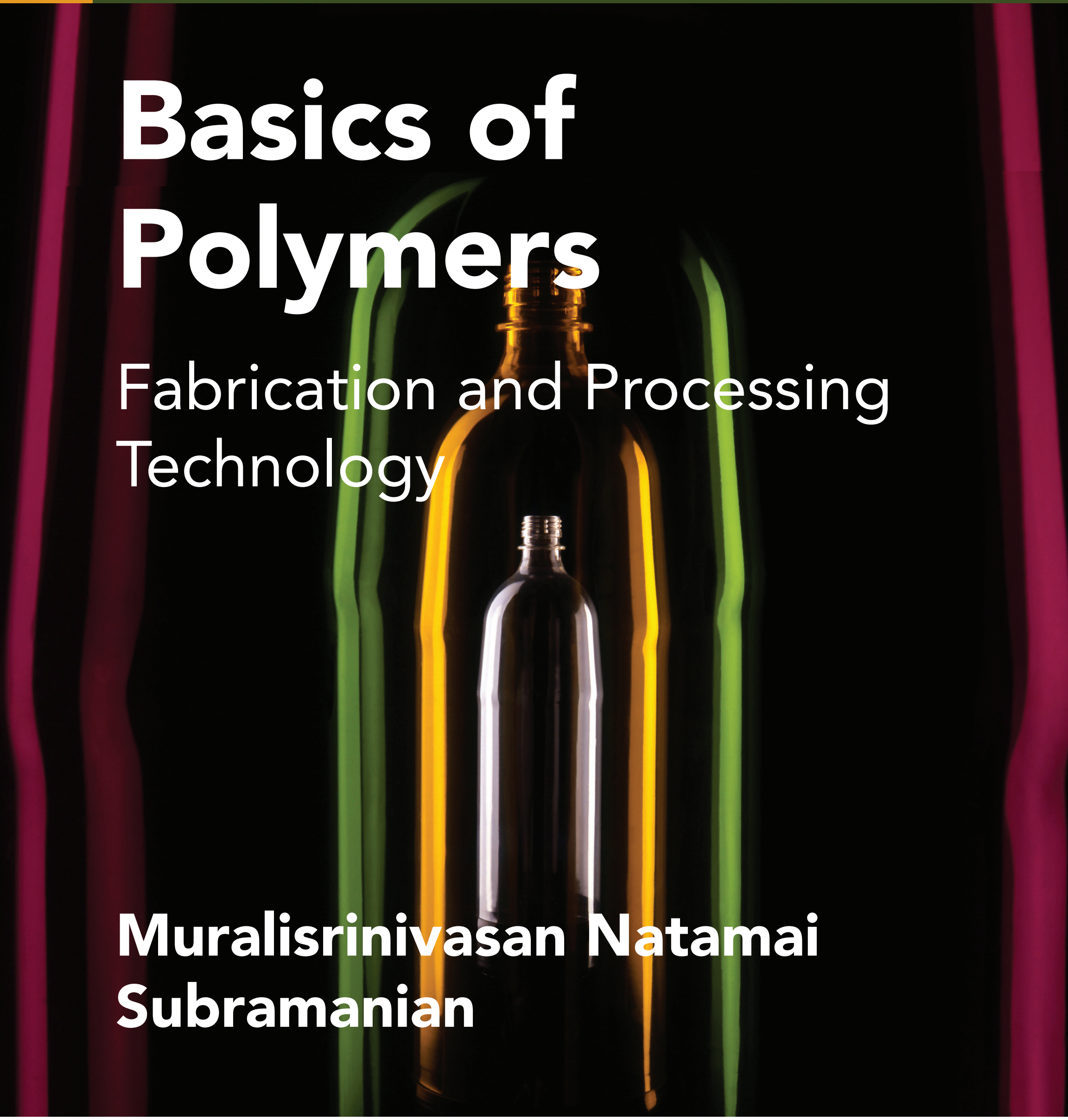
PLASTICS AND POLYMERS COLLECTION



Basics of Polymers

Fabrication and Processing Technology

Muralisrinivasan Natamai Subramanian

MOMENTUM PRESS
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Abstract

This book constitutes one of the most important aspects of polymer processing and technology. The performance of polymers is evolving the most rapid increasing volume of production. Polymers are an important commodity in the modern lifestyle. Polymers are undoubtedly superior materials in terms of their costs, processability, and functional properties. The fabrication and processing technology is showing higher growth than the number of polymer grades in the market.

The growth rate of the polymers continues with the following important points: (1) commercialization of polymers, especially with respect to the processing technology, (2) growth of polymers, and (3) increasing number of processing technologies such as injection blow molding and extrusion blow molding. Additives mixing and compounding with polymer materials facilitates processing technology with increase in production. More precise and expensive processing equipment results in higher productivity with better polymer properties. However, from the processing point of view, equipment requires much finer control, which results in higher productivity rate of better end product.

To improve the processing in polymers, it is often necessary to know about polymers based on

- structure
- properties
- molecular weight distribution

Fabrication and polymer processing should be considered as resources for the manufacture of new products. Scientific knowledge about the polymeric materials during their processing and end product development for the quality is the fundamental to guarantee the performance of applications. Additives can be used to upgrade the processing technique and properties.

Fabrication and processing technology is essentially a simple teaching program designed for students and industrial trainees who have little or no background in science or in the technology of polymers. It is essentially set out in simple form, that is, a series of short notes, diagrams, machines, die design, and processes. The basic principles associated with polymer properties and machine and operation are related. Text teaching along with the elements of processing technology forms active material from a practical angle.

Keywords

amorphous, anionic polymerization, morphology, processing, molecular weight, polymer properties, crystalline, polyethylene, polypropylene, acrylonitrile–butadiene–styrene, nylon, polycarbonate, stress relaxation, injection molding, extrusion, thermoforming, rotational molding, compounding, melt flow rate, thermomechanical, melting point, screw extrusion, hollow parts, research, process simulation

Contents

Preface

Polymers are an extraordinarily large class of materials with promising applications and have been developed to the point of highly successful commercialization. In this book, topics are organized according to the polymer processing as distinct from a method-based classification. Polymers have served as an important material throughout the world in large scale and the consumption has increased tremendously. More researches have spurred a new wave of demand for polymers.

Despite the tremendous growth in the global consumption of polymer, there are still many technological challenges that must be met to improve the quality of the end product. The contents of this book are to a great extent a transcript of my training courses delivered at various parts of the world. These training materials have been considerably amplified.

The book "Basics of Polymers—Fabrication and Processing Technology" describes research in development and will serve as a platform for scientific studies leading to polymer processing and quality. The objective of this book is to provide an overall increasing awareness related to polymers and the processing is highlighted.

The aim of the book is to classify and systematize rather than to describe. I have endeavored to furnish the student with a kind of skeleton of polymer. The great amount of labor an earnest student expends in noting down the polymers and their processing is presented in this book. The chief objective of this book has been to relieve students from such labor and distractions.

Acknowledgment

I deeply thank my professors for their valuable guidance during my studies, and many thanks to Mr. Joel Stein, Ms. Rene Caroline, Ms. Charlene Kronstedt and other members of M/s. Momentum Press. Many thanks to my wife (Mrs. Himachala Ganga) and my children (Venkatasubramanian who is studying in KLN College of Information Technology and Sailesh who is studying in Velammal College of Engineering and Technology) who worked hard with me to get this book finished in timely manner. My sincere thanks are extended, above all to god and parents who brought me to the earth to enhance my writing.

CHAPTER 1

Introduction

Plastics processing technology is one of the important methods traditionally used to produce polymer products. It is limited by equipment and has seen a rapid growth due to the development of new application areas in the automotive, sports and leisure, electronics, transportation, and packaging industries [1]. Processing technology is the major contributor in the production of plastic parts. Today, polymers are an integral part of lifestyle, with application varying from commonplace articles to sophisticated scientific and medical instruments. In polymers, processing and design criteria may often succeed with tools. Therefore, polymers have been referred to as one of the major technological ages.

Polymers are of profound interest to society and are replacing metals in diverse fields of life, which can be further modified according to modern application. They are more desirable than traditional materials in such areas as packaging, construction, and medical applications. Polymer processing has gone through considerable changes; the basics of polymer processing remain dynamic as well, thoroughly to demonstrate the precision and accuracy of the end products obtained from the technology. Polymer technology represents important areas of work owing to everyday presence of polymers. Processing of polymeric materials basically depends on applied heat and pressure.

Polymer processing technology accounts for all polymeric materials processed and is widely used for mass producing products and parts of complex shape cost-effectively with high precision [2]. The complexity of processing technology calls for a much better understanding of the process, machining and material behavior, and its effects on the performance of the final product. Continuous improvement in the processing should, however, ensure that there will be pressure from in the direction of production of polymeric products. Therefore, polymer processing technology may cause pressure in some applications; however, the greater infrastructure will assist in limiting any major swings.

Summary

- Polymers are replacing metals in diverse fields of life.
- Polymer processing technology is widely used to process all polymeric materials.
- Processing technology often succeeds entirely with tools and design.
- Processing technology is the major contributor in the production of plastic parts.
- Processing of polymeric materials depends on applied heat and pressure.

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CHAPTER 2

Principles of Polymers and Polymerization

Polymeric materials are based on both precise control of molecular structure through polymerization and subsequent processing techniques. The necessary requirements for designing and processing of polymeric materials are functionality, composition, topology, and chain uniformity. The structure of polymer materials consists of designed architectures and this property helps accomplish various applications.

Polymers are macromolecules built up by large numbers of much smaller molecules called monomers. Because of the increased reliability of polymeric materials, they are extensively used in many applications.

2.1. Polymer Classification

Polymers can be classified according to one or more of the following criteria:

- chemical nature of monomers
- molecular structure of polymers
- polymer chain growth mechanism
- type of polymerization process

2.1.1. Chemical Nature of Monomers

Monomers contain the following [1]:

- Bifunctional or multifunctional reactive groups include hydroxyl and carboxyl amines and can undergo condensation polymerization reactions.

- One or more pairs of double bonds such as >C=C< and >C=O can form polymers by conversion of their double bonds into saturated linkages; for example, vinyl chloride can undergo free-radical addition polymerization to form polyvinyl chloride.
- Ring-type monomers such as cyclic ethers, lactams, and lactones can be polymerized via ring scission reactions to high-molecular-weight polymers.

2.1.2. Molecular Structure of Polymers

Classification of polymers based on the number of different structural units present in the chain:

- Homopolymers that link together a large number of single repeating unit.
- Copolymers that form more than one type of monomers such as bipolymers, terpolymers, and multipolymers on the basis of different structural units in polymer chain.

Classification of polymers according to their chain structure:

- linear polymers
- branched polymers
- comb-like polymers
- star-like polymers
- cyclic polymers
- dendrimer polymers

Classification of polymers based on the degree of stereoisomerism relative to arrangements of configurational units in a chain:

- Geometrical isomerism—arises from different configurations of substituents on a carbon–carbon double bond or on a cyclic structure.
- Optical isomerism—arises from different configurations of substituents on a saturated carbon atom.

2.1.3. Polymer Chain Growth Mechanism

Classification based on polymer chain growth mechanism results in

- Step-growth polymerizations (polycondensations)
- Chain polymerizations (e.g., free radical, anionic, and cationic).

2.1.4. Polymerization

In producing good-quality polymeric materials, monomer purity is of prime importance. Catalysts are poisoned by oxygen, carbon monoxide and dioxide, sulfur compounds, and water. Therefore, crystallinity and molecular weight are altered. The reactions by which monomers combine are termed polymerizations. There are polymerization processes, each having advantages and disadvantages [2–4].

2.1.4.1. Important Rector Operations [5]

- Flow—an important variable in polymerization and relies on need to know material being transported from one point to another. It is inferred from liquid velocity or from changes in kinetic energy where the driving force is a pressure difference.
- Level—an important measurement that is common not only in polymerization reactors but, in general, for chemical process industry [6].
- Pressure—a commonly measured variable and its measurment can be divided into absolute pressure, gauge pressure, and differential pressure.
- Temperature—a routinely measured parameter in polymerization reactions. The principle of temperature measurement is based on the transmission of the thermal energy from the medium.

Styrene is obtained industrially by the reaction of ethylene from petroleum or natural gas and benzene from coal or synthetically from petroleum. Styrene may be synthesized directly from acetylene via vinylacetylene or from acetylene and benzene. In coal-tar during aromatization of aliphatic hydrocarbons, some styrene is formed. The reaction of

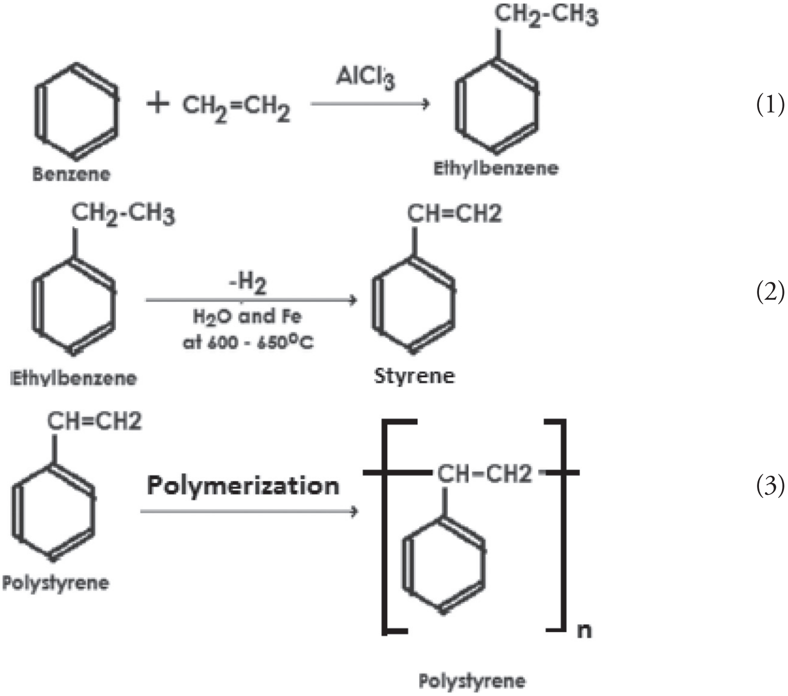


Figure 2.1 Manufacture of polystyrene from benzene and ethylene

styrene and ethylene in the presence of Friedel–Crafts catalyst forms ethylbenzene; further on dehydrogenation of ethylbenzene (Eq. 1), Styrene (Eq. 2), and polystyrene (Eq. 3) (Figure 2.1) is obtained.

Polymer manufacturing involves mass polymerization by batch or continuous, solution polymerization, and suspension polymerization techniques using radical initiators. Mass polymerization yields transparent material with broad molecular weight distribution, which leads to difficulty during processing. Solution and suspension polymerization processes produce polystyrene with greater control of molecular weight with impaired clarity. Temperature is an important parameter in all polymerization techniques. Low temperature results in a slow rate of reaction with few byproducts and yields tough polymers with higher molecular weight, whereas high temperature yields brittle polymers with lower molecular weight.

2.1.4.2. Chain or Addition Polymerization

Polymer chains grow by repeated addition of monomer molecules to an active chain center contrary to step-growth polymerization. Chain polymerization can proceed via free-radical and ionic mechanisms. It requires a chain initiator for the formation of primary active centers. It is possible to prepare a polymer with narrow-molecular-weight distribution in the absence of chain transfer and chain termination [7–10]. Chain-reaction polymerizations produce polymers with a distribution of molecular weights, which is governed by the random nature of the termination reaction.

In any addition type of polymerization, there are three basic steps, namely:

- Initiation leads to the smallest entity and may reproduce the growing end-group by addition of monomer.
- Propagation consecutively adds to a growing center, regenerating it every time and producing an ever lengthening polymeric chain.
- Termination and transfer deprive the growing polymer, and the ability is lost irrevocably and the reaction may continue only through creatine of new growing centers by some initiation step. In case of transfer reaction, the growth of a polymeric molecule is terminated simultaneously with the formation of new growing center and the chain reaction is continued.

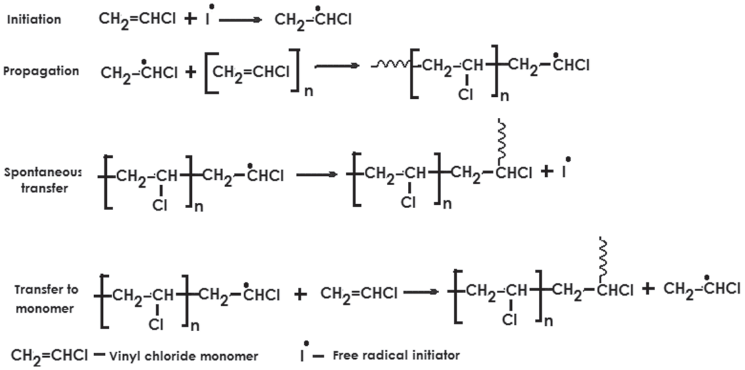
The essential requirements to form narrow molecular weight distribution in chain or addition polymerization are

- Growth of each polymer molecule must proceed exclusively with the addition of monomer consecutively to an active terminal group.
- Only all active termini must be equally susceptible to reaction with monomer and this condition must prevail throughout the polymerization.
- No chain transfer or termination or interchange in polymerization.
- Irreversible propagation.

2.1.4.3. Free-Radical Polymerization

In free-radical polymerizations, three basic reactions occur during polymerization. They are initiation, propagation, and termination reactions. In initiation reactions, continuous generation of free radicals takes place. In propagation reactions, the free radicals are responsible for the growth of polymer chains by monomer addition. Termination reactions end the polymer chain growth with the addition of radical center and bimolecular reactions between two radical centers. This reaction results in net consumption of radicals. In free-radical polymerization (Eqs. 4–7),

- Monomer concentration decreases throughout the polymerization.
- Reaction mixture contains only monomer, high polymer, and growing polymer chains.
- Lifetime of live polymer chain is of the order 0.1–1.0 seconds [9].
- High-molecular-weight polymers are formed from the beginning of the polymerization.
- Chain microstructure and molecular weight distribution are independent of initiation mechanism and type and function of reaction variables such as temperature and concentration of reactants.
- Polymers are largely atactic and in some cases, such as polyethylene, highly branched.



(4)

(5)

(6)

(7)

Free radicals may be generated by the chemical decomposition of azo and peroxide compounds thermally and by γ-irradiation. In the polymerization reactions (4)–(7), vinyl chloride monomer and free-radical initiator are involved, resulting in polyvinylchloride (PVC) by free-radical polymerization.

2.1.4.4. Ionic Polymerization

Ionic polymerization is a chain process, which is industrially employed for the production of thermoplastic polymeric materials.

2.1.4.4.1. Anionic Polymerization. Anionic polymerizations (Eqs. 8–9) are industrially employed for the production of thermoplastics, most notably that of formaldehyde and ε-caprolactam and block copolymers (e.g., thermoplastic elastomers of the styrene–butadiene–styrene type). Initiation by alkali metals is achieved by adding across the double bond in anionic polymerization.

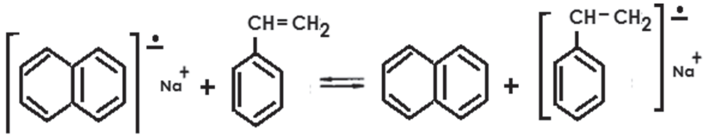
Initiation in anionic systems takes place normally by either reaction (8) or reaction (9). Even in some cases, initiation can take place simultaneously by both reactions [11–12].

Initiation reaction

$$CH_2{=}CHR + X^- \longrightarrow XCH2{-}\bar{C}H \qquad (8)$$

$$\left.\begin{array}{l} CH_2{=}CHR + X^- \longrightarrow {}^{\bullet}CH2{-}\bar{C}HR + X \\ 2\left({}^{\bullet}CH2{-}\bar{C}HR\right) \longrightarrow RH\bar{C}-CH2\,CH2{-}\bar{C}HR \end{array}\right] \qquad (9)$$

Sodium naphthenate and styrene monomer reactions eqs. (10)–(12) undergo anionic polymerization.



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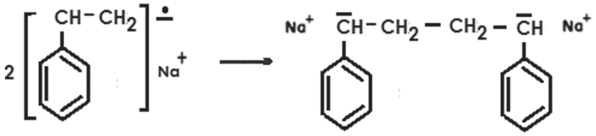

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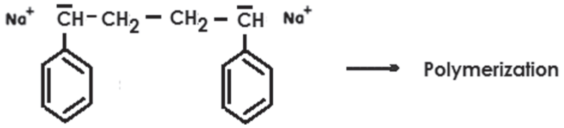


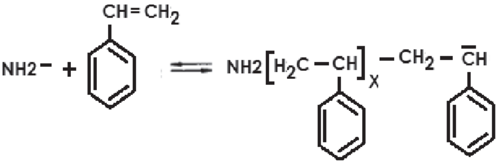
(12)

A similar situation of styrene by potassium amide in homogeneous solution in liquid ammonia due to the necessary use of a high degree of chain transfer to the solvent is introduced [13] in reactions eqs. (13)–(15).

In reaction (15), which is a chain transfer step and not a termination step, the molecular weight of the product is strongly influenced.

The base-catalyzed polymerization of cyclic siloxane [14] undergoes initiation, propagation, and termination reactions as shown in eqs. (16)–(18)

$$KNH_2 \rightleftharpoons K^+ + NH2^- \qquad (13)$$



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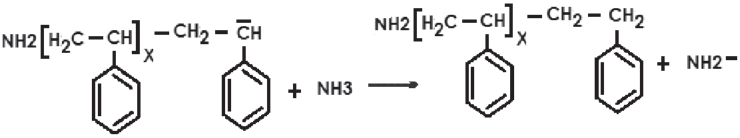


(15)

$$\text{Initiation} \quad R_3SiOK \longrightarrow R_3SiO^- + K^+ \qquad (16)$$

$$\text{Propagation} \quad R_3SiO^- + D_4 \rightleftharpoons R_3SiO\,[D]_x^- \qquad (17)$$

$$\text{Termination} \quad R_3SiO\,[D]_x^- + K^+ \longrightarrow R_3SiO\,[D]_x K \qquad (18)$$

where R_3SiOK represents a potassium silanolate initiator. It can be formed by the reaction of KOH with the cyclic monomer and D_4 represents the cyclic monomer. D represents the $(CH_3)_2SiO$ group.

In anionic polymerization, the outstanding feature is the absence of any fortuitous chain termination step; therefore, the system enables control in the synthesis of polymers as follows:

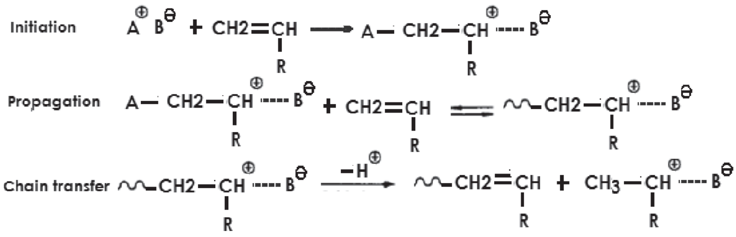
- It is initiated by bases or Lewis bases such as alkali metals, alkoxides, amines, phosphines, Grignard compounds, and sodium naphthalene. It is carried out at low temperatures in solvents of low polarity, giving lightly bound ion pairs rather than mainly separate ions. It is also sensitive to traces of moisture and air.
- Polymers having a predictable molecular weight average, from simple stoichiometry.
- Formation of living polymer chains such as synthesis of true block copolymers by sequential addition of different monomers.
- Formation of polymers with functional end groups by selective termination with appropriate reagents.

- It may have termination and transfer reactions rare. However, initiation reactions are faster than propagation.
- Formation of very narrow molecular weight distribution by proper adjustment of initiation versus propagation kinetics.
- It has a number of growing chains, which is simply equal to the number of catalyst molecules added.
- Lifetime of the chains is of the order 10 to 10^6 seconds [10].
- Deliberate termination is to be carried out by the addition of proton donors such as alcohol or acid to give saturated hydrocarbon groups.

A major drawback of this anionic system is the difficulty of living anionic polymerization of functionalized derivatives, since most functional groups are not normally compatible with anionic initiators and the propagating chain-end polyanions [15].

2.1.4.4.2. Cationic Polymerization. Cationic polymerization is defined as an addition polymerization reaction mediated by a propagating carbocation. Commercially high polymers are produced by cationic polymerization. The reaction is carried out in chlorinated solvents using aluminum trichloride ($AlCl_3$) as catalyst. Carbonium ions are very sensitive to polar impurities, and this often precludes the establishment of a stationary state. It is difficult to establish the production of growing polymer chains by the proportion of catalyst.

In cationic vinyl polymerization reactions eqs. (19)–(21), the propagating carbocation $–CH_2–CH\ (R)^+\ B^-$. This carbocation is derived from vinyl monomer and an initiator [16–20]. The growing carbocations are highly reactive but unstable and subject to a number of side reactions such as chain transfer and termination, among which chain transfer to monomer is most important.



Initiation $\overset{\oplus}{A}\ \overset{\ominus}{B} + CH2{=}\underset{R}{CH} \longrightarrow A-CH2-\underset{R}{\overset{\oplus}{CH}}\text{-----}\overset{\ominus}{B}$ (19)

Propagation $A-CH2-\underset{R}{\overset{\oplus}{CH}}\text{-----}\overset{\ominus}{B} + CH2{=}\underset{R}{CH} \rightleftharpoons \sim\!CH2-\underset{R}{\overset{\oplus}{CH}}\text{-----}\overset{\ominus}{B}$ (20)

Chain transfer $\sim\!CH2-\underset{R}{\overset{\oplus}{CH}}\text{-----}\overset{\ominus}{B} \xrightarrow{-\overset{\oplus}{H}} \sim\!CH2{=}\underset{R}{CH} + CH_3-\underset{R}{\overset{\oplus}{CH}}\text{-----}\overset{\ominus}{B}$ (21)

2.1.4.5. Step-Growth or Condensation Polymerization

Step-growth polymerization involves in reactions between two different functional groups. It forms lifetime of a growing polymer chain until the functional group reactions end. Even single monomers containing both types of functional groups can be polymerized. Polyamides can be obtained from the reaction of aminoacids with themselves without the addition of any other monomer. Condensation polymers such as polyesters form from diacids and diols of two different bifunctional groups with elimination of water.

Step-growth polymerization includes the following characteristics:

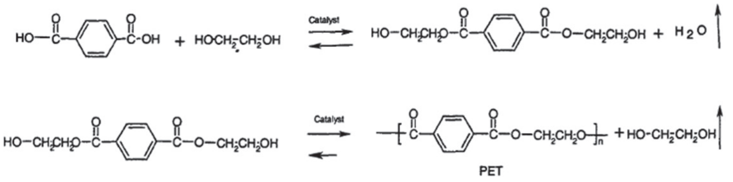
- It is an exothermic reaction.
- At high conversions, only viscosity of the reaction mixture increases.
- Monomers disappear early in the reaction.
- Molecular weight increases throughout reaction in a steady manner.
- High-conversion reactions (greater than 99%) take place.
- Absence of deleterious side reactions results in the loss of functionality.
- The reaction is controlled by functional group stoichiometry.
- It is improved with high monomer purities.
- Removal of any polymerization condensates makes the process efficient.
- It has relatively fast polymerization rates.

The general reaction of step-growth polymerization (Eq. 22) is mentioned as below:

$$R_m + R_n \longrightarrow R_{m+n} + C \tag{22}$$

where Rm and Rn are the growing monomers with degree of polymerization of m and n, respectively, and C is the condensate of small molecules such as H_2O and CO_2.

To obtain polyethylene terephthalate (PET) and other polyesters by step-growth polymerization (Eqs. 23–24), a variety of metal catalysts have been employed at acceptable rates with minimization of side reactions [21, 22].



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(24)

Polyethylene Terephthalate (PET)

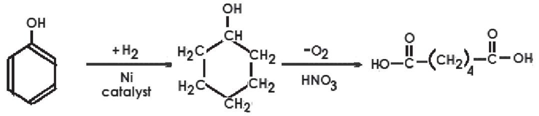
Step and chain polymerizations are typical examples of condensation polymerization of difunctional monomers and addition polymerization of olefinic monomers, respectively [23–26]. Bayer's phenol–aldehyde reaction is a step polymerization and Simon's styrene reaction is a chain polymerization(Eqs. 25–26).

$$\text{Difunctional monomer} \quad X{-}R{-}Y \xrightarrow[\text{single-bond reaction}]{\text{step polymn}} X{+}R{+}_{n}Y \quad \text{Condensation polymer} \tag{25}$$

$$\text{Vinyl monomer} \quad C{=}C \xrightarrow[\text{double-bond reaction}]{\text{chain polymn}} {+}C{-}C{+}_{n} \quad \text{Vinyl polymer} \tag{26}$$

Molecules of a difunctional monomer such as X–R–Y (where X and Y are mutually reactive functional groups) are polymerized via the elimination of small molecule by-products of XY, a linear condensation polymer with a general formula of X–(–R–)*n*–Y is formed, whereas when molecules of an olefinic monomer such as $H_2C{=}CHR$ are polymerized, a vinyl polymer with a structure of –[–H_2C–CH(R)–]*n*– is produced. The difunctional and olefinic monomers have been the major monomer sources, and their step and chain polymerization reactions have been the main synthetic routes to the "conventional" polymers such as polyester and polystyrene, respectively [27].

2.1.4.5.1. Nylon 6,6. Phenol is hydrogenated, or cyclohexane is catalytically oxidized with air, and the resulting cyclohexanol is oxidized to adipic acid. Dehydration of ammonium adipate then yields adiponitrile, which is hydrogenated to hexamethylenediamine. Equivalent amounts of adipic acid and hexamethylene diamine are used to prepare a solution of hexamethylenediammonium adipate which, when heated first under pressure then under reduced pressure and in the absence of oxygen, condenses to a linear polymer. In contrast to the polymerization of caprolactam, the condensation proceeds almost to completion (Eqs. 27–29).



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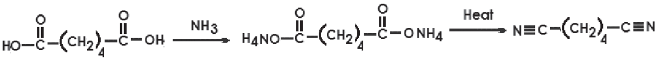
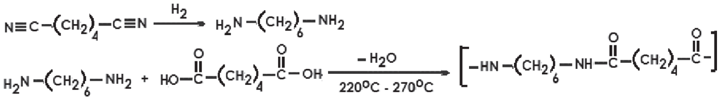


$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NH_3} H_4NO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-ONH_4 \xrightarrow{Heat} N\equiv C-(CH_2)_4-C\equiv N \quad (28)$$



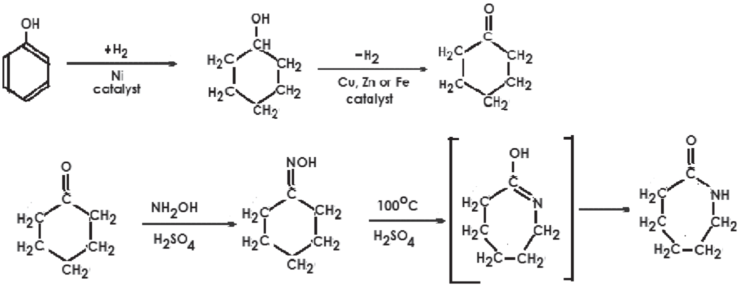
$$N\equiv C-(CH_2)_4-C\equiv N \xrightarrow{H_2} H_2N-(CH_2)_6-NH_2$$

$$H_2N-(CH_2)_6-NH_2 + HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[220^\circ C - 270^\circ C]{-H_2O} \left[-HN-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right] \quad (29)$$

2.1.4.6. Ring-Opening Polymerization

Nylon 6 is produced from caprolactam. Phenol is hydrogenated to cyclohexanol. This cyclohexanol is dehydrogenated to cyclohexanone, which is then converted to its oxime. Beckmann rearrangement of the oxime gives caprolactam, which is largely converted to a linear polymer on heating under pressure (Eqs. 30–31).

Nylon 6



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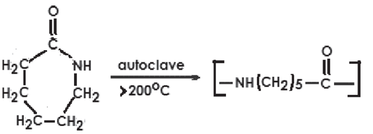

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2.2. Summary

- Polymerization is a multidisciplinary field with the combination chemistry, physics, and colloidal and interfacial phenomena.
- Needs to have an outstanding technical background in chemical reaction.
- Polymer molecules are polydisperse.
- Polymers are macromolecules having a unique molecular architecture such as molar mass, composition, and branching distribution.
- Th reactions in polymerization are highly exothermic and highly viscous, often carried out in a heterogeneous dispersion medium.

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CHAPTER 3

Polymer Structure and Property

Polymers are long-molecule chemical substance with complicated structure and properties. They are strong in their structural features. Polymer processing does not only depend on their chemical structure but also depend on their distribution of molecular mass, distribution and kind of short- or long-chain branches, persistence of chain length, distribution of additives, their nature, and composition [1]. Polymers are functional materials used in everyday life. They are cheap, light, tough, and seen in large amounts with different fabrication techniques.

Polymers are synthetic in nature and composed of small molecules known as monomers—identical units of chemical molecules. Polymers normally show a large variation of physical and mechanical properties with temperature. Viscosity is a physical property that is often embedded in equipment and process models used by process engineers to design and optimize equipment and chemical processes.

Polymers have very interesting rheological properties. They can exhibit both elasticity and viscosity [2]. Polymers are formed by polymerization, which occurs by addition, condensation, step-growth, ionic (cationic or anionic), and free-radical techniques. The molecular weight polymer formed is of several thousands of Daltons or higher. Polymers are used for different applications on the basis of their requirements.

Polymeric materials have structurally different combination of properties:

- Low effect of moisture resulting in excellent retention of properties and good dimensional stability
- Good high-temperature properties

- Melting point range resulting in low coefficient of thermal expansion
- Chemical resistance

3.1. Structure and Properties

Polymer properties are strongly influenced by variables such as molecular weight, molecular weight distribution, and the degree of branching [3].

Polymeric material undergoes strain, which is dependent upon the applied stress. Once the stress is removed, the material may not always return to its original dimensions, which means certain amount of permanent deformation. The ability of polymer molecules is to slide each other under the influence of an applied force.

Therefore, the specific factors affecting the properties of a bulk polymeric material can generally be divided into three groups: (1) the size and geometry of the polymer chains, including such factors as molecular weight and chain branching, (2) the nature of the chain repeating units and regularity of the chain as determined by the mechanism of polymerization, and (3) the forces between polymer chains and the way these forces affect the arrangement of molecules in the bulk phase.

The melt viscosity of polymer that contains different short- or long-chain polymer is much more difficult to predict than the viscosity of polymers with low-molecular-weight components. Polymers [4, 5] have the following properties:

- Long-chain polymers arranged in the order of magnitude
- More spatial conformations than small molecules
- Mixtures of polymer components with varying chain length, chain chemical composition, and degree of branching
- Polydispersity in a variety of ways to varying degrees
- Non-newtonian flow in nature during its processing
- Stronger sensitivity to temperature, composition, and shear rate
- Simple chains may differ in molecular weight, degree of branching with long or short chain, stereo-structure, or composition.

3.1.1. Polymer Structure—Principle

The structure of polymers determines the principle and their usefulness as durable materials such as film, plastic, and rubbery forms. In polymeric materials, the chains are based on various factors such as crystallinity, flexibility, inflexibility, stiffness, and cross-link (Figure 3.1). Therefore, the chains are

- capable to arrange in crystalline or ordered form,
- based on their degree of stiffness, flexibility, or inflexibility,
- either chemically cross-linked or not.

In principle, with the combinations of chain arrangement, it is possible to achieve various properties [6].

During processing, polymers evolve primarily from molten state into final products. Molten state evolves as an intermediate stage of processing. The effect of order that exists upon subsequent chain arrangement becomes important. Many polymer properties are affected in the melt, which includes crystalline properties such as melt history effect, rate of crystallization, and nucleation intensity. Other properties such as electrical conductivity, solubility, and rheology are not restricted to crystalline polymer.

In the molten state, polymeric materials are composed of flexible chain molecules. These long-chain molecules may coil into balls forming

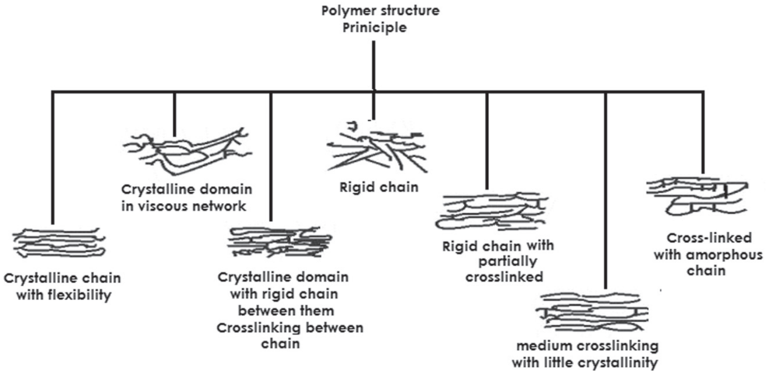

Figure 3.1 Schematic representation of structure of polymeric material

globular structures—a completely irregular chaotic pattern becoming interwoven with each other or gradually acquiring a certain order by paralleling chain segments. The effect of processing (shear and heat) is expected to have an effect on the polymer at the molecular level, reducing molar mass and altering its distribution [7].

3.2. Summary

- Polymer chains are flexible during melting.
- Polymer melt is the intermediate stage in processing.
- Polymer chains are based on various factors such as crystallinity, flexibility, inflexibility, stiffness, and cross-link.

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CHAPTER 4

Polymer Materials and their Processing

Polymers are formed by the repeat units of monomers by addition or condensation reactions. They are long-chain molecules, which comprise main monomer unit repeats throughout the structure. Hundreds and even thousands of repeated monomers form one polymer chain.

Polymer materials enable optimization of processing with product performance. They are widely used in many important emerging technologies; every day applications such as housing materials, medical applications and appliances, and automotive and aerospace parts; and also in communication. Processing techniques are critical to the performance of polymeric materials and products used in a wide range of industries. Therefore, polymer technology has advanced to great extent through the discovery of new or improved materials to upgrade the product improvement.

Polymers differ from other materials by the size of their molecules. They consist of thousand or tens of thousands of atoms. They also have a macroscopic rectilinear length. The atoms of macromolecules are firmly held together by valence bonds, forming a single entity. The weaker van der Waals forces have an effect on the components of the macromolecules. The structure of polymer is more complicated.

4.1. Polymers

Polymers are viscoelastic in nature. They have interesting rheological properties, which exhibit elasticity and viscous flow [1]. During the application of stress, the polymeric material undergoes a strain, which is dependent upon the applied stress. Removal of stress on the material may not return to its original dimensions, which has certain permanent deformation. Polymer molecules slide each other under the influence of an applied force.

In the manufacturing finished products, polymeric materials are useful for a variety of end use, which includes many light engineering applications. Advantages of polymers over metals can be quickly summarized as follows [2]:

- Outstanding resistance to both atmospheric and chemical corrosion.
- Light weight, that is, one-fifth of mild steel and one half that of aluminum.
- Can be worked by all usual operations.

4.1.1. Polyethylene

Polyethylene (PE) is globally produced and consumed as commodity polymer. It has high-impact strength, low brittleness temperature, flexibility, and outstanding electrical properties. It is partially crystalline, with increase in molecular weight, and it provides better tensile and environmental stress–cracking resistance [3].

Solubility of PE increases with increasing melt flow index (MFI) but decreases with increasing density and crystalline nature. PE will dissolve slowly above 50°C in hydrocarbons, chlorinated hydrocarbons [4], and higher aliphatic esters and aliphatic ketones [5], but is insoluble below 50°C in all common solvents.

PE is used as packaging polymer for high-volume supermarket bags, food packaging, and rubbish sacks. High-density polyethylene (HDPE) is an important material for rigid packaging. PE is capable of being injection molded, blow molded, and extruded. It is also processed as powder material in processing such as rotational molding. They are difficult to vacuum-form because they are slow to heat up, resulting in semicrystalline structure; hence, the forming temperature tends to be close to the melting point. PE is difficult to obtain smooth dimensionally stable sheets during calendering. However, film is readily produced by extrusion blowing or chill roll casting.

Linear low-density polyethylene (LLDPE) has short chains attached to the main chain. The short chains reduce regularity and ability to crystallize. It is used in water tank manufacturing and drip irrigation pipes. It has better thermal and mechanical properties such as stiffness, puncture, and elongation, but it is more difficult to process due to its poor optical property. It is widely used in blown film extrusion. LLDPE is mixed with low-density polyethylene (LDPE) in order to improve the processability of the polymer in terms of bubble stability during blown film extrusion.

PE is described by its density, strength, molecular weight, crystallinity, and melts flow or rheological characteristics. Environmental stress–cracking resistance of PE is specific application oriented. Rheological characterization involves measurement of viscosity and viscoelasticity of the molten polymer (Table 4.1).

4.1.1.1. Low-Density Polyethylene

LDPE has both long- and short-chain branches attched to the main chain occasionally (Table 4.2). It has limited ability to crystallize and is quite

Table 4.1 Typical properties of PE

Properties	Unit	Value	Reference
Density	kg cm^{-3}	920	[6]
Heat of combustion	kJ g^{-1}	46.5	
Glass transition temperature	°C	–120	[7]
Processing temperature	°C	205–260	[8]
Heat deflection temperature at 445 kPa	°C	42	[6]

Table 4.2 Typical properties of LDPE

Properties	Unit	Value	Reference
Density	kg cm^{-3}	0.91–0.925	[11]
Melting temperature, T_m	°C	95	
Glass transition temperature, T_g	°C	60–70	
Crystalline temperature, T_c	°C	95.1	[12]
Thermal linear expansivity	10^{-5} K^{-1}	11–13	[6]
Specific heat capacity	kJ kg^{-1} K^{-1}	2.31	
Thermal conductivity	W m^{-1} K^{-1}	0.44	
Melting temperature, T_m	°C	120	[13]

flexible. LDPE is soft and flexible, whereas HDPE is harder and stiffer [4, 9]. Resistance to stress cracking increases with decrease in density increase in molecular weight and molecular weight distribution. PE is generally stable and it undergoes photo-oxidation [10].

4.1.1.2. High-Density Polyethylene

HDPE has strong dependence on temperature, shear rate, molecular weight, and molecular weight distribution [14]. It is semicrystalline with a combination of amorphous and thin lamellae crystals [15]. High-degree crystalline material tends to be brittle because of weak crystal–crystal interface. High amorphous material will behave as a rubbery or glassy material depending on its glass transition temperature. HDPE has both structures, which give high toughness at room temperature. Therefore, toughness tends to decrease at low temperature as it behaves more like brittle and glassy material (Table 4.3).

HDPE is a virtually unbranched polymer with most regular structure. It is more crystalline and has high strength, stiffness, and softening point of the PE. HDPE pipes are useful in drainage applications for acid waste, effluent, or laboratory discharge. These pipes are produced by extrusion [2]. Cross-linked PE pipes and tanks are capable of handling a wide variety of materials in industrial and domestic applications, including water,

Table 4.3 Typical properties of HDPE

Properties	Unit	Value	Reference
Density	kg cm^{-3}	961	[16]
Melting temperature, T_m	°C	145	[13]
Crystallinity	%	77	[16]
Crystalline temperature, T_c		117	
Glass transition temperature, T_g	°C	–120	[6]
Melting temperature, T_m	°C	137	
Thermal linear expansivity	10^{-5} K^{-1}	13–20	
Specific heat capacity	kJ kg^{-1} K^{-1}	1.90	
Thermal conductivity	W m^{-1} K^{-1}	0.35	
Heat deflection temperature at 445 kPa	°C	85	

fluid waste, gas, and chemicals. PE pipes of different dimensions are used in electrical applications.

4.1.2. Polypropylene

The mechanical properties of polypropylene (PP) mainly vary on degree of crystallinity, molecular weight, and molecular weight distribution. The degree of crystallinity is mainly responsible for mechanical properties in which small deformations are involved, such as dynamic elastic modulus, heat distortion temperature, and hardness.

PP has a high self-ignition temperature and flame and surface pyrolysis temperatures. It is difficult to make PP flame retardant because of excessive thermal degradation, which liberates a large amount of fuel into the flame. High crystallinity of PP under normal processing conditions may inhibit effective dispersion of additives. It has contributed to automotive industries, land transport, home appliances, and other industrial applications due to its low price, excellent chemical properties, good processing ability, and modifying its mechanical properties with the help of additives.

PP is a semicrystalline polymer produced by addition polymerization of propylene monomer. PP replaces much small-volume engineering polymer as primary matrix polymer used in processing [17–19]. PP is stiffer than PE. It has high heat distortion temperature. PP is not suitable for rotomolding due to thermo-oxidative degradation during rotomolding cycles. The MFI of PP is higher than that required for rotomolding. It is autoclavable, and it offers excellent chemical resistance, environmental stress cracking resistance, and surface hardness. Thermoforming process of PP can only be performed over a very narrow range of temperature that is close to the melting temperature of the polymer. PP is thermoformed in the range of 143–166°C [20]. PP has sharp melting point but poor melt strength (Table 4.4) [21].

4.1.3. Poly(vinyl chloride)

Poly(vinyl chloride) (PVC) is a commercially important polymer. Rheological behavior of PVC is very important in processing. The process of PVC gelation is affected by additives. The investigation of rheological properties of the formulations is important for PVC processing. It is important

Table 4.4 Typical properties of PP

Properties	Unit	Value	Reference
Density	kg cm^{-3}	900	[16]
Crystallinity	%	50	
Melting temperature, T_m	°C	165	
Crystalline temperature, T_c	°C	123	
Glass transition temperature, T_g	°C	18	
Heat of combustion	kJ g^{-1}	46.0	[6]
Thermal linear expansivity	10^{-5} K^{-1}	6–10	
Specific heat capacity	kJ kg^{-1} K^{-1}	1.93	
Thermal conductivity	W m^{-1} K^{-1}	0.24	
Heat deflection temperature at 445 kPa	°C	115	

Table 4.5 Typical properties of PVC

Properties	Unit	Value	Reference
Density	kg cm^{-3}	1400	[6]
Glass transition temperature, T_g	°C	87	
Melting temperature, T_m	°C	175–212	
Heat of combustion	kJ g^{-1}	19.9	
Thermal linear expansivity	10^{-5} K^{-1}	5.25	
Specific heat capacity	kJ kg^{-1} K^{-1}	1.05	
Thermal conductivity	W m^{-1} K^{-1}	0.15–0.16	

to have a fundamental understanding of how PVC formulations are affected by heat during processing (Table 4.5).

PVC is a linear polymer. Normal PVC contains a few (<10) branches per molecule and the existence of more than one long chain per molecule is not probable [22]. The intrinsic thermal stability of PVC material is far less than that of any of the other major polymers. It is also much less than that of compounds containing vinyl chloride monomer units that are arranged in the same head-to-tail fashion [23]. The properties of products depend on the composition of the PVC compound and its processing conditions [24–27]. The change of properties as a function of temperature of processing, often with impact strength or elastic modulus,

Table 4.6 Typical properties of PMMA

Properties	Unit	Value	Reference
Density	kg cm^{-3}	1190	[42, 43]
Melting temperature, T_m	°C	160	[42]
Glass transition temperature, T_g	°C	107	[44]
Maximum operating temperature	°C	150	[45]
Thermal conductivity	W m^{-1} K^{-1}	0.15–0.2	[46]
Solubility parameter (calculated)	δ	9.25	[47]
Heat of combustion	kJ g^{-1}	26.2	[6]
Thermal linear expansivity	10^{-5} K^{-1}	4.5	
Specific heat capacity	kJ kg^{-1} K^{-1}	1.39	
Thermal conductivity	W m^{-1} K^{-1}	0.19	
Heat deflection temperature at 445 kPa	°C	93	

depends significantly on the degree of gelation of PVC [26–28]. The beginning of gelation is extremely important for the course of processing. However, PVC suffers from poor thermal and light stability. It undergoes rapid autocatalytic dehydrochlorination upon exposure to heat [29, 30] and light [31–34] during its molding and use, respectively.

4.1.4. Poly(methyl methacrylate)

Poly(methyl methacrylate) (PMMA) is a typical transparent amorphous polymer and has been widely used as an important material for optical devices. It has several advantages such as good flexibility, high strength, and excellent dimensional stability and disadvantages such as poor heat resistance, weak mechanical surface, and low refractive index (Table 4.6) [35, 36].

PMMA has been extensively employed because of their potential applications in light-emitting devices, batteries, optics, electromagnetic shielding, and corrosion-resistant coatings. However, their poor mechanical strength limits their range of applications. Nanoscale reinforcement is considered to improve the mechanical and electrical performance of PMMA effectively.

PMMA is a thermoplastic polymer commonly employed as the main component of positive resists for electron and UV photolithography [37, 38], as well as an imprintable material for hot-embossing soft lithography [39]. Because of its excellent transparency in the visible spectrum, PMMA is widely used in optical applications, especially as a matrix for nonlinear optical composite materials [40, 41]. The process of thermoforming PMMA sheets has been used to produce a variety of dental prostheses that include splints, stents, and bases for occlusal rims.

4.1.5. Acrylonitrile–Butadiene–Styrene

Acrylonitrile–butadiene–styrene (ABS) is a graft copolymer, which is widely used in many industrial applications. It consists of styrene and acrylonitrile as continuous phase grafted to a dispersed butadiene phase. Impact properties are provided by butadiene. The presence of double bonds in polybutadiene is susceptible to oxidation. Therefore, acrylonitrile–styrene helps to preserve impact-modifying properties during melt processing and product use toward UV light from the degradation of polybutadiene [48]. It has good processability and chemical resistance and is economical. However, it has limitations such as low thermal stability, poor flame retardancy, and poor chemical resistance [49, 50]. Thermoforming of ABS has a temperature range of 127–182°C (Table 4.7) [20].

Acrylonitrile–butadiene–styrene terpolymer is one of the most successful engineering thermoplastics. It consists of styrene–acrylonitrile copolymer (SAN) mixed with and to some extent grafted to polybutadiene

Table 4.7 Typical properties of ABS

Properties	Unit	Value	Reference
Density	kg cm^{-3}	1050	[52]
Glass transition temperature, T_g	°C	95	[53]
Transition temperature	°C	105	–
Limited oxygen index		18.3	[54]
Deflection temperature	°C	80–90	–
Volumetric coefficient of expansion with 15% rubber β_{ABS}	K^{-1}	2.7×10^{-4}	[55]

rubber. ABS is widely used in the automotive industry, telecommunications, business machines, and consumer markets, mainly because both the properties and price are intermediate between the lower priced commodity thermoplastics and the more expensive high-performance engineering plastics [51]. ABS is a graft copolymer; during extrusion and injection molding, it is necessary to protect the polybutadiene phase from degradation with the help of additives. This phase is particularly susceptible to oxidation due to the presence of residual double bonds [48]. ABS polymer is important for its melt processing such as extrusion, injection, thermoforming, and blow molding.

The durability of ABS polymers is important in many applications and depends on composition, processing and operating conditions, environmental weathering, heat aging, and installation damage. ABS is subject to UV degradation, which causes embrittlement and darkening. The availability of a durability prediction model for ABS would allow material types to be selected according to their expected environmental and operating conditions, and would significantly reduce the risk of in-service failures.

ABS is one of the most frequently used polymers in electrical and electronic equipment, as well as having widespread applications in automobiles, communication instruments, and other commodities. Recycling of ABS can be used as an aid to reducing environmental, economic, and energy issues.

4.1.6. Polystyrene

Polystyrene (PS) is a thermoplastic polymer with linear structure. It is a conventional product being atactic and amorphous, and therefore transparent. Isotactic PS was also synthesized in the laboratory, but it offered only a slight advantage in mechanical properties. As a matter of fact, it is characterized by increased brittleness and more difficult processability due to a high melting point. Like other resins, PS is relatively inert to inorganic chemicals. It is resistant to alkalies, acids, and oxidizing and reducing agents. However, at high temperatures, PS can be sulfonated or nitrated by strong mineral acids (sulfuric or nitric acids); either sulfonation or nitration makes it moderately soluble in water (Table 4.8) [56].

Table 4.8 Typical properties of PS

Properties	Unit	Value	Reference
Density	kg cm^{-3}	1060	[6]
Glass transition temperature, T_g	°C	95–100	
Melting temperature, T_m	°C		
Heat of combustion	kJ g^{-1}	42.2	
Thermal linear expansivity	10^{-5} K^{-1}	6.8	
Heat deflection temperature at 445 kPa	°C	82	
Specific heat capacity	kJ kg^{-1} K^{-1}	2.34	[57]
Thermal conductivity	W m^{-1} K^{-1}	0.0976	

Table 4.9 Typical properties of Nylon

Properties	Unit	Value	Reference
Density	kg cm^{-3}	1140	[6]
Glass transition temperature, T_g	°C	50	
Melting temperature, T_m	°C	265	
Heat of combustion	kJ g^{-1}	31.9	
Thermal linear expansivity	10^{-5} K^{-1}	9	
Specific heat capacity	kJ kg^{-1} K^{-1}	1.70	
Thermal conductivity	W m^{-1} K^{-1}	0.25	
Heat deflection temperature at 445 kPa	°C	245	

4.1.7. Nylon

Nylon is an attractive engineering polymer widely used in engineering applications. It exhibits high resistance to crack initation and imparts high unnotched impact toughness. Presence of notch leads to crack propagation and finally to embrittlement [58, 59].

Nylon has high mechanical strength and better resistance to elevated temperature (Table 4.9). "Nylon" is a generic term applied to a family of polyamides. Previously, nylon tubing has been manufactured from nylon molding materials by centrifugal casting and more recently by extrusion. Even though nylon absorbs water more seriously by solutions of acids

Table 4.10 Physical properties of PC

Properties	Unit	Value	Reference
Density	kg cm^{-3}	1.2	[6]
Glass transition temperature, T_g	°C	145	
Melting temperature, T_m	°C	230	
Heat of combustion	kJ g^{-1}	30.8	
Thermal linear expansivity	10^{-5} K^{-1}		
Specific heat capacity	kJ kg^{-1} K^{-1}		
Thermal conductivity	W m^{-1} K^{-1}		
Processing temperature	°C	270	
Heat deflection temperature at 445 kPa	°C	1.38	

and alkalis, which may cause hydrolysis, nylon tubes should prove very suitable for the conveyance of many organic solvents. Generally, nylon is soluble in formic acid and phenol.

4.1.8. Polycarbonates

The processing of polycarbonates (PC) is challenging because of their high melt viscosity (Table 4.10). In general, to overcome this, additives are dissolved into the melt during processing to decrease the melt viscosity. There are several processing additives that improve processing at lower temperatures, but they may cause negative effects on the final products. Under dry conditions, PC undergoes only limited degradation below 250°C, but injection molding is often carried out at ~300°C [60].

4.1.9. Poly(ethylene terephthalate)

Poly(ethylene terephthalate) (PET) is a commercial polymer used in bottles, films, and molded articles due to its excellent mechanical and thermal properties and commodity cost (Table 4.11). Like all polymers, the use of various stabilizer chemistries in polyesters may enhance esthetics, performance, or durability of the polymer during manufacturing, during converting operations, or in end-use application [61].

Table 4.11 Physical properties of PET

Properties	Unit	Value	Reference
Density	kg cm^{-3}	1360	[6]
Heat of combustion	kJ g^{-1}	21.6	
Thermal linear expansivity	10^{-5} K^{-1}	10	
Specific heat capacity	kJ kg^{-1} K^{-1}	1.01	
Thermal conductivity	W m^{-1} K^{-1}	0.14	
Heat deflection temperature at 445 kPa	°C	38	
Melting temperature, T_m	°C	240	[62–64]
Crystallinity	%	37	
Glass transition temperature, T_g	°C	89	[65]

4.2. Summary

- Melt strength of polymer is one of the most important processing parameters in melt processing operations along with stretching and drawing. Melt strength is a measure of its resistance to extensional deformation.
- Thermoforming requires better forming temperature range and melt strength to overcome the sag problem in melt phase thermoforming. Amorphous polymers such as ABS and PS can be thermoformed over a much wider temperature than semicrystalline polymer such as PP.
- Polymers are highly viscous and challenging during processing.
- Polymer durability is important in many applications and depends on composition and processing and operating conditions.
- High-crystalline polymers may inhibit effective dispersion of additives during normal processing conditions.

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CHAPTER 5

Polymer Processing Technology

Polymer production has been growing rapidly and majority of plastics are synthesized from petrochemicals. Polymers have facilitated their development to meet the convenient needs of the modern consumer [1, 2].

5.1. Polymer Processing Technology

Polymer processing is influenced by the thermal characteristics of polymer. They are melt temperature, glass transition temperature, thermal conductivity, thermal diffusivity, heat capacity, coefficient of linear thermal expansion, and decomposition temperature. The effect of processing (shear and heat) is expected to have an effect on the polymer at the molecular level, reducing molar mass and altering its distribution [3].

Polymer processing techniques are used to meet the requirements or specification as required by the industries and end-product applications. During processing, improved mechanical, thermal, optical, and other properties are optimized during manufacturing using optimized polymerization conditions. Polymers are reliable in many applications with confidence and also in many specialized applications. They are accompanied by improvements in manufacturing methods with enhanced properties in particular predicted applications.

Polymer processing technology aids the manufacture of articles with various colors, complicated shapes, and designs [4]. It helps to convert into long-life applications for use in areas such as transportation, appliances, electronics, and construction markets [5].

Polymer processing operations are extrusion and injection molding, calendering, blow molding, thermoforming, and rotational molding.

Injection molding is labor intensive and extrusion is material intensive. Both these processes involve the following sequence of steps: (a) heating and melting the polymer, (b) pumping the polymer to the shaping unit, (c) forming the melt into the required shape and dimensions, and (d) cooling and solidification. In polymers, shear and elongational flow are two primary flow mechanisms. Shear flow describes the response of the polymer to an imposed shearing force. Elongation flow is the response of the polymer to an imposed stretching or pulling force. As the shear rate increases, the rate of increase in shear stress decreases and this is described as shear thinning [6].

Polymer processing includes stress relaxation and normal stress differences. In process such as injection molding and extrusion, the slow stress relaxation is responsible for frozen-in stresses. During processing and extrudate swelling in extrusion, the normal stress differences are responsible for flow instabilities. Extrudate swelling is the significant increase in cross-sectional area when a molten material is extruded out of a die.

5.2. Processing Technology Versus Melt Flow Index

The suitability of a material for processing is usually based on the melt flow index (MFI) given in Table 5.1. It may also be called as melt flow rate. It is a measure of inverse viscosity involving extrusion through a die of standard dimensions under the action of standard weight to push the material. Low MFI indicates high-viscosity and high-molecular-weight material, whereas high MFI indicates low-viscosity and low-molecular-weight material. MFI values for the processing technology are tabulated.

During processing, the material is to be added with additives in the formulation to produce unique and versatile products. Compounding or

Table 5.1 Processing technology versus MFI requirement for different processing techniques

Processing technology	MFI
Extrusion	0.01–10
Injection molding	1–100
Blow molding	0.01–1
Rotational molding	1.5–20

mixing produces materials with additives to enhance the required properties with automated facility. Heat generated during compounding is removed in a controlled process that ensures optimum dispersion and dryness to prevent melting or generation of excess heat. Compounded materials are made ready-to-mold or extrude as natural or pre-colored by compounding or by means of masterbatch used in processing for applications.

5.2. End-Product Requirements

In polymer processing, a proactive approach on measurement, analysis, prediction, and prevention of problems is required. Therefore, a greater emphasis is needed to prevent defects and errors. End-product quality must be based on process utilization rather than inspection [7].

It is important in any processing techniques to attain higher productivity by means of

- minimizing the defects,
- optimizing the production process,
- investigation of the problem,
- process improvement,
- quality improvement.

In any polymer production, processing and efficiency are of key importance. However, processing techniques to be used depend on factors such as product size, shape, type of polymer, quantity required, quality and accuracy, design performance, cost, and time schedule. The traditional approach is about detecting and correcting the problems. Therefore, in any of the processing techniques, there should be a reactive to a proactive approach to avoid expense of high rework [8].

Polymers can be processed by conventional technologies such as extrusion, injection molding, blow molding, and thermoforming. During processing, the mechanical and rheological properties are likely to change, and it is important to understand these changes. The addition of additives and fillers generally results in an increase in viscosity.

5.3. Summary

- Injection molding technique can be used for obtaining end products in different shapes and sizes.
- Extrusion technique can be used for manufcturing pipe, profiles, sheet, etc.
- Extrusion and sometimes injection molding technique can be performed through an addition processing stage such as blow molding and blown film.
- Calendering sheets are limited in their width by the width of the material rolls, but are unlimited in length.
- Thermoforming is not greatly limited by pressure although even a small vacuum distributed over a large area can build up an appreciable load.
- Blow molding is limited by equipment that is feasible for the mold sizes.
- Rotational molding can produce relatively large parts.
- Polymer processing techniques are influenced by the thermal characteristics of polymer, such as melt temperature, glass transition temperature, thermal conductivity, thermal diffusivity, shear capacity, coefficient of linear thermal expansion, and decomposition temperature.

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CHAPTER 6

Injection Molding

Injection molding is one of the important industrial fabrication techniques for polymeric materials to produce thin products. It produces products with complex three-dimensional polymeric parts. Injection molding of thermoplastics involves injecting molten resin into a mold at high pressure and ejecting the cooled part. A better understanding of the friction conditions during the molding process can lead to improved injection mold and part designs [1].

Therefore, injection molding is a process with [2]

- high-pressure squeezing of complex and compressible hot melt polymer fluid,
- hot melt that flows through a very small gate into a cold cavity mold with high velocity,
- end product having an apparent hierarchical structure, macroscopically as a skin–core structure,
- higher versatility,
- end product with little or no finishing required.

The polymer material solidifies under homogeneous stress and cooling conditions in injection molding. The inner structures of the molded article are inhomogeneous, which influences the product properties. Therefore, it is necessary to clarify the influences of the structure of polymer and molding conditions on the inhomogeneous structure of the molded article.

6.1. Machinery

Injection molding machine (Figure 6.1) consists of an injection and plastication unit, mold clamping unit, and hydraulic and control unit. In the injection unit, the polymer is melted by heating and shearing. The

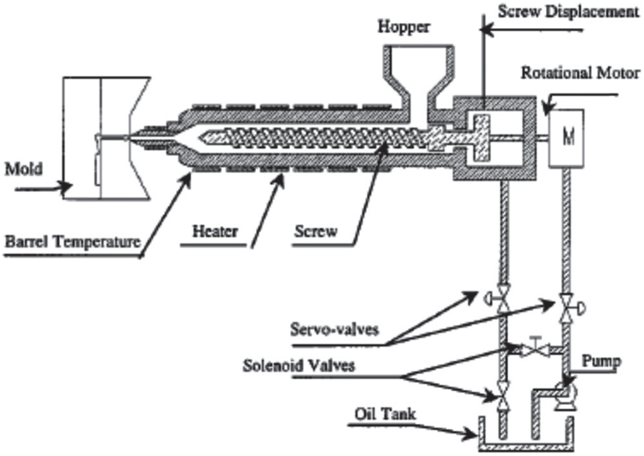

Figure 6.1 Schematic diagram of an injection molding machine [Reprint with permission from Yu-Chu Tian and Furong Gao. (1999). Ind. Eng. Chem. Res. 38(9), 3396. Copyright © 1999, American Chemical Society. All rights reserved [3]].

polymer is injected under pressure into a mold cavity, which is held by the mold clamping unit. By the application of cooling agent, the polymer melt solidifies into a shape of the mold cavity. Hydraulic unit serves manipulator for the injection unit. Finally, control unit supervises the process and provides overall control and sequences of the machine.

Polymer Melt

- The polymer melt enters into mold cavity in parabolic profile flow.
- Front melt undergoes considerable stretching.
- Melt deposits on the cold wall and at the same instant form a thin, frozen layer.
- Flow in the mold cavity exposes to complex thermomechanical environment.
- Additional flow appears within the envelope created by the frozen layer.

The thermomechanical environment is characterized by high cooling rate and strong stress field. The solidification rate of the melt close to the mold wall is higher than that of the melt far away from the mold wall.

6.2. Functional Areas

The purpose of injection molding is to produce polymer end products with high efficiency and to shape the products with complicated forms. Scientific molding is an important initial practice to make proper short shot. To start up with any mold, short shot is to be made for the safety of the machine and mold. Therefore, functional areas such as barrel and heating zones are important for their individual functions.

6.2.1. Barrel

Inside barrel surface, the following conditions should be considered.

- No holdup spots, cracks, or spaces between the mating inside surfaces of barrel, adaptor, and/or nozzle when assembled.
- No insulation around the heater, which could interfere with the performance of the temperature controllers. However, an insulated shield can be attached but not in complete contact to the outside diameter of the barrel.

6.2.2. Heating Zones

Injection molding, to have higher output rates, corresponds to the heating zones on the barrel. For close tolerance in molding, the nozzle temperature must be precisely controlled with separate temperature controller to prevent freeze-off or drool. During processing, the hopper area should be with separate temperature controller, in order to not affect the ability of the sensor in the feed heating zone to control temperature.

6.2.3. Screw

Screw length to diameter should be important to have uniform melt at higher output and also for uniform melt temperatures. Improved performance comes from radius between the flights and root diameter of the screw. It should be equal to or greater than the flight depth in the respective zones. Screw decompression (screw suck back) and reduction in nozzle temperature can be used to control drooling into the mold. However, it is necessary to identify and correct the cause of drooling.

Some of the causes of drooling are too high melt temperature, wet resin, long holdup time, polymer degradation, poor nozzle temperature, high back pressure, and poor nozzle design.

Wear and corrosion of the screw should be made from or surface coated with corrosion and abrasion-resistant metals. Coating screws with wear and corrosion-resistant metals should also be considered. The bimetallic barrel liner and the flight tip metal must be compatible. Otherwise, excessive wear may occur between these two metal surfaces during screw recovery and injection.

6.2.4. Mold

Molds are complex tool and to be reliable in operation and cost. They are expected to be time-effect at their design and manufacturing stages. In production, molds play an important role of fulfilling the product section with smooth operation [4–6]. The melt polymer flows in injection molding through several gates. The melt must unite or weld during their meet. Careful gate design with proper process control can allow welds to occur where stresses will be minimal. Polymeric materials have been molded in various types of molds. The mold must be capable of handling temperatures to have good dimensional stability and surface appearance of the end product.

The cooling and heating channels in the mold must be sized and located, so that fast and exact heat-up/cool-down and mold temperature uniformity are achievable by oil heat. If the mold is heated by electricity, then the cartridge heaters must be located to give temperature uniformity. To facilitate high injection rates, also a requirement for good part surface, the melt flow should not be restricted. Various types of gates have been successfully used to mold polymeric materials. The gate area will experience wear during molding.

Venting the mold at the proper locations, for example, at parting lines, ejector, or dummy knockout pins, will prevent part burning and mold damage, and at the same time it will improve mold filling and weld line strength. The area of the relief passage should increase rapidly in proportion to its distance from the edge of the cavity.

Tolerances for parts molded in polymeric materials vary according to the complexity of the part design, part thickness, and part thickness uniformity. Predicting the dimensions of parts molded in the glass-reinforced resins can be difficult because it depends on a large degree on the glass fiber orientation in the part. The mold shrinkage of polymeric materials depends on the composition, the amount and orientation of the glass fibers, part thickness and part design, mold design, and processing conditions.

6.2.5. *Sprue and Runners*

Sprue and runners should be as small as possible to avoid rework of the polymeric material. The entrance diameter of the sprue should be larger in diameter than the nozzle diameter. Full round and trapezoidal runners have been used successfully to mold polymeric materials. Runner layout should be balanced and generously radius for smooth and uniform melt flow. Holdup spots can cause resin degradation, color changes, and property loss, especially in the flame-retardant and toughened grades.

6.2.6. *Nozzle*

To prevent drool and nozzle freeze-off, good nozzle temperature should be maintained. The heater band is provided and should be as far forward as possible on the nozzle and should not touch the platen. Nozzle can also be heated by heat pipes. Nozzle designs have been successfully used, with the radius of the nozzle tip being less than the radius of the sprue bushing.

6.2.7. *Shot Size*

Shot size confirms the cutoff or switch-over position from fill to pack. Filling part in the melt should fill most of the part but not begin packing. Shot size evaluates the machine response or amount of screw travel, to understand the balance of filling in multicavity mold. It also checks the parting line for flashing in the filling stage. Short shot helps to evaluate the viscosity of different materials, colors, grades, dry material status, and information for appropriate holding stage pressure. During troubleshooting, the shot size helps to reduce flash, shorts, sinks, bubbles, and splay and to calculate pressure loss over the flow path in filling. It also helps to check non-return valve function and the machine function for minimum hold pressure [7].

6.2.8. Ejection

Required ejection forces have a direct impact on mold durability and part quality, and the friction between the mold core and the molded part directly affects the ejection forces. The ejection system for the production of parts that are difficult to extract from the mold cores assumes a relevant importance in the product quality [8–10].

6.3. Injection Molding Process

Typical injection molding process is illustrated in Figure 6.2 [11–13].

- Polymer pellets are simultaneously conveyed, melted, and plasticated within a barrel.
- Injection is done under pressure in the mold.
- Mold is filled and packed.

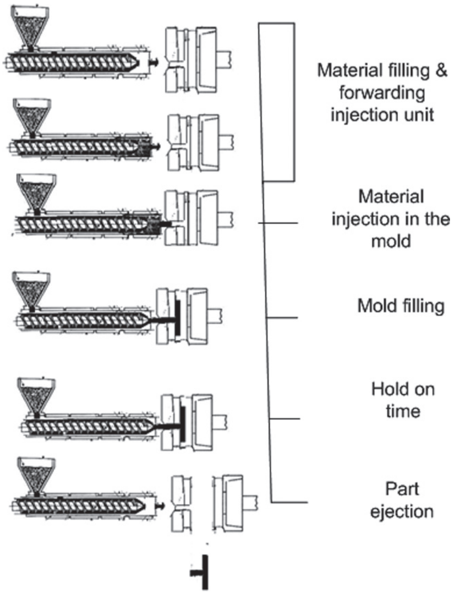

Figure 6.2 Typical injection molding process

- Polymeric material is cooled below its glass transition temperature (T_g).
- Cooling process consumes major share of the molding cycle.
- The mold is then opened and the part is ejected, and the cycle is repeated.

Injection molding is used to produce molded parts with quality in terms of mechanical characteristics, dimensional conformity, and appearance. The end product is affected by process parameters such as nozzle temperature, injection pressure, coolant temperature, and injection speed.

6.4. Processing Technology

Injection molding is a key process in the polymer processing industry. This technique is economical and efficient to produce a wide range of polymer parts for industrial, agricultural, electronic, and household articles. It is a typical cyclic process in which filling, packing, holding, and cooling take place.

During filling, the mold is closed first and then the nozzle moves forward and comes into contact with the mold orifice. The injection begins with screw axial movement at a determined speed by the velocity profile. At the time when the cavity in the mold is filled, the process switches to the packing and holding phase in which the pressure in the injection cylinder is maintained to compensate for material shrinkage. The process then enters the cooling phase during which the polymer melt is cooled and solidified in the mold cavity. When the product reaches a significant rigidity, the mold opens and the product is ejected. At the same time, the polymer is plasticized in the injection unit by a screw rotation for a period of time for next shot. The process repeats for the next cycle.

The dynamic behaviors of injection molding are determined by a complex interaction among material properties, mold and machine geometry, and a number of process variables, including injection velocity, cavity pressure, nozzle pressure, hydraulic pressure, barrel temperature, nozzle temperature, and so on. Among these variables, injection velocity plays a critical role in the quality of the end product. The injection velocity affects the cavity pressure and product quality with respect to residual stress, shrinkage, impact strength, product morphology, and surface characteristics. Productivity is also directly related to the injection velocity setting.

Barrel temperature in injection molding should gradually increase from the hopper to the nozzle. It should be controlled according to the injection molding machine, shape and size of the product, and the mold structure. Injection pressure should be controlled to mold full parts with acceptable appearance. Many parameters affect injection pressure, which include injection temperature, product shape, nozzle and gate size, runner dimensions, and mold temperature. It is important that injection pressure should drop off to holding pressure immediately after filling up.

Mold temperature should be controlled to improve the surface quality and the level of residual stress in the end products. Moreover, higher mold temperature may cause production loss due to long cycle time and leads to warpage problem.

The process parameters that affect the quality of injection molding products include cooling time, injection pressure, injection speed, injection time, filling time, melt temperature, ejecting pressure, mold temperature, mold geometry shape, material property of melt, melt speed, and heat transfer action of flow field.

Among these parameters, mold temperature is the significant one. As soon as the polymer melt begins to enter the cavity, it starts to cool. In order to obtain high weld strength, the temperature of the melt must remain high enough for a period sufficient for the segments of a chain to become entangled. With high mold temperature, the melt will not cool too rapidly [14]. A packing (hold) pressure is applied to cause the melt to flow and to fusion bond the parts. Weld line strength can be increased by increasing the packing pressure, resulting in the increase of the molecular diffusion at the weld interface [15, 16]. During the ejection phase, friction forces develop between the polymer surface and the mold surface, which is usually made of steel [17].

6.5. Summary

- Polymers can be molded in standard screw injection molding machines.

- With injection molding technique, the products are produced with different shapes, sizes, and applications. Based on polymer characteristics such as density and ease of processing, the polymers can be shaped to different forms, which are more economical and easier than metal and ceramic materials.
- The quality of injection parts is determined by several important factors, which results in complex combination of the materials used, the part, and mold designs along with processing conditions such as temperature and pressure.

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CHAPTER 7

Extrusion

Extrusion is one of the most important polymer processing methods used to enhance the uniaxial strength and stiffness of polymer materials. It makes up the material much higher strength along the polymer chain than that exhibited by the material properties before processing. It involves solid conveying, melting, mixing, venting, and homogenizing and affects the quality of polymer products considerably. Single-screw extruder (Figure 7.1) and counter-rotating twin-screw extruder (Figure 7.2) are used during extrusion of polymeric materials.

7.1. Extrusion

7.1.1. Extruder

Extruder represents a very complex machine to process various types of polymeric materials and viscosities under high temperature and pressure with very strong shear forces and short residence time in the barrel. During extrusion, the extruder treats the material with mixing, kneading, heating, shearing, and finally through a die appropriately designed to form the product under expansion and rapid fall in pressure.

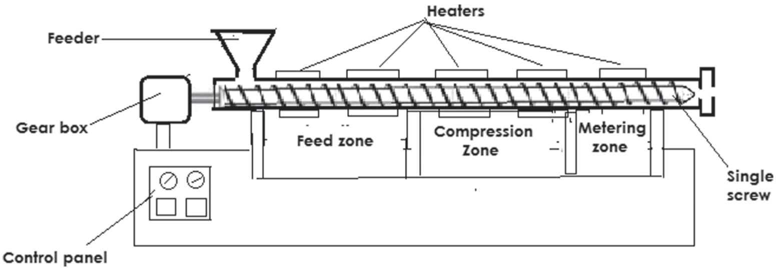

Figure 7.1 Schematic representation of single-screw extruder

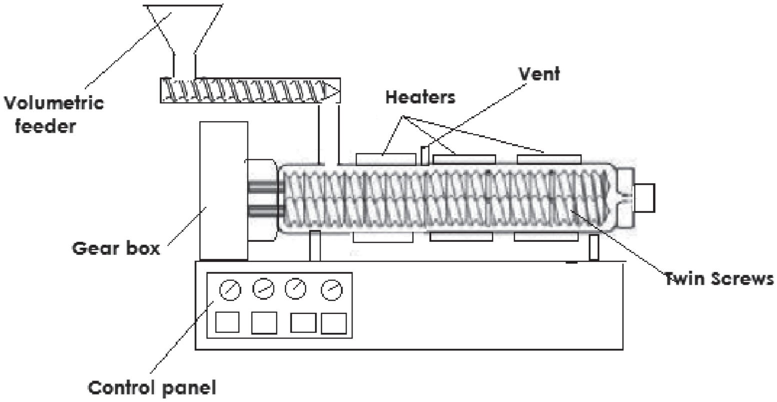

Figure 7.2 Schematic representation of twin-screw extruder

Extruder is used to extrudate polymeric materials with a series of subprocesses, including motor-drive control systems and barrel heating/cooling system. Operation and process reflect the input and output of the extrusion process. During extrusion process, each material undergoes a different temporal, thermal, and/or mechanical history. As a result, its final properties may be different from those of the materials subjected to extrusion process [1–4].

Single- and twin-screw extruders differ in conveying mechanism. In single-screw extruder, the process is highly dependent on the frictional and viscous properties of the material. In this extruder, the frictional and viscous forces help in the melt conveying. Twin-screw extruders are designed to have positive conveying characteristics. These extruders can be classified according to their geometrical configuration. The polymeric material may be more or less trapped in compartments formed by the two screws and barrel due to their full intermeshing nature of the twin screw. Better the intermesh between the screws, the more positive conveying occurs. In twin-screw extruder, the frictional and viscous forces have a minimal effect on the conveying behavior. These extruders are preferred for higher output of better quality extrudate from a machine of a given size or cost that have stimulated from single-screw extruders.

7.1.2. Single-Screw Extruders

Single-screw extruders operate normally in a flood-fed mode in which the granulate or powder polymeric material is compacted in the solid conveying zone. These extruders act and operate as a dry friction pump. Therefore, the pressure rises exponentially with the length along the axis. During the material residence time in the solid conveying zone, the boundaries of the material are compressed by the hydrostatic pressure. Individual particles of polymeric material are pressed against one another, thus forming agglomerates. There is an increase in the critical shear stress that is needed to break them up during their subsequent residence time in the melting zone and in the pumping zone of the extruder [5]. The general configuration of a single-screw extruder with 24:1 to 30:1 L/D (length-to-diameter ratio) and a barrier screw is to have a feed section, barrier (compression) section, and metering section with temperature zones.

In the compression or barrier zone of single screw, the melting occurs approximately 85–90 percent with drive power requirement. The same mechanism occurs in metering zone too. At the metering zone, the melt film thickness equals the channel depth due to complete melting at the point [6].

The screw extrusion process consists of three distinct zones, namely feed, compression, and metering zone. The polymer is either conveyed in the solid state or melted under the action of conducted heat and shear, and the resulting melt is mixed and pumped. The three sections of the screw, feed zone having the constant channel depth in the section, tapering compression or transition section, and the constant depth metering section, are normally associated with these three functions although there is often considerable overlap. Melting starts in the feed section of the screw and continues into the metering section.

7.1.3. Twin-Screw Extruder

Twin-screw extruder has been extensively used in the polymer industry, particularly counter-rotating involves in various applications, including melting, pressurization, and mixing, which leads to different end products such as pipe, profile, sheet, and flat film [7–11].

Twin-screw extruders are usually operated at a specific throughput; therefore, portions of the extruder are completely filled, whereas other locations are partially filled. Filled regions are formed behind restrictive and reverse pumping elements in extrusion screws.

7.1.4. Screw

Geometry of the screw's cross section helps in self-cleaning of extruder. Screw geometries of counter-rotating screws differ in flight flank angle and they can be developed for counter-rotating extruders with improved mixing and conveying and high-speed capability. The leading flight flank can be different from the trailing flank and can be used to design for efficient dispersive mixing.

Screw design is used to

- improve distributive and dispersive mixing,
- alter the residence time distribution (RTD) of material inside the extruder to meet processing requirements,
- separate processes such as melting, mixing, and devolatilization, which occur along an extruder's length.

Among these three processes, devolatilization by vacuum is more efficient for the renewal of surface volatiles and better heat transfer from the polymer melt in the channel to the barrel [12, 13].

Screws bored for water or oil cooling are useful in certain critical situations. The bore is normally plugged, so that cooling extends only into the midpoint of the first transition section of the screw. Therefore, the melting of the polymer can be fine-tuned if necessary.

7.1.4. Barrel

High-quality barrel and die temperature controllers are desirable to minimize fluctuations in machine temperatures. Heater zones with cast-in channels are desirable for water cooling of the barrel.

7.1.5. Haul-Off Equipment

Smooth and glossy finish of the end products requires the use of high-quality belts, polishing rolls, or rubber rolls. Rubber rolls are used in pipe, profile, and sheet extrusion. Either polished rolls or rubber rolls are used, which depend on the end product finish. These haul-off should be equipped with accurate speed controls for better results. In film or sheet extrusion, the polished rollers can be controlled even with independent temperature and speed controls along with rubber pull rolls for better results.

7.1.5.1. Sheet or Film Extrusion Haul-Off

In sheet or film extrusion haul-off rolls in a three-roll stock should be on trial and error to give the best appearance of the flat sheet. The maximum roll temperature is normally limited by sticking of the polymer material to the roll. The larger the roll diameters, the better effectiveness and heat transfer occur. In this extrusion process, the buildup of bank of polymer in the nip of the rolls should be avoided, which leads to excessive orientation in the end product. This excessive orientation can cause brittleness in across-the-machine direction and such film or sheet is difficult to thermoform.

7.2. Extrusion Die

The swell of the extrudate as it leaves the extrusion die is an important phenomenon in polymer melt extrusion [14]. Die entrance angle plays an important role in the die pressure in the extrusion pressure. Die pressure is affected by flow rate of polymer melt, cross section of the die, die temperature, and material viscosity [15]. Controlling the die pressure can achieve a maximum production rate and an optimal application of extruder. Therefore, the entrance angle in die should be optimum to minimize the pressure drop [16]. Die entrance angle has no considerable effect on mechanical strength of the product, but the land length has some effects [17].

As the polymeric material is forwarded along the screw channel, heat is generated by viscous flow and transferred through both the screw and barrel surfaces. A die at the end of the channel causes a resistance, resulting in an adverse pressure gradient in the channel. These factors influence the temperature distribution between the two surfaces.

Extrusion is a suitable plastic forming method for fabricating a variety of shapes with constant cross section, not only for flat shapes, but also for structural shapes, such as I-sections, channels, pipes, and tubes.

Streamlined die with production will eliminate degradation problem or make it insignificant. Therefore, streamlining the die surface and adaptor promotes minimal drag on the material; hence, the polymer layer is not spending excessive time in the machine.

7.3. Processing

Extrusion consists of processing polymeric materials through an extruder that heats, softens, and forces the molten plastic through a die to give the desired shape. It is essential to have proper machine operation and a successful final product. The extruder used depends upon the output and size of the final product. Before processing the polymeric material, the machine is to be ready to start up and purges to eliminate the contaminated or degraded material, which may produce wastage.

7.4. Material Consideration

7.4.1. Drying

Majority of the resins are absorbents (hygroscopic), which absorb moisture in proportion to environmental humidity. The absorbing process of moisture is reversible. Therefore, wetted pellets can be used to remove moisture in the environmental air with lower humidity. Dried pellets should absorb moisture until the amount touches equilibrium amount with the moisture in the air. The absorbing moisture content depends on the relative humidity in the air, that is, how long the resin was exposed. The material is essential

- To avoid contamination of polymer and compounds with other plastics. Contaminations compromise behavior of the materials, optical and mechanical properties of the finished product.
- To dry due to absorption of moisture from the atmosphere. The moisture level in the polymer or compound should be less to achieve a better transparency and surface gloss. The presence of moisture in the material leads to surface streaks and/or bubbles in the end product.

7.5. Start-Up and Purging

Before start-up of the extruder, the barrel and die should be preheated to operating temperatures. The screw speed is gradually increased at slow rate to the desired level to avoid excess motor load current and pressure levels in the barrel. Initially melt to some extent viscous to a short period during purging. Once purging is over, the contaminated or degraded material is removed, extrusion process produces an optimum-quality end product. If the material in the extruder is present for long periods or at excessive temperature, a long purge may be needed, which is also used to manually clean the screw, barrel, or die. During shutdown, it is necessary to run as much material out of the machine as possible and to turn all heaters off.

7.6. Processing Temperature

The barrel zone temperature is not to be compared with the recommended processing temperaure for the resin being run. It is common in extruder, the barrel temperature zones set lower than the desired melt temperature. If this type of operating condition is used, then the control of the extrudate temperature is totally dependent on screw geometry and the viscous heat developed from shear generted by channel depth, flight clearances, and screw speed. Die and adaptor zones should be set at the melt temperature recommended for the resin. Feed section should be set to temperature that is warm to the touch. This warm temperature is enough to help preheat the material as it enters the extruder, yet cool enough to prevent bridging in the feed throat. It is good to monitor feed-throat temperaure.

The feed zone has the most effects on solid conveying of the resin. Three coefficients of friction take place, namely friction between barrel and pellet, between pellet and pellet, and between root of the screw and pellet. Solid conveying is the process wherein the material must stick to the barrel and slip on the screw. Hence, cooling root of screw will reduce the coefficient of friction between the screw and the plastic pellets. Screw cooling should be installed in the core of the screw in the feed section to give another zone of temperature control on the extruder.

Heat necessary for plasticating a polymer originates from the hot barrel by conduction and from the viscous dissipation caused by the rotation of the screws.

- Setting barrel temperature involves dynamically changing input.
- Barrel heating or cooling involves dynamics, which reflects in the output of the machine.
- In processing, primarily melting takes place in the extruder and the melt becomes viscous dissipation. The melt results from the rotation of the screw with external heat provided outside the barrel. Therefore, the melt film adheres to the barrel during screw rotation. The flight of the screw wipes the melt from barrel wall and continuously pushes in the front side of the flight. The channels become shallower in the compression section of the screw, causing the unmelted resin to be pushed continuously toward the barrel wall. This renewal process allows the polymer to be melted faster without relying solely on the conduction of heat from the melt film on the barrel wall.
- Melt polymers have low thermal conductivity. As the volumetric flow rate decreases, the pressure gradient increases and hence the back flow, that is, negative velocity zone becomes more pronounced. The flow in the down channel direction is a combination of drag and pressure flows during extrusion.

7.7. Screw Speed

Increases in screw speed result in

- Increase in output of the machine due to increase of torque and die pressure, which indicates the effort of motor drive to overcome the inertia of screw shaft.
- Increase in screw speed at constant feed rate would result in decrease in the degree of fill in the barrel. Degree of filling is dependent on the ratio of feed rate and screw speed.

7.8. Polymer Melt

The melting process in all screw machines can be divided into two sections:

- Compacting of the fluffy products in order to minimize air pockets. The air in most cases escapes through the feed opening. Simultaneously, a melt film is formed on the barrel walls and the product fuses due to heat and pressure.
- Generation of melt through the shearing section of the product and mixing of the unmolten particles with the already formed melt. As a result, a large heat exchange surface is generated between the solid particles and the melt.

7.9. Operating Variables

- Screw speed
- Barrel temperature
- Motor torque
- Die pressure
- Material temperature

Screw speed and barrel temperature are used as forcing functions to disturb the extrusion systems. Therefore, the motor torque, die pressure, and material temperature shift from initial steady states to new equilibrium.

7.10. Effect of Different Parameters

A variable that affects the plastification rate should have some impact on the processing rate. The mixing quality and the average time that the polymer stays in the extruder will directly affect the final product properties. The mean residence time is related to the transport delay time, which has enormous impact on the stability of feedback loops over the length of the extruder [18–20].

- The higher the melting point of the polymer, the lower the plastification rate.

- The higher the barrel temperature, the greater the plastification rate.
- The higher the screw speed, the greater the amount of heat generated by viscous dissipation, but lower the amount of heat transferred to the polymer by conduction due to reduced residence time.
- Decreasing plastification with increasing screw speed implies that the barrel heating is the main heat source for polymer plastification.
- Increasing feed rate amounts to increasing the screw speed in terms of the plastification rate.
- Thermomechanical history is known to affect the molecular arrangement (morphology) of many polymers, such as poly(vinyl chloride) and branched polyethylene, thus inducing specific properties [21].
- When the melt temperature is constant, the viscosity will also be constant. To continue extrusion without degradation, a stable polymer in steady-state extrusion the effect of changing shear rate, inherent variations in the feed material or the effect of residence time and mechanical shear on the polymer does not allow variations. Furthermore, the temperature instrument must be capable of detecting temperature variations across the bulk flow of polymer [22].

7.11. Residence Time Distribution

RTD in an extruder depends on both throughput and fill lengths or fill volumes in an extruder. The shear and temperature history of extruded product, amount of mixing, conversion, etc., are directly dependent on the RTD.

Screw configuration has a pronounced effect on the RTD. The effects of different screw configurations on the broadness of mixing compared their subtle differences. Specific throughput is defined as the ratio between throughput and screw speed. The residence time of a material element is the time it spends in the extruder. All material elements do not necessarily spend the same period of time in the extruder. Residence times have a distribution called RTD.

7.12. Quality of Extrudate

Quality of extrudate has a significant effect on

- the product or the requirements of subsequent processing,
- the functional qualities such as mechanical properties and chemical or heat resistance, which are fundamentally dependent on the choice of material,
- actual extrusion conditions.

In the extruder, filled lengths can affect the stability of the process. A too large fill length may result in blocking of feed ports and in some cases material may flow out from the feed port, into feeding or venting equipment. The conveying sections of an extrusion screw can only develop pressure when they are fully filled. Fill length is an important indicator of process performance. It is very important to understand fill lengths in relationship to operating conditions. During polymer melt extrusion, at high flow rates, polymer melt flow exhibits large pressure oscillations, commonly referred to as spurt [23].

7.13. Output

Extruder output exhibits a complex and periodic fluctuation, resulting in superimposed effect of external disturbances entering the process from various sources and internal flow instabilities. The amplitudes of the fluctuations are large enough to cause the output undesirably effects such as surging or spurt flow, bamboo fracture, sharkskin, and other forms of product nonuniformity.

Process variations are caused by

- die flow instability,
- melting instability,
- periodic nature of feeder screws,
- heating elements,
- nonuniform feed material quality,
- extrusion screw.

Small amplitude variations in pressure could result in large variations in throughput [24]. Screw speed can be used to control output flow rates, provided that the time period of the input variations is shorter than the transient period.

7.14. Extrusion Technology

Extrusion is a suitable plastic forming method for fabricating a variety of shapes with constant cross section, not only for flat shapes, but also for structural shapes such as I-sections, channels, pipes, and tubes [25]. A decrease in extrusion pressure is of benefit to dies and extruders.

Extrusion process is used in major pipe, profile, sheet, and flat film manufacturing process. In this process, an extruder (of one or two screws) moves molten materials through a barrel by pushing it through a die to produce uniform shape of products [26].

7.15. Summary

- In processing of all polymers, it is important to avoid creating hot spots where the melt is overheated, causing degradation (breakdown of the molecular composition) and resulting in deterioration of material properties.
- Instability in melting and conveying in the extruder may result in "cold" spots of incompletely melted material in the extrudate. This will affect dimensional stability and surface finish, and can lead to weaknesses or failure of the product.
- Fluctuation in the melt viscosity will also result in fluctuating die stresses, which may induce viscoelastic instabilities. It also follows that inhomogeneity in the melt exiting the extruder will affect the stability of further processes, such as cooling, stretching, and forming.
- In processing, the delivery of a consistent, homogenous melt is paramount to prevent many defects. Consistent melt viscosity corresponds to the ideal melt state in terms of the molecular arrangement, resulting in the desired product properties.
- Viscosity is monitored indirectly through control of the melt temperature/pressure, as these parameters are much easier to monitor than viscosity itself.

- Melt pressure may be considered a function of viscosity, since fluctuations in viscosity will result in a change in pressure. However, pressure will also be a function of throughput, disturbances in the extruder and complexities of flow such as elastic responses. As a result, control of viscosity in this way is difficult to achieve.
- Measuring viscosity directly would allow clear detection of the homogeneity of the melt and furthermore would prove useful in identifying a viscosity range corresponding to optimum product quality.

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CHAPTER 8

Blow Molding

In polymer processing technology, blow molding is the third largest technique in the world [1]. This technique is used to produce hollow, thin-wall objects from polymer materials. It is not only used for the production of packaging items, but also used in increased industrial applications such as fuel tanks and ventilation components and in the fields of electrical and medical engineering [2]. It is also used in the automotive, sports and leisure, electronics, transportation, and packaging industries [3]. Blow molding processes can be divided into two main categories:

- extrusion blow molding,
- injection stretch blow molding.

Both processes involve the inflation of a parison (extrusion blow molding) or a preform (injection blow molding) into the final part.

8.1. Extrusion Blow Molding

Extrusion blow molding is a continuous process capable of high production rates. This process (Figure 8.1) involves three main stages: parison formation, parison inflation, and part solidification. It has a number of

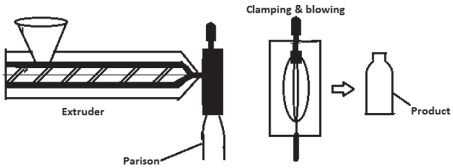

Figure 8.1 Schematic representation of extrusion blow molding

technical and economic advantages concerning the low-pressure characteristics of the process and the facility to produce complex shaped parts with very thin walls.

Extrusion blow molded parts must meet strict dimension distribution requirements to provide the necessary strength and rigidity with minimum material usage. The final part dimension distributions are directly influenced by parison dimensions [4].

Extrusion blow molding is the process employed in the production of large containers such as drums, as well as complex automotive parts. This process is widely used to produce containers of various sizes and shapes. It is also adapted to make irregular, complex, hollow parts, such as those supplied to the automobiles, office automation equipment, and pharmaceutical sectors. In this process, the extrudates swell [5], as well as sag or draw down during parison extrusion stage.

8.2. Injection Stretch Blow Molding

Injection stretch blow molding (Figure 8.2) is employed in the production of smaller fine detail parts prevalent in the food and pharmaceutical industries [6]. This molding process is extensively used in the commercial production of bottles for food, beverages, and pharmaceutical industries [7].

This is a two-stage process in which the material is injection molded around a core rod to form a preform. Then the preform is stretched through the action of a stretch rod. Finally, it is inflated and cooled, which results in a lighter biaxially orientation product. This process is used to produce scrap-free, close-tolerance, completely finished products that require no secondary operations such as trimming, which is used in extrusion blow molding.

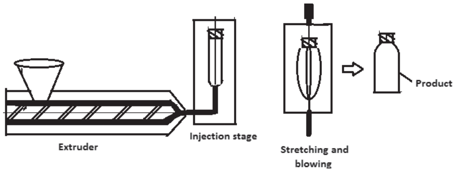

Figure 8.2 Injection stretch blow molding

8.3. Processing

Polymer materials in the form of powder or pellets are fed to screw extruder in which they are heated into a homogeneous melt. The melt is forced through a die. The die forms the polymeric melt into a parison shaped as a cylindrical tube. Compressed air is introduced into the parison by a blow pin at the top. The air pressure forces the parison to conform to the inner shape of the mold. Indirect cooling water that passes inside the mold halves solidifies the blown melt into its final product shape. When the part has sufficiently cooled to hold the desired shape, the mold halves open and the part is stripped from the mold.

8.4. Optimization

Operating parameter is considered to optimize the main challenge for the blow molding process. This is due to the high sensitivity of the process to the smallest variations in the settings and/or the surrounding environment. After a thorough investigation of the existing processes, the factors that affect the volume and mass of the produced bottles were identified as

- screw speed,
- melt temperature,
- blow pressure,
- blowing time,
- mold temperature,
- cooling time.

The temperature history during processing is a critical parameter in dictating final part strength. This temperature history depends upon the rate at which the extrudate cools upon leaving the extrusion head. The thermal history imposed on the material has important repercussions on the final product. The mold temperature depends on ambient temperature, which affects expansion or shrinkage based on the product after production and process during manufacturing [1].

8.5. Summary

- Blow molding improvements are related to production rates and to minimization of post-blowing finishing operations.
- Injection stretch blow molding has become one of the major manufacturing methods for containers.
- Optimization of manufacturing processes and parameters control is known to have direct impact on the production line maintenance and operations.
- Cycle time of the processing includes opening time and closing time of the mold, closing speed, and mold positioning.
- Blow pressure, screw speed, cooling time, and melt temperature have significant effects on blow molding process.

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CHAPTER 9

Rotational Molding

Rotational molding is an economical process used to produce medium- to large-sized hollow parts from polymeric materials. It is a shear- and pressure-free process with processability of limited polymeric materials. Viscosity, surface tension, and thermal properties of polymer influence the sintering behaviors. Changes in economy and competition with other process methods shift from these techniques to rotational molding. The type of materials could be used in the process is mainly limited to polyethylenes [1].

With rotational molding

- The mold is inexpensive in comparison to injection and blow molding.
- Complex shapes can be handled.
- There is a wide range of product sizes and variable thicknesses.

Typical applications of rotational molding include chemical tanks, automotive and commercial aircraft parts, backyard play equipment, toys, etc. Rotational molding requires long cycle time, which puzzles the overall success of the technology. The cycle times are restricted by the time required to heat up and cool down the mold and the product by the slow heat convection process.

9.1. Parameters

- Polymer melt viscosity is the most important rheological property, which is dominant in sintering. Increased viscosity lowers the mobility of the melt, resulting in the reduction of sintering rate, which increases the cycle time of the process.

- Melting, percentage crystallinity, and crystallization point of the polymer strongly affect the onset of sintering.
- Crystallinity affects the mechanical properties of the end product while processing with rotational molding.

9.2. Processing

The fundamentals of processing with rotational molding are the melt deposition and densification of polymer melt material. Cycle time is the completion of powder coalescence, which controls a major part of the heating time in the molding cycle [2]. Sintering has a significant impact on the end product properties. The molded part exhibits high porosity and poor mechanical properties with incomplete sintering (Figure 9.1).

Rotational molding is the process of producing hollow parts by adding plastic powder to a shell-like mold and rotating the mold about two axes while heating the mold and powder. During rotation, the powder fuses against the inner mold surface into a bubble-free liquid layer. The polymer is then cooled to near room temperature, and the resulting hollow part is removed. The cyclical process is then repeated.

The material viscosity, surface tension, and powder properties control particle coalescence, whereas diffusion controls the bubble shrinkage [4]. Particle size of the polymer powder acts as a thermodynamic driving force to lower the surface energy by means of reducing the surface area. Surface tension is the driving force and the viscosity of the resin is the opposing factor. Sintering rate is expressed by rate of the neck growth between the two particles [5].

Rotational molding is the most important processing technology for producing polymeric hollow articles [6]. In this process, polymer material in the form of powder is placed in the mold and the mold is closed and subjected to biaxial rotation in an oven at a temperature of 200–400°C. Polymer powder present inside the mold is melted [7–9] by heat transferred through the mold wall. During processing, all the powder melts, and the mold is moved out of the oven by maintaining the biaxial orientation. The complex rotations of the mold, heating

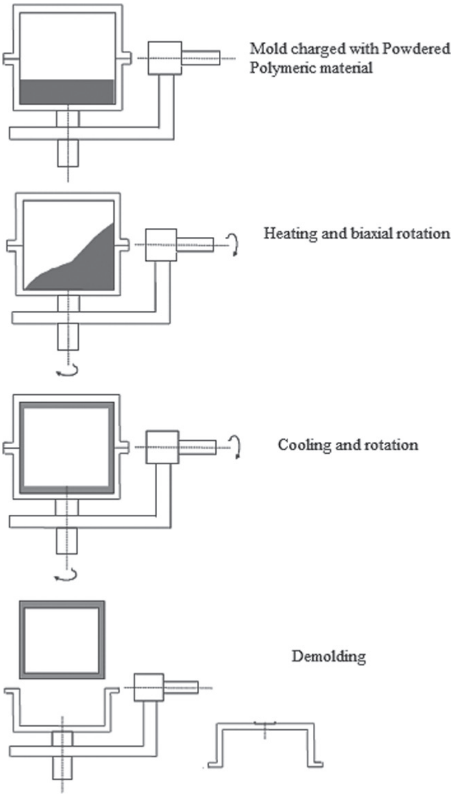

Figure 9.1 Schematic representation of rotational molding [Reprint with permission from Lim, S.-J. and Fu, K.-H. (2008). Polym. Testing. 27, 210. Copyright © 2007 Elsevier Ltd. All rights reserved [3]].

and cooling are most commonly achieved by convection to the external surfaces of the mold using air as the heat transfer medium. Air, fan, or water shower is usually used to cool the mold. When the product reaches sufficient rigidity below forming temperature, the mold is opened and the product is removed [10–12].

Heating time is defined as the time needed to heat up the internal air temperature from room temperature to 150°C. The cooling temperature is the time interval needed to cool down the internal air temperature from 150 to 100°C (Figure 9.2).

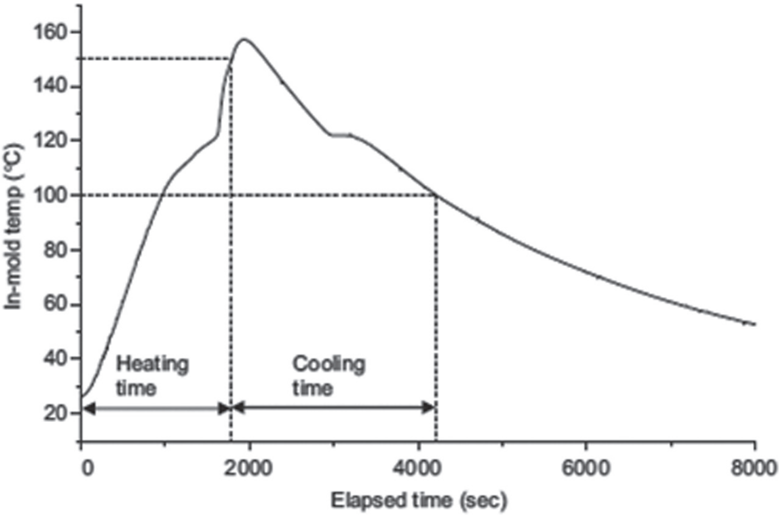

Figure 9.2 Schematic representation of typical internal air pressure of rotational molding [Reprint with permission from Lim, S.-J. and Fu, K.-H. (2008). Polym. Testing. 27, 213. Copyright © 2007 Elsevier Ltd. All rights reserved. [3]]

9.3. Summary

- Power and material properties are the most important factors.
- Molding process requires zero shear and pressure.
- Viscosity of the melt is to allow the polymer to form a uniform melt pool on the wall of the mold.
- Melt elasticity should hold the melt layer on the wall of the mold.
- Surface tension is an important process parameter during heating cycle, which acts as a driving force of powdered particle in particle coalescence.

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CHAPTER 10

Thermoforming

Thermoforming is one of the most economical methods of producing polymeric parts. It is an established process, which offers freedom to develop complex shapes and forms with cost-to-performance characteristics. It has significant advantages over other traditional methods of production. Low cost tooling, large part production, and reduced lead times are the advantages of producing sheet products.

Thermoforming is basically a very simple primary conversion process. However, there are variations in different processing, design, and finishing steps. The major advantages of thermoforming are cost-effective tools and processing of any kind of polymeric sheets. This technique is used to shape heated semi-finished products in the form of sheet by three-dimensional stretching.

Thermoforming equipment ranges from inexpensive single-station prototype or sample machines to massive units producing industrial components. Small manual operation machines provide for economical short-run production. High-production equipment can produce thousands of parts and requires the use of automatic, continuous-operation equipment.

10.1. Processing

Polymeric sheet is heated to its rubber state by either mechanical or pneumatic means. The sheet is formed into a three-dimensional part. The complete thermoforming process (Figure 10.1) may be described in terms of the following sequences of phases:

- Sheet material is clamped at its edge and heated. The sheet expands and becomes less rigid, and may sag under gravity due to the temperature increase.

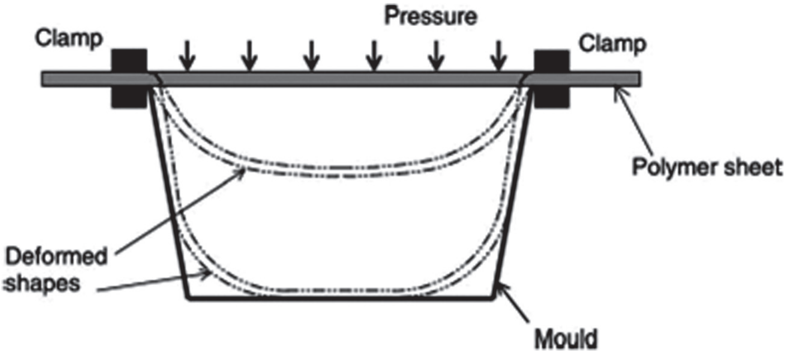

***Figure 10.1** Schematic representation of pressure thermoforming process [Reprint with permission from Warby, M.K., Whiteman, J.R., Jiang, W.-G., Warwick, P., and Wright, T. (2003). Math. Comput. Simul. 61, 209–218. Copyright © 2002 IMACS. Published by Elsevier Ltd. All rights reserved. [1]].*

- Heaters are removed.
- Pressure is applied immediately either to the upper face of the sheet or by evacuation of the volume between the sheet and the mold.
- Deformation takes place and the hot sheet comes into contact with the mold, gets cooler, and takes up the mold shape.
- Pressure is maintained until the thin-walled structure gets cooled. The structure at this stage remains in contact with the mold.
- The pressure is removed however, at this stage the sheet remains in contact with the mold.
- The sheet is blown off the mold, possibly charging shape, and takes up its final equilibrium shape.

The sheet is softened to an extent such that to stretch, enable, or ease without tearing. The softening behavior purely depends on the thermomechanical behavior in the form of orientation, stress, and crystallinity of the polymeric material. Therefore, the sheet memory is partially removed because of comparatively low temperatures over short periods of time. Polymer with amorphous nature is thermoformed above its glass transition temperature. The forming temperature is slightly above the melting temperature of their crystalline domains. The polymeric sheet is heated by contact, convection, or radiant heater. Then, the heated sheet is formed by vacuum or compressed air, which is called vacuum forming or pressure forming. The forming is carried out as two- or multistep process. Shear thinning of the polymer sheet material in comparison to its initial thickness results in thermoforming process. First step of thermoforming is pre-stretching and final step is obtaining final shape of the end product.

10.2. Orientation

The degree of orientational strain in sheet or film can affect its forming characteristics. Allowable orientation varies depending on thermoforming technique and end product. Low orientation is needed for preprinted forming since a distorted sheet distorts the printed product. Low and uniform orientation is also needed for forming processes using contact heat. Uneven orientation causes a sheet to ripple during the heating cycle, leading to uneven surface contact. This leads to nonuniform heat distribution and causes mottled spots or webbing in the end products.

10.3. Mold

Molds may be either male (raised) or female (recessed). Female molds are preferred, with plug assist process. A female mold will provide a thicker flange area, sharp definition on the outside area, and easy ejection. A male mold is usually cheaper to construct and provides for a deeper draw. Disadvantages include a tendency to web, form a weak flange area, and provide an extremely difficult release.

10.4. Mold Design

The variety of forming equipment also provides wide contrast in thermoforming mold design. Factors to be considered are as follows:

- Mold is for production or prototype.
- It should be male or female mold.
- Materials to be used.
- Material to be cast or machined.

- Mold shrinkage, finish, and cooling design.
- Requirement of trimming.
- Having mating component with a container or lid.

Shrinkage to be allowed depends on the material. Venting is provided for possible best results. Draft angle is to be provided based on female and male molds. All radii, undercuts, and vertical draw should be polished. Flats should have finish to prevent air entrapment. It is necessary to have uniform cooling. Uneven cooling distribution may cause shrinkage strains within the part. When forming, the mold temperature should be slightly below material distortion temperature.

10.5. Thermoforming Process

If the sheet is formed over the male or positive mold and the inner surface of the thermoformed part touches and replicates, the mold is called positive forming (Figure 10.2a). In other way, if the thermoformed part is in the cavities of a female or negative mold and the outer surface of the part replicates, the mold is called negative forming (Figure 10.2b) [2, 3].

Thermoforming results in characteristic thickness distributions of the part's walls. Once the sheet contacts the mold surface, it sticks and locally cools. The wall thickness distributions are due to hindering and stretching of the hot sheet material. Thermoformed sheet once formed as product is cooled below its softening to freeze is normally performed by conduction via the mold surface. The mold is kept at a constant temperature by cooling or heating. Finally, the thermoformed product is demolded and cut out or trimmed by various means around the formed regions.

10.6. Parameters

Forming of polymeric sheet is illustrated in Figure 10.3. The hot sheet placed and forced with pressure results in the product formation. The following parameters help to improve the thermoforming technique:

Heating. High-speed forming is achieved by adjusting heat control settings, which provide controlled temperature range. Surface degradation

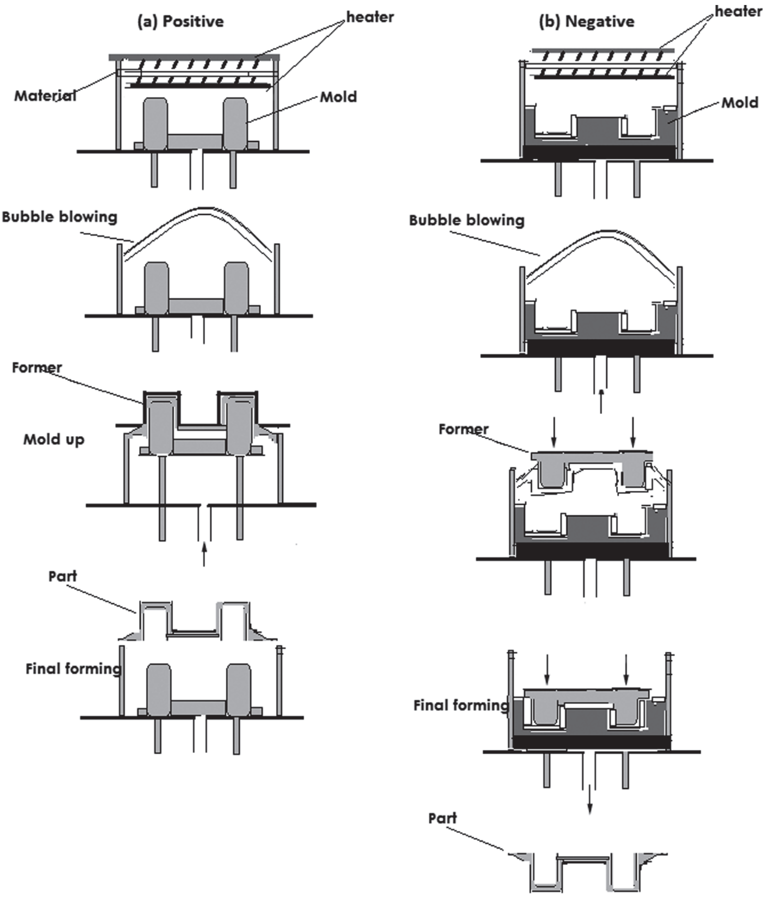

Figure 10.2 Two basic types of thermoforming processes: (a) positive and (b) negative forming

occurs with excessive heat. Using low, uniform heat and extended residence time is to achieve the best clarity of the product.

Pressure. The higher the pressure, the better the definition. Pressure should always be high. However, purging within the air line can cause forming problems and it is better to have an accumulator within the forming unit, which helps to troubleshoot the problem.

Mold temperature. The mold is designed for uniform thermal conductivity. Operating temperature below the material heat distortion temperature leads to better production. Uneven mold temperature may result in excessive stress.

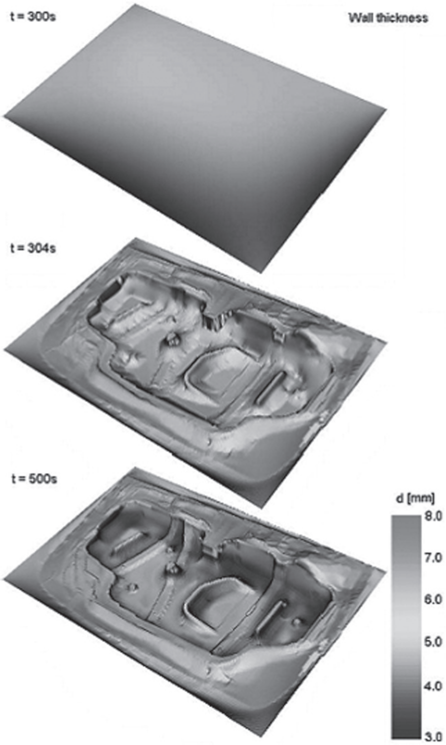

Figure 10.3 Forming of heated polymeric sheet. [Reproduced with permission from aus der Weische, S. (2004). Appl. Therm. Eng. 24, 2391–2409. Copyright © 2004 Elsevier Ltd. All rights reserved. [4]].

10.7. Summary

- Packaging technology concerned with thermoforming has grown synergistically with impressive processes and products with tailoring properties and continued evolution will undoubtedly lead to more
- Sheets are produced by extrusion or calendering in rolls of several hundred feet. As thermoforming process has become important, emphasis has been focused on producing sheets. Every polymeric sheet can be thermoformed depending on the material thermal properties.

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CHAPTER 11

Research on Polymer Processing

Research has recently focused on projects with important insights in terms of coordination and communication. The more spontaneous and opportunistic activities in polymer with different perspectives are based on technologies with integration. Rapid growth of polymer materials has commanded many new products emerged from the research activities. Polymers appear with their unusual properties that need processing technique to a high degree of commercial development. Polymer fabrication technology harmonizes with and support by filling opportunistic gaps. It may shrink and expand until without demanding conscious coordination. Therefore, research supports multitasking and defers to external contingencies.

In polymer research, particularly to estimate the processing techniques or process parameters, it requires extensive experimental data that are needed to obtain reason and complex search is required to minimize the desired objective function. Research is motivated by a desire to understand the fabrication techniques, which are impacted and constituted in technology use. Theories argue for an increase in spatial and temporal range of influences to study of time use that measures multitasking and time strategies during processing and fabrication.

Research on polymer fabrication is used to develop parameters that allow obtaining polymer processing parameters from a determined set of macroscopic properties, which yields parameters that are suitable for the thermodynamic properties and phase behavior of polymeric materials during its melt condition. It is necessary to have an extensive experimental detail to minimize the troubles during polymer processing. Therefore, knowledge of thermodynamic properties and phase equilibria behavior of polymer systems plays a fundamental role in the design and operation of equipment used in polymer processing and manufacturing.

11.1. Process Simulation

Process simulation is taking an increasing significance in research activity in polymer processing technology. The mold design can be optimally tailored to the process parameters that are to be expected, or the parameters can be optimized for an existing process [1, 2].

Simulation techniques in polymer processing are increasingly being used for understanding and optimizing polymer processes. Its advantages are that the whole process can be set up on a low-cost computer, and all of the variables can be changed at will to study their effects. This saves time, machinery investment, costly raw materials, and operation expenses. In addition, simulation can allow a visualization of effect, which cannot be seen or measured normally in the process. When investigating the thickness distribution of a bottle, we normally can see only the starting position and the end result. With simulation, the whole operation can be studied and understood [3]. New processes merge continuously such as injection stretch blow molding, gas-assisted injection molding, reactive extrusion, and nanotechnologies [4].

11.2. Research Problems

Important research problems in polymer processing techniques are

- heat transfer phenomenon between the processing equipment and polymeric materials during processing,
- melt polymer movement in the processing equipment, such as injection molding, extrusion, blow molding, and calendaring,
- material morphological changes during feeding and within residence time in the processing equipment,
- material and processing behavior under high stress in the processing equipment.

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Basics of Polymers

Fabrication and Processing Technology

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Basics of Polymers: Fabrication and Processing Technology constitutes one of the most important aspects of polymer science and technology. The performance of polymers is evolving into the most rapidly increasing volume of production. Polymers are an important commodity in the modern lifestyle. They are undoubtedly superior materials in terms of their costs, processability, and functional properties. The fabrication and processing technology are showing higher growth than that of the number of polymer grades in the market.

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