling time too short, thick part sections
Short shot	Partial fill of part	Low injection speed, low dosage stroke, cold mold
Splay marks	Circular pattern around gate	High moisture in plastic, trapping of gas in rib
Stringiness	String-like articles	Nozzle temperature too high, gate not freezing off, decompression of the screw, no sprue break, poor placement of the heater bands
Voids	Empty space within the cross-section of a plastic part	Low holding or pack pressure, poor tooling condition
Weld line	Visual flow pattern from two flow fronts coming together	Too low a melt temperature, too low a mold temperature, low injection speed and pressure
Warping	Twisted or distorted part	Pack pressure too low, pack time too low, cooling time is too low, mold temperature may be too high

Source: From Belofsky (1995b).

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APPENDIX B

Extrusion

B.1 INTRODUCTION

The extrusion process is the foundation of many plastic processing methods including injection molding, blown film extrusion, blow molding, profile extrusion, and others. The main purpose of an extruder is to heat plastic materials and then convey the plastic under pressure through a die.

Plastic extruders encompass several types that include single-screw, twin-screw, and ram-screw extruders. The plastic pellets are placed in the hopper and fed through the extruder in three main heated zones as shown in Figure B.1. Extruders have a hopper that transports the plastic pellets or powder into the extruder, one or more vents along the length of the extruder, and an exit die that shapes the plastic exiting the extruder.

The extruder screw design is an essential component of extrusion. The long cylinder with a helical flight is shown in Figure B.2. The screw has several functions during extrusion that includes plastics conveying, shear heating, and mixing of plastics. Special low-shear screws are needed for PVC and nylon materials. Several types of screws are available with different types of shearing zones. Screw types can include EVK screws, barrier screws, plastic screw, cavity mixer, and other shearing screws (Hensen 1997).

The temperature profile in the three zones is dependent on the plastic type. The first zone is called the feed zone. The second zone is called the

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Sustainable Plastics: Environmental Assessments of Biobased, Biodegradable, and Recycled Plastics, First Edition. Joseph P. Greene.

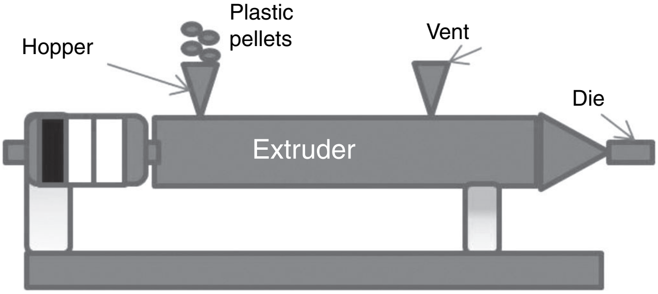

FIGURE B.1 Extrusion process.

compaction zone. The third zone is called the metering zone. The first zone has the largest opening between the rotating screw and the barrel. The metering zone has the largest screw diameter and the smallest flight depth or gap between the screw and the barrel.

The feed zone has the lowest temperature of the three zones and the largest flight depth on the screw. The flight depth is the gap between the screw and the barrel. The flight depth ratio is the ratio of the flight depth in the feed section and the flight depth in the metering section (Screw Designs BASF). The flight depth ratio is typically between 2 and 3 for injection molding.

The compaction zone has an increasing screw diameter from the small diameter in the feed zone to the larger diameter in the metering zone. The gaps between the screw and the barrel are reduced in the compaction zone. The plastic is melted in the compaction zone due to increased temperature and shear heating from the small clearance between the screw and the barrel.

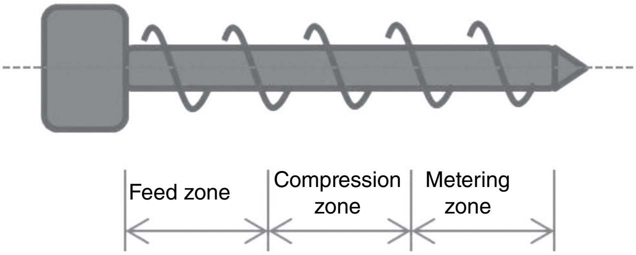

FIGURE B.2 Single-flighted extruder screw.

The metering zone has a constant diameter and gap between the screw and barrel. Plastic is transported with the rotating screw at a rate specified in the machine process parameters.

The length and diameter of the screw and flight depth are important parameters for extrusion. The *L*/*D* ratio is typically 40 or higher for better mixing and blending of plastics. The plastic flows through a breaker plate at the end of the extruder with a screen pack. The screen pack is used to trap contaminants and to improve mixing of the plastics.

The hot plastic exits the extruder through a die. The extrusion die can be many configurations that mold the plastic into a desired shape. Annular dies are used to make tubing, pipe, and wire coating. Slit dies are used to produce flat film and sheet. Profile dies are used to produce shapes other than annular, circular, or rectangular (Rauwendaal 1998).

The extrusion die has three main elements, that is, inlet channel, manifold, and land region. The inlet channel of the die matches the exit of the extruder. The design of the extrusion die should include features that allow for slow, laminar flow across the die channel and maintain a uniform velocity profile.

B.2 EXTRUSION PROCESSING

Extrusion is used in four major plastic processes, including twin-screw compounding, blown film and sheet, tubing and pipe, and profile extrusions. Each of these extrusion operations has a resin handling system, drying system, extruder, shaping device, cooling device, and take-up device.

B.2.1 Twin-Screw Extrusion

Twin-screw extrusion process is used to compound and blend plastic materials into uniform plastic pellets. Twin-screw extrusion can be classified with intermeshing and non-intermeshing extruders. The twin-screw extrusion machine is very similar to a single-screw extruder as shown in Figure B.1. The screws can be co-rotating or counter-rotating configurations as shown in Figure B.3.

Plastic material transport is different in a twin-screw than in a single-screw extruder. In single-screw extrusion, plastic is conveyed with a drag-induced type or transport. In a twin-screw extruder, plastic

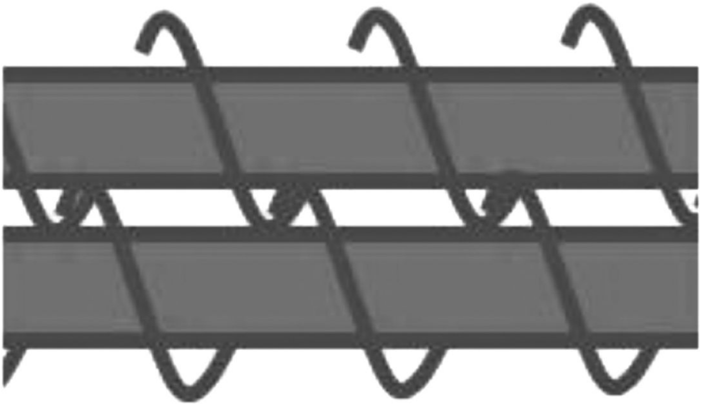

FIGURE B.3 Twin-screw extrusion.

materials are conveyed with a positive type of transport from the gap of the positive flight of one screw and the opposing channel in the other screw (Rauwendaal 1986). The velocity patterns in a twin-screw extruder have a different profile than with a single-screw extruder. The velocity profiles in a single-screw extruder are well defined and dependent upon the screw speed and the back pressure. The velocity profile in a twin-screw extruder is more complicated and involves screw speed, back pressure, and secondary flows that create distributive mixing.

Twin-screw extrusion is used to blend additives, fillers, and reinforcements to polymers as well as blending of two or more polymers. For instance, additives are combined with biopolymers in a twin-screw extruder to increase the strength and mechanical properties. PHA materials are compounded with acrylic impact modifiers and boron nitride nucleating agent in a twin-screw extruder to improve the strength of PHA and increase the crystallinity percentage (Greene 2013).

An American Leistritz Model ZSE-18HP twin-screw extruder system, with 40:1 *L/D*, provided uniform plastic pellets. In the feed zone, the particles are conveyed away from the hopper and fed into the heated barrel. In the transition zone, particles are melted and the melt is homogenized, completing a process that started at the end of the feed zone. This section is designed to enhance the friction and contact with the barrel. Finally, in the metering zone, screw section is designed to act efficiently as a pump by generating pressure in the new homogeneous molten mass of plastic.

The temperatures of the eight zones were between 160°C and 190°C. The screw rpm was between 30 and 66. The side-stuffer speed was 30 rpm. The water bath was warmed to 45°C with a barrel heater. The PHA extrudate was cut into pellets at the take-up roll.

B.2.2 Blown Film Extrusion

Blown film extrusion is a method of producing plastic film that can be used for the production of plastic bags. The blown film process utilizes and extruder and film die to blow a plastic film as shown in Figure B.4 with an annular blown film die and film tower (Rauwendaal 1998).

Plastic materials are evaluated by density and melt index for proper process control on the blown film production line. The density and melt index of several extrusion grade plastics are listed in Table B.1.

The melt index is a measure of the viscosity of the plastic material at very low-shear rate. The melt index is the amount of mass of a plastic that flows through a small orifice in a die over a 10-minute time period. A melt index test machine is shown in Figure B.5. The temperature for plastics can range from 190°C to 300°C and the plunger mass can vary

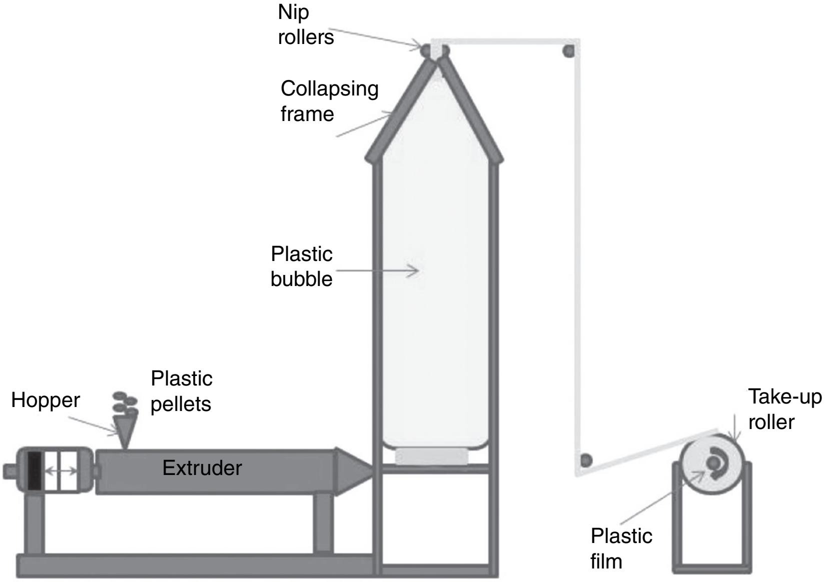

FIGURE B.4 Blown film extrusion system.

TABLE B.1
Plastic Material Melting and Glass Transition Temperatures

Plastic material	Density (g/cm^3)	Melt flow (gram in 10 minutes at temperature)
Acrylonitrile butadiene styrene (ABS)	1.02–1.15	1.0–62
Nylon 6	1.13–1.3	1.0–198
PHA	1.29	N/A
Polyethylene (LDPE)	0.915–0.94	0.18–16
Polyethylene (HDPE)	0.95–0.985	0.04–39
Polyethylene terephthalate (PET)	1.35	9–64
Polypropylene (PP)	0.9	20
Polystyrene (PS)	1.04–1.06	8
Polyvinyl chloride (PVC)	1.40–1.55	2–25

Source: www.matweb.com.

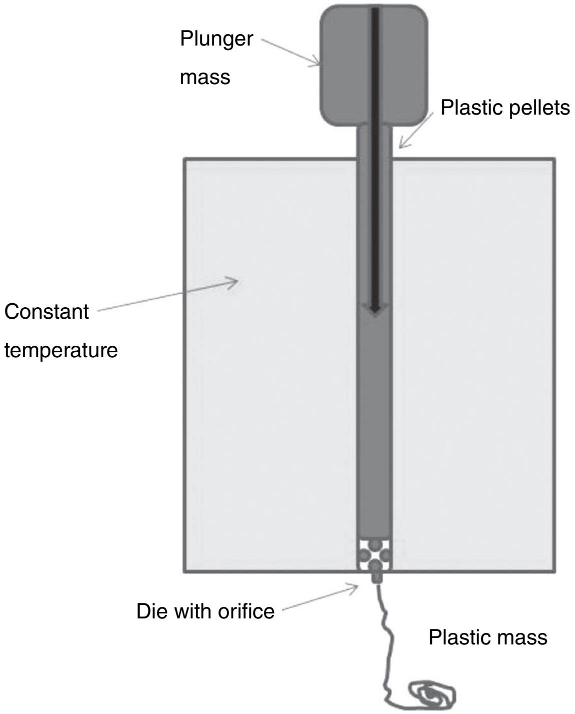

FIGURE B.5 Melt index test for plastics.

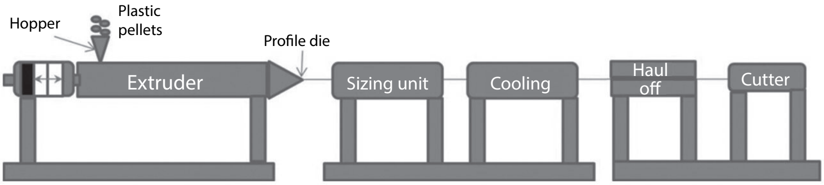

FIGURE B.6 Profile extrusion for plastics.

from 2.06 to 16 kg. The temperature and plunger mass for polyethylene and polypropylene is typically 190°C and 2.16 kg.

The melt index of extrusion or thermoforming grade of plastics is typically less than 1 gram per 10 minutes. The melt index for injection grade plastics is typically greater than 1 gram per 10 minutes.

B.2.3 Profile Extrusion

Many plastic profile shapes are made with a profile extrusion system. Figure B.6 provides a sketch of a profile extrusion line. The profile extrusion system includes an extruder with a profile die, a sizing unit that calibrates the diameter or dimensions to a specified value, a cooling tank, haul-off section, and cutting mechanism (Rauwendaal 1998).

B.3 EXTRUSION PROCESS CONTROL

The extrusion can be controlled by monitoring four areas of the molding process, namely temperature, pressure, time, and screw speed. The four parameters are shown in Figure B.7. Melt temperature is an important control parameter for extrusion. The melt temperatures of several plastics are listed in Table A.1. The temperature of the plastic can be increased in the extruder through shear heating. The screw speed directs the plastics through the screw extruder as the plastic melts into a continuous flow of plastic. The plastic flows relative to the screw along a channel that is related to the helix angle of the screw flight. The plastic flows across the screw channel until the end of the channel where the plastic flows across the flight and along the barrel. The tumbling motion of the plastic is repeated along the screw. The plastic flow along the channel of the screw is proportional to the screw speed. The plastic is

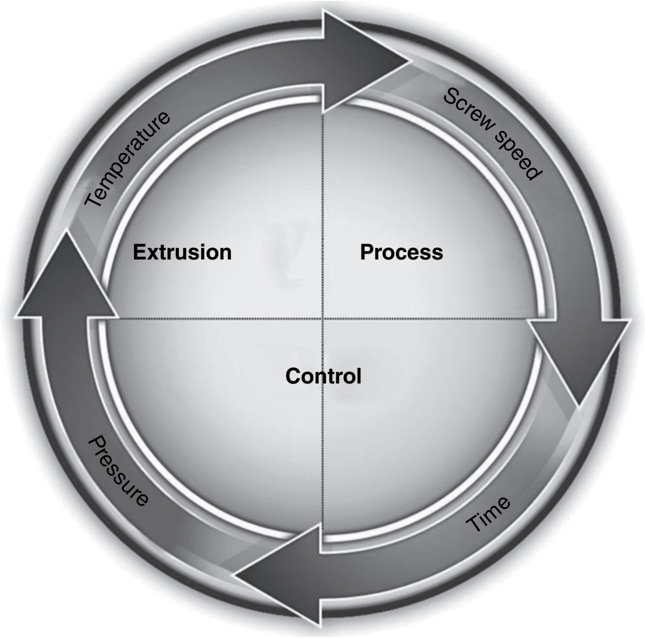

FIGURE B.7 Process control variables for extrusion.

mixed in the screw with a distributive mixing method that recirculates the plastic onto itself. The mixing of the plastic can be improved with mixing elements in the screws. Other resources can better explain the use of mixers in extrusion (Rauwendaal 1986; 1998).

The transportation of the plastic in the extruder is retarded by the pressure that builds up at the die. The plastic flows along the extruder until it reaches the die where the plastic flows through the restrictive opening and conforms to the shape of the die. The pressure in the extruder is highest at the die exit and lowest at the feed zone at the hopper. Thus, the faster the screw is turning, the higher the pressure at the die. The pressure at the die will restrict the flow of the plastic. The pressure drop across the die can contribute to the quality of the plastic in the extrudate.

The residence time in the extruder can also affect the quality of the plastic in the extrudate. Polymer degradation can occur in the extruder if the plastic is heated too long in the extruder. Degradation can result in a drop in mechanical properties in the plastic as well as surface imperfections in the extrudate. Thermal stability of plastics can be improved with the addition of additives.

B.4 EXTRUSION DEFECTS

Surface defects in the plastic extrudate can occur due to flow instabilities or degradation of the plastic during the extrusion process. Some common defects and possible causes are listed in Table B.2.

TABLE B.2
Molding Defects in Plastic Parts

Molding defect	Description	Causes
Blister	Raised or layered zone on the surface of the part	Plastic material temperature may be too high, causing thermal degradation of the plastic
Color streaks	Localized change of color in plastic part	Masterbatch was not mixed properly or the *L*/*D* of the screw is not high enough
Gels	Small round surface defects that resembles distorted plastic	Poor mixing of plastic, thermal degradation of plastic at the barrel walls, un-melted plastic
Melt fracture	Severe distortion of the extrudate leading to defective appearances of spiraling, bambooing, ripples, and random fractures	Occurs when a critical shear stress is exceeded in the die. Causes can be too small, an entry angle in the die or pressure oscillations
Streaks	Straight lines in the machine direction at regular intervals along the width of the sheet in a multilayer extrusion	Non-uniform temperature distribution in the cooling or calendaring rolls
Shark skinning	Surface defect of a regular ridged surface distortion, with ridges running perpendicular to the extrusion direction	Rapid acceleration of the surface layers of the extrudate when the polymer exits the die. This can be caused by too high extrusion velocity, or too high a extrusion temperature

Source: From Rauwendaal (1998) and Prakash and Moitra (2006).

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APPENDIX C

Blow Molding

Plastics can be made into bottles with the blow molding process (Argarwal 2008, Dempsey and Atkins 2008, and Chen 2007). Blow molding can involve injection blow molding, extrusion blow molding, or stretch blow molding process depending on the plastic material properties. The injection blow molding process is used to produce polyethylene terephthalate (PET) and polylactic acid (PLA) plastic bottles. The PET or PLA plastic is injection molded into preforms in one operation and then subsequently cooled and reheated in a separate operation to form the bottle.

C.1 EXTRUSION BLOW MOLDING

Extrusion blow molding is a one-step blow molding process that heats the plastic pellets in an extruder, extrudes the parison into a mold, and then blows air into the parison to form a bottle, as shown in Figure C.1.

Extrusion blow molding can be used to produce PHA bottles. PHA materials were blow molded in a Rocheleau R4 Laboratory Blow Molder. The machine is shown in Figure C.2. The R4 utilizes a 38-mm feed screw with 24/1 *L/D* ratio. The R-4 machine has a reciprocating screw design that allows for fewer moving parts than continuous extrusion machines. PHA bottles were produced on a single parison die with a 125-mm width and 280-mm height bottle. Figure C.3 shows the examples of PHA bottles produced with the R4 extrusion blow molder (Greene 2013).

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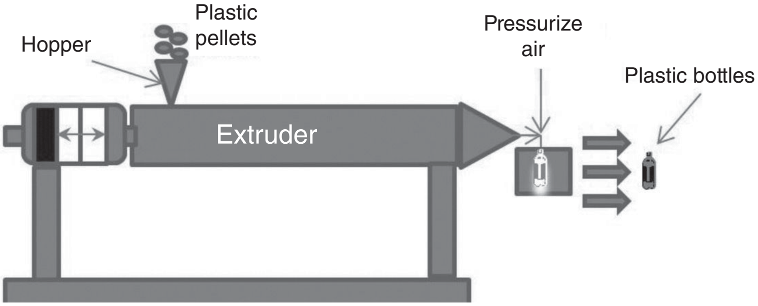

FIGURE C.1 Extrusion blow molding process.

Processing conditions that produced PHA bottles are listed in Table C.1. The optimal conditions are rear temperature of 320°F, front temperature of 300°F, block temperature of 300°F, injection pressure of 1000 psi, blow pressure of 60 psi, mold temperature of 120°F, and mold close time of 60 seconds.

FIGURE C.2 Rocheleau R4 extrusion blow molding machine.

FIGURE C.3 PHA bottles.

C.2 INJECTION STRETCH BLOW MOLDING

Injection stretch blow molding is a two-step blow molding process that is used to produce plastic bottles. Figure C.4 provides an illustration of the injection blow molding process. Multi-cavity injection molding dies are used to produce multiple preforms of plastic. The preforms are heated and stretched in a series of stations. After appropriate time, the

TABLE C.1
Processing Information for PHA Bottles

Molding parameter	Setting
Injection pressure	1000 psi
Blow pressure	60 psi
Rear temperature	320°F
Front temperature	300°F
Shut-off block temperature	300°F
Head temperature	280°F
Mold temperature	120°F

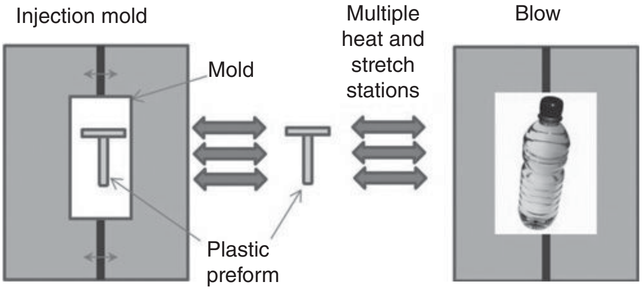

FIGURE C.4 Injection blow molding process.

heated preforms are placed in a blow molder machine and blown into a bottle.

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APPENDIX D

Industrial Compost Biodegradation Testing

D.1 METHODOLOGY

The biodegradation of the compostable materials was tested in a controlled experimental environment. The experimental setup for the laboratory experiment is based upon procedures outlined in ASTM D5338. The procedures to measure the gases were done with detectors as allowed in the ASTM standards. Each of the compostable materials was added to compost soil in a 5-liter glass-canning jar and placed in an oven maintained at 58°C. The room temperature was between 22°C and 27°C during the course of the experiment. The jar containers have a rubber seal on the top.

The samples were prepared by adding 100 grams of plastic sample to 600 grams of mature soil compost in a 5-liter glass jar. The mature compost, 2-3 months old, had a pH of 8.7, ash content of 35%, and Carbon/Nitrogen (C/N) ratio of 10. The C/N ratio was calculated based upon carbon dioxide and ammonia measurements taken with the Solvita instrument on the compost at the beginning of the test. Solvita is an easy-to-use test that measures both carbon dioxide (CO_2) and ammonia (NH_3) levels in the soil and also indicates a Maturity Index value. The index is useful for maturity level of the compost soil (Solvita® Test Kit 2013). The blank compost had a Solvita overall maturity index of 7

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with carbon dioxide rating of 7 and ammonia rating of 5. The mature compost rating indicates well-matured, aged compost and cured with few limitations for use. The blank compost was screened with a sieve of less than 10 mm. The dry solids content was 95% and the volatile solids were 63%. The volatile solids percentage is calculated by the ratio of the difference between the dry weight and the ash content divided by the dry weight.

The biodegradation of the compostable materials was tested in a controlled experimental environment. The experimental setup for the laboratory experiment is based upon procedures outlined in ASTM D5338. The procedures to measure the gases were accomplished with gas detectors as allowed in the ASTM standards. Each of the compostable materials was added to compost soil in a 5-liter glass-canning jar and placed in an oven maintained at 58°C. The jar containers have a rubber seal on the top.

Testing began with 100 grams of test samples, 600 grams of compost soil collected from a 2–3-month-old green yard waste compost facility in Chico, CA. The CO_2 gas evolution was measured with a hand-help digital CO_2 detector from PASCO with the detector placed in the sample jars on a weekly basis. The detector was calibrated weekly. The PASCO IR detector is shown in Figure D.1. The detector was placed in the 5-liter test jar. The experimental equipment is illustrated in Figure D.2.

Avicell microcellulose was used as a positive control material. Polyethylene plastic sheet, called Clingwrap, from Glad was used as a negative control as required in the ASTM standard. Polylactic acid (PLA) and polyhydroxyalkanoate (PHA) materials were cut into small pieces and then ground into powder. The materials are added to a 5-liter vessel, which was filled with 600 grams of compost and 100 grams of test sample. The sample materials occupied 1.5 liters of the vessel and left 3.5 liters of open volume for the gas to occupy. Our experiment met the ASTM D5338 specification that a maximum of 75% of the container can be filled with the test sample and compost.

The moisture content of the samples was regularly monitored with a digital Sartorius moisture analyzer. Distilled water was added, as needed, to achieve an overall moisture content of 50%. The moisture content is found by drying the sample with infrared heat until the mass is unchanged. The composting vessels were placed in an oven with temperature of 58°C (±2°C) for 180 days. The temperature of the air in the laboratory was between 22°C and 27°C throughout the 180 days. The

FIGURE D.1 CO$_2$ measurement with PASCO IR detector.

FIGURE D.2 Experimental setup for laboratory environment.

vessels were rotated and shaken weekly to maintain uniformity. Excess liquid was noted on the daily log and removed by adding air. Oxygen levels ranged between 17% and 21% during the experiment, which met the ASTM requirements of greater than 6% during the experiment.

D.2 MATERIALS

The test materials are all commercially available plastics that are made from corn, namely PLA and PHA. ASTM biodegradation standards are applicable for plastic molded products and not plastic pellets. The samples for the ASTM D5338 test included the following:

- PHA plastic film
- PLA film
- Avicell microcellulose powder (positive control)
- LDPE film (negative control)

The positive control material is cellulose powder from Avicell and the negative control is LDPE film.

D.3 CARBON CONTENT TESTING RESULTS

The amount of carbon can be directly determined experimentally by calorimetry. A bomb calorimeter is a constant-volume device made from stainless steel that measures the change in temperature of a known volume of distilled water as a combustible material is ignited. The bomb calorimeter is capable of withstanding the large pressure and force of explosive reactions. A bomb (Parr Series 1300 Calorimeter with model 1101 stainless steel oxygen bomb) was used to measure the carbon content of the samples by igniting the sample and measuring the amount of carbon dioxide that is produced with the PASCO detector. The carbon content was calculated based on converting the ppm measurement to mg/m^3 in the sample container with Equation A.1 in Appendix A.

The CO_2 gas was vented through the exhaust port at the end of the test and gathered in the 320-mL sampling tube. The ppm of CO_2

was measured with the PASCO CO_2 gas detector. The volume of the calorimeter was 0.340 liters. The pressure in the vessel was 25 atmospheres. The plastic samples were also measured for moisture content. The LDPE film and PLA film had higher heats of combustion than the cellulose material. The cellulose samples had approximately 7% moisture content, whereas LDPE, PHA, and PLA samples had 1% or less moisture content. The moisture content is an average of three measurements.

The average carbon content of PHA, PLA, cellulose, and polyethylene were measured to be 81.09%, 82.45%, 92.42%, and 82.86%, respectively.

D.4 BIODEGRADATION RESULTS

The biodegradation rate can be determined from the amount of CO_2 measured during the 180-day experiment and the amount of initial carbon present in the sample with the use of Equation D.1 below. The CO_2 was measured with a PASCO CO_2 gas detector at weekly intervals by placing the detector inside the 5-liter sealed jar. An example of the measured CO_2 concentrations in ppm for the biodegradation of cellulose is listed in Figure D.3.

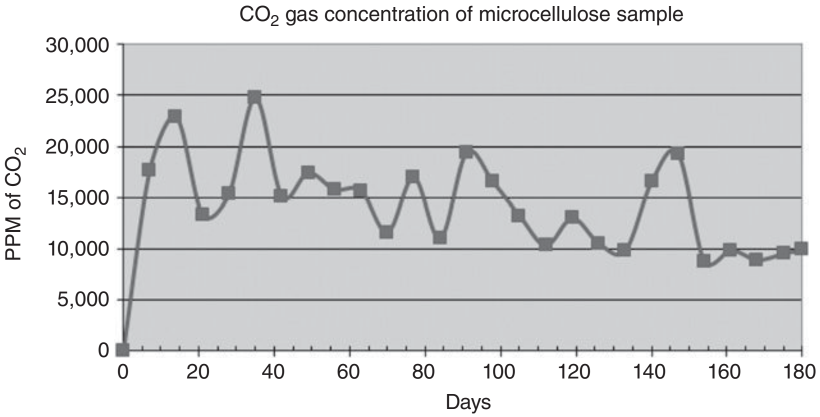

FIGURE D.3 CO_2 ppm measurements of microcellulose sample for 180 days.

The concentrations of CO_2 vary during the experiment and demonstrated a cyclic nature of biodegradation. The concentration of CO_2 was higher at the beginning of the test and then slowly decays over the course of the experiment.

The concentration of carbon dioxide gas in ppm can be converted to percentage biodegradation by calculating the mass of carbon produced and then dividing by the initial mass of carbon in the sample. Equation D.1 lists the conversion factor from carbon dioxide gas concentration to grams of carbon produced. The ppm concentration is divided by 10,000 to convert the ppm to volume fraction of carbon dioxide gas. The volume fraction of carbon dioxide gas is multiplied by the liters of free air of gas and then by the density of carbon dioxide to yield the mass of carbon dioxide. The mass of carbon dioxide is multiplied by the ratio of the atomic mass of carbon and the molecular mass of carbon dioxide.

$$\begin{aligned} \mathrm{gC} = {} & \frac{\mathrm{ppm\ CO_2}}{10{,}000} \times \text{liters of free air} \times \frac{1\,\mathrm{m}^3}{1000\,\mathrm{L}} \times \frac{1.987\,\mathrm{kg}}{\mathrm{m}^3} \\ & \times \frac{1000\,\mathrm{g}}{1\,\mathrm{kg}} \times \frac{12\,\mathrm{gC}}{44\,\mathrm{g\,CO_2}} \end{aligned} \tag{D.1}$$

The conversion of the organic materials in each of the eight materials into CO_2 can be represented by graphing the total conversion percentage on a daily basis as depicted in Figure D.1. The results represent an average of three samples per material. The curve demonstrates degradation throughout the 180-day trial.

The CO_2 concentrations are measured for control materials and biodegradable plastic samples. The amount of CO_2 was measured daily over a 180-day period. The amount of carbon resulted from the CO_2 concentration is calculated for each day. The concentrations of CO_2 that was released over the 180-day experiment from the cellulose control sample are listed in Figure D.3.

The biodegradation rate can be determined from the amount of CO_2 measured during the 180-day experiment and the amount of initial carbon present in the sample with the use of Equation A.1. The CO_2 was measured according to the procedure outlined previously.

The results are listed in Table D.1, and shown graphically in Figure D.4. The results show that PHA film, PLA film, and the cellulose positive control degraded at least 90% in 180 days and met the degradation performance requirement in the ASTM standard. ASTM

TABLE D.1
Degradation Rates for Compostable Samples after 180 Days

Material	Total biodegradation conversion (%)
PHA film	91.69
Cellulose positive control	90.66
PLA film	90.43
Polyethylene negative control	3.98

D6400 biodegradation standard requires at least 90% degradation over 180 days. Cellulose samples had comparable degradation conversion and degradation rates as the PHA film and PLA film. The polyethylene plastic bag had negligible biodegradation in the compost environment.

D.5 PHYTOTOXICITY TESTING

The compostable materials must not release toxic materials into the compost soil during and after degrading. The compost soil can be tested to assess phytotoxicity, which indicates poisonous environment to plants. The germination of tomato seedlings in the compost soil was evaluated after a 10-day duration. The phytotoxicity test was based upon the

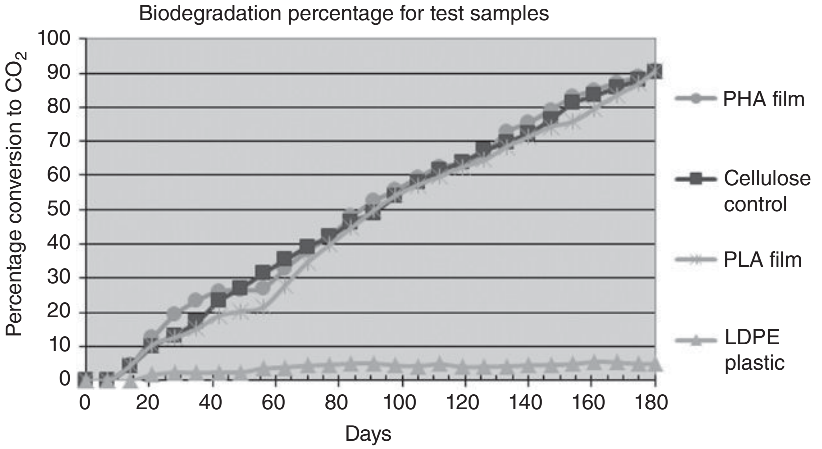

FIGURE D.4 Carbon conversion percentages for samples under industrial composting conditions per ASTM D5338 standards.

TABLE D.2
Phytotoxicity of Compost Soil

Material	Average germination (%)	Average length (mm after 10 days)	Average germination index	Average pH
Blank compost control	46.67	24.33	11.35	8.5
Avicell cellulose control	83.33	18.33	15.27	8.7
PHA film	63.33	16	10.13	8.83
PLA film	70.00	20	14.00	8.5
Polyethylene negative control	70.00	25	17.50	8.63

ISO 11269 standard. The tomato seeds are a "Tiny Tim" variety form Vaughans Seed Company. Ten seeds were planted in small beverage cups (280 mL) that were filled with approximately 50 grams of compost for each of the test samples.

The sample containers were watered with tap water frequently while in a greenhouse. The greenhouse was warm and moist with a temperature of 25°C and relative humidity of 80%. After 10 days in the greenhouse with ambient light, the number and length of shoots were recorded for each sample. The lack of emerging seedlings could indicate phytotoxicity. The percentage of seeds that germinated and the average length of the seedlings are listed in Table D.2. Ten seeds were placed in each container. A germination index is determined by taking the product of percent germination and the average length and dividing by 100.

All of the samples had tomato seedlings grow and pass the phytotoxicity test. Similar results were found with the degraded plastic samples compost with cucumber seeds and cress seeds at 25°C, 80% relative humidity, and atmospheric pressure in the greenhouse. The cucumber seedlings exhibited similar germination percentage growth as the tomato seedlings but had much higher growth length. The cress seedlings also had similar germination percentages as the tomato seedlings, but had much lower seedling height after 10 days. The tomato seedlings had the optimum growth height and were adopted as the standard seed source for the experiment.

D.6 REGULATED HEAVY METAL TESTING

The degraded materials should not leave any regulated heavy metals in the compost soil after degradation. The compost soil from each of the degraded samples was tested for lead and cadmium for all of the materials. The acceptable limit is 30 mg/kg for lead and 0.3 mg/kg for cadmium. The compost soil for each sample was put into solution and the regulated heavy metal in the compost soil was measured with Fisherbrand (2013) hollow-cathode single-element 2-inch-diameter lamps with elements for lead and cadmium.

Lead and cadmium were measured by flame atomic absorption spectrometry using a Jarrell-Ash Model. Lead and cadmium absorption was measured at 283.3 nm and 228.8 nm, respectively. The background correction was measured at 281.2 nm for lead and at 226.5 nm for cadmium. The detection limits are 0.02 ppm lead and 0.005 ppm cadmium in the analytical solution. For a 1-gram sample, the detection limits are 0.2 ppm Pb and 0.05 ppm Cd.

The soil samples that were used during the phytotoxicity testing were also used to measure the lead and cadmium levels. Approximately, 10 grams of compost soil from each sample was dried for 24 hours at 105°C. The average moisture loss was about 30%. About 3 grams of each sample was weighed into a 150-mL beaker to which 50 mL of 8 M HNO_3 was added. The samples were heated for 4 hours at 85°C with occasional stirring. After 4 hours, 50 mL of deionized water was added to each sample followed by vacuum filtration through a Whatman GF/A glass filter with 1% (v/v) HNO_3. The filtrate was quantitatively transferred to a 250-mL volumetric flask and filled to the mark with 1% (v/v) HNO_3. The resulting samples all had a relatively intense orange-red appearance.

Sample preparation included adding a 0.8239-gram sample of $Pb(NO_3)_2$ to a 500-mL volumetric flask, dissolved and diluted to the mark with 1% (v/v) HNO_3 yielding a 1099.5 ppm Pb^{2+} solution. Various standard solutions in the range of 0.220– 1.10 ppm Pb^{2+} in 1% (v/v) HNO_3 were prepared along with a 1 M HNO_3 solution. Standard solutions were prepared by dissolving 0.2460 grams Cd in approximately 3 mL of 6M HCl and approximately 2 mL of 8 M HNO3 in a 250-mL volumetric flask and diluted to the mark with 1% HCl (v/v) yield on 984 ppm Cd solution. Various standard solutions including a blank from mature compost alone were prepared from 0.0984 ppm to 9.840 ppm Cd in 1% HCl.

D.6.1 Regulated Heavy Metal Testing Results

The standard solutions and eight sample solutions were analyzed using a ThermoElectron S Series Flame Atomic Absorption Spectrophotometer and an air-acetylene flame and equipped with a Pb hollow-cathode lamp detecting at 283.3 nm, a Co hollow-cathode lamp, and a Cd hollow-cathode lamp. The sample solutions gave absorbance at or very near the lowest standard employed, which was just above the detection limit of the instrument. Using 0.022 ppm Pb^{2+} as the detection limit leads to an upper limit of 20 ppm Pb^{2+} in the original soil samples. The 20-ppm value equates to 0.02 mg/kg for Pb. The Cd concentrations were lower than 1 ppm, which equates to 0.001 mg/kg Cd.

All of the soil samples from the compostable materials had lead concentrations much lower than the limit of 30 mg/kg Pb and Cd concentrations lower than the limit of 17 mg/kg Cd. In fact, the measured values for Pb and Cd were at the lower detection limits of the Pb and Cd detectors.

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APPENDIX E

Marine Biodegradation Testing

E.1 METHODOLOGY

Marine biodegradation is measured according to ASTM D6691 test methods with measurement of CO_2 evolution from the plastic samples. As per ASTM standards of using actual marine water rather than synthesized one, ocean water was retrieved from beaches in Half Moon Bay, California, with a surface temperature of approximately 20°C. Water was maintained at room temperature until testing began. The marine water was not characterized for sea microorganisms.

E.2 MATERIALS

The test materials used are all commercially available plastics that are made from corn, namely, polylactic acid (PLA) and polyhydroxyalkanoate (PHA). PLA and PHA materials have passed the ASTM D6400 compostability standard and biodegraded in a simulated industrial compost environment in 180 days. ASTM standards are applicable for plastic molded products and not plastic pellets. The samples for the ASTM D6691 test included the following:

- Mirel PHA-2200 plastic film

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- NatureWorks™ PLA bag with aluminum coating
- Avicell microcellulose powder (positive control)
- LDPE Glad trash bag (negative control)

The positive control material is cellulose powder from Avicell and the negative control is LDPE plastic trash bag from Glad.

E.3 EXPERIMENTAL SETUP

Plastic samples were pulverized with a blender and then mortar and pedestal. ASTM D6691-09 allows for testing of plastic products in the form of film, foam, powder, or fragments of molded product. According to ASTM, powder samples should have a mean particle size of less than 25 mm. Our powder samples had a mean particle size less than 25 mm based on visual observations. CO_2 biogas was measured with a PASCO detector with computer-controlled equipment as shown in Figure E.1. The samples are kept in an oven and held at 30°C for 26 weeks according to ASTM standards.

Samples were placed in 5-liter jars that have approximately 1 gram of each sample along with 400 mL of ocean water and approximately 100 grams of ocean bottom soil. The amount of plastic samples and ocean water was significantly larger than those specified in ASTM D6691. The larger samples were needed to provide a larger signal for the PASCO CO_2 sensor. CO_2 biogas was measured by placing the PASCO CO_2 detector in the jar. Previous tests with the smaller sample size per the ASTM standards did not result in a consistent reading with the sensor.

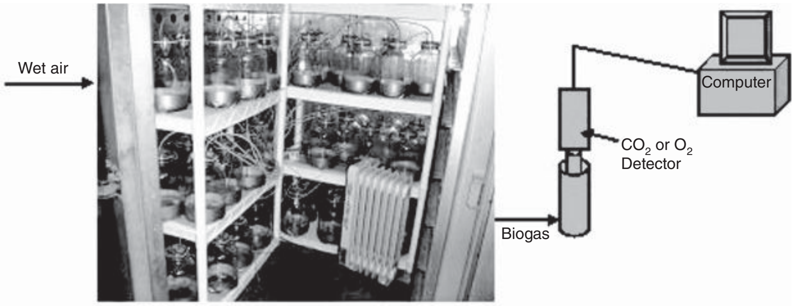

FIGURE E.1 Experimental setup for laboratory experiment.

Testing began with 1 gram of test samples, 400 mL of ocean water, and 100 grams of ocean sand and sediment. The ocean water was retrieved from Half Moon Bay, CA. The computer-controlled testing apparatus with the analog PASCO IR detector experienced some equipment malfunctions and did not provide consistent results early in the testing. The testing was restarted with a new procedure after 3 weeks of testing. The CO_2 evolution was measured with a hand-help digital CO_2 detector from PASCO with the detector placed in the sample jars on a weekly basis. The detector was calibrated weekly. The PASCO IR detector is shown in Figure E.2. The detector was placed in the 5-liter test jar.

The amount of carbon in a sample can be directly determined experimentally by calorimetry. A bomb calorimeter is a constant-volume device made from stainless steel that measures the change in temperature of a known volume of distilled water as a combustible material

FIGURE E.2 CO_2 measurement with PASCO IR detector.

is ignited. The bomb calorimeter is capable of withstanding the large pressure and force of explosive reactions. A bomb (Parr Series 1300 Calorimeter with model 1101 stainless steel oxygen bomb) was used to measure the carbon content of the samples by igniting the sample and measuring the amount of carbon dioxide that is produced with the PASCO detector. The carbon content was calculated based on converting the ppm measurement to mg/m^3 in the sample container with the use of Equation D.1.

The CO_2 gas was vented through the exhaust port at the end of the test and gathered in the 320-mL sampling tube. The ppm of CO_2 was measured with the PASCO CO_2 gas detector. The volume of the calorimeter was 0.340 liters. The pressure was 25 atmospheres. The plastic samples were also measured for moisture content. The carbon content of PHA, PLA, cellulose, and polyethylene were measured to be 81.09%, 85.67%, 92.42%, and 82.86%, respectively.

E.4 MARINE BIODEGRADATION RESULTS

ASTM D6691-09 states the report should include the following information: carbon content of the sample, cumulative average carbon dioxide evolution, and percentage of theoretical aerobic biodegradation for each plastic and control. Table E.1 lists the biodegradation results. The results are also shown in Figure E.3. The calculation methodology is provided in Appendix A**.** Biodegradation is measured based on ppm measurements that are then converted to volume percentage of CO_2. The volume percentage of CO_2 is converted to liters based on an air space of 4.25 liters

TABLE E.1
Marine Biodegradation Results for PHA, PLA, and Control Test Samples after 180 Days

Materials	Initial % CO_2 in 1 gram sample	Cumulative CO_2 evolution after 180 days (grams)	% Biodegradation after 180 days
Cellulose powder	90.68	0.2071	33.31
PHA film	80.91	0.3380	38.22
PLA film	80.68	0.0279	4.45
LDPE film	83.45	0.0254	3.3

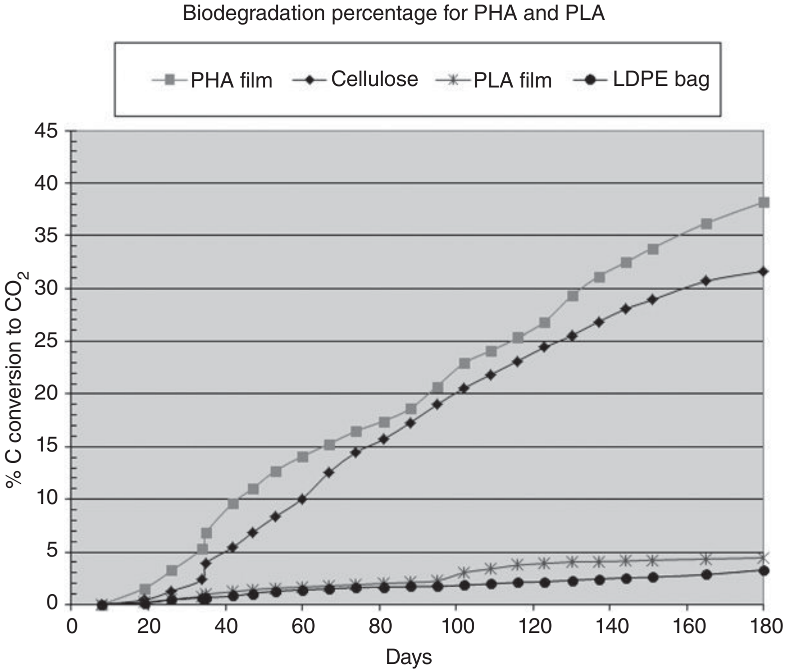

FIGURE E.3 Marine biodegradation results for PHA and PLA after 180 days.

in the test jar. The CO_2 concentration is converted to grams of carbon based on molecular mass of carbon and carbon dioxide. The PASCO IR reading of ppm of CO_2 is the amount of carbon measured in CO_2 and is divided by the initial mass of carbon from the sample to determine the percentage of biodegradation. ASTM D7081 standard requires 30% of the carbon in the test sample to convert into CO_2 after 180 days.

After 180 days as displayed in Table E.1 and Figure E.3, Mirel 4100 and 2200 samples and microcellulose samples passed the ASTM criterion for greater than 30% biodegradation, whereas PLA bottle biodegraded 3%, PLA bag has biodegraded 4%, and the negative control LDPE film biodegraded 3%. LDPE film does not biodegrade in the marine environment in 180 days, but does provide an indication of the experimental noise of the CO_2 measurement device. Therefore, the background noise in the test method is 3% total or ±1.5%.

APPENDIX F

Answers to Selected Questions at the End of Each Chapter

CHAPTER 1

Q.1.1	False
Q.1.2	True
Q.1.3	False
Q.1.4	False
Q.1.5	True
Q.1.6	True
Q.1.7	False
Q.1.8	False
Q.1.9	True
Q.1.10	True

P.1.1	d.
P.1.2	d.
P.1.3	c.

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P.1.4	a.
P.1.5	c.

CHAPTER 2

Q.2.1	True
Q.2.2	True
Q.2.3	False
Q.2.4	False
Q.2.5	False
Q.2.6	True
Q.2.7	False
Q.2.8	True
Q.2.9	True
Q.2.10	False

P.2.1	c.
P.2.2	a.
P.2.3	d.
P.2.4	b.
P.2.5	d.
P.2.6	c.
P.2.7	d.
P.2.8	d.
P.2.9	d.
P.2.10	b.

CHAPTER 3

Q.3.1	True
Q.3.2	False
Q.3.3	False
Q.3.4	False

Q.3.5 False
Q.3.6 True
Q.3.7 False
Q.3.8 True
Q.3.9 True
Q.3.10 True

P.3.1 b.
P.3.2 d.
P.3.3 c.
P.3.4 c.
P.3.5 c.

CHAPTER 4

Q.4.1 False
Q.4.2 True
Q.4.3 True
Q.4.4 False
Q.4.5 False
Q.4.6 True
Q.4.7 True
Q.4.8 False
Q.4.9 True
Q.4.10 True

P.4.1 c.
P.4.2 a.
P.4.3 b.
P.4.4 c.
P.4.5 d.
P.4.6 b.
P.4.7 a.

P.4.8	a.
P.4.9	c.
P.4.10	c.

CHAPTER 5

Q.5.1	True
Q.5.2	False
Q.5.3	False
Q.5.4	False
Q.5.5	True
Q.5.6	True
Q.5.7	False
Q.5.8	True
Q.5.9	False
Q.5.10	True

P.5.1	c.
P.5.2	a.
P.5.3	c.
P.5.4	c.
P.5.5	b.
P.5.6	c.
P.5.7	a.
P.5.8	b.
P.5.9	b.
P.5.10	c.

CHAPTER 6

Q.6.1	False
Q.6.2	False
Q.6.3	True

Q.6.4 True
Q.6.5 False
Q.6.6 True
Q.6.7 False
Q.6.8 True
Q.6.9 True
Q.6.10 False

P.6.1 b.
P.6.2 c.
P.6.3 d.
P.6.4 c.
P.6.5 c.

CHAPTER 7

Q.7.1 True
Q.7.2 True
Q.7.3 False
Q.7.4 True
Q.7.5 True
Q.7.6 True
Q.7.7 True
Q.7.8 False
Q.7.9 True
Q.7.10 True

P.7.1 b.
P.7.2 b.
P.7.3 d.
P.7.4 c.
P.7.5 b.
P.7.6 b.

P.7.7	c.
P.7.8	c.
P.7.9	c.
P.7.10	d.

CHAPTER 8

Q.8.1	True
Q.8.2	False
Q.8.3	False
Q.8.4	False
Q.8.5	True
Q.8.6	True
Q.8.7	True
Q.8.8	True
Q.8.9	False
Q.8.10	False

P.8.1	c.
P.8.2	c.
P.8.3	c.
P.8.4	d.
P.8.5	b.
P.8.6	c.
P.8.7	a.
P.8.8	c.
P.8.9	c.
P.8.10	c.

CHAPTER 9

Q.9.1	True
Q.9.2	True

Q.9.3 True

Q.9.4 False

Q.9.5 True

Q.9.6 True

Q.9.7 True

Q.9.8 True

Q.9.9 False

Q.9.10 True

P.9.1 d.

P.9.2 a.

P.9.3 a.

P.9.4 c.

P.9.5 d.

CHAPTER 10

Q.10.1 True

Q.10.2 True

Q.10.3 True

Q.10.4 False

Q.10.5 False

P.10.1 d.

P.10.2 d.

P.10.3 b.

P.10.4 a.

P.10.5 d.

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