Polymer Degradation and Stability 129 (2016) 56–62

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

A new approach for reclaiming of waste automotive EPDM rubber using waste oil

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ARTICLE INFO

Article history:
Received 28 July 2015
Received in revised form
6 January 2016
Accepted 4 April 2016
Available online 5 April 2016

Keywords:
Waste EPDM
Mechanochemical reclaiming
DSO
Mechanical properties

ABSTRACT

The disposal of polymeric and especially rubber materials is an important global issue. In this work we have used disulfide oil (DSO), the oily waste produced in gas refineries, as a chemical agent for mechanochemical reclaiming of waste EPDM rubber at a specific operation condition. The devulcanization reaction was performed using different concentrations of DSO (5 and 7 phr) and different temperatures (220, 250 and 290 °C). The results confirmed the effectiveness of DSO in decreasing the crosslink density up to 73% at specific reaction conditions. Subsequently, two different portions of the devulcanized rubber (RR) (20 and 40 wt %) were blended with the virgin EPDM rubber to assess the reusability of the recycled product. Accordingly, replacing 40 wt% of RR had no effect on the scorch and the optimum curing time and similar curing rates were obtained. Moreover, the mechanical properties of the revulcanized blends were not worsened and surprisingly were improved in some cases including tensile strength and elongation at break up to 14% and 26% respectively. These results can be used to propose a new method for solving both rubber and disulfide oil disposal issues.

1. Introduction

Ethylene–propylene–diene rubber (EPDM) has applications in wide variety of areas specifically in automotive industry. The world consumption of both natural and synthetic rubbers has been 24.845 kt in 2010 [1]. Nowadays, the disposal and recycling of the discarded EPDM automotive parts is a growing issue, and the associated economy is significant. Different recycling methods for the scrap rubber have been proposed including rubber incineration and pyrolysis [2–5], application of ground rubber powder (GRP) in civil engineering [6–9], pulverizing [10,11] and direct addition of recycled material to the virgin rubber. However, the remaining crosslinked structure of the rubber and the weak interfacial adhesion between the rubber particles and matrix has been reported to cause poor mechanical properties [12]. Devulcanization is superior process developed for plastisizing ground rubber powder and to improve the final properties of the recycled material. The selective crosslink scission in the latter method transforms the vulcanized rubber back to its original form, while reclaiming process includes combination of both crosslink and main chain scission resulting in formation of shorter chains and consequently leading to poor mechanical properties. An ideal reclaiming process would only break the crosslinks and leave the main chains intact [13]. However, there is always a balance between crosslink scission and backbone breakdown. The challenge is to shift this balance towards devulcanization as far as possible and avoid main chain degradation [14].

There are several technologies that use different processes for reclaiming including mechano chemical [15–18], thermo mechanical [19,20], microwave [21,22], ultrasonic [23,24], biotechnological [25–27], devulcanization in supercritical carbon dioxide [28–30] and chemical reclaiming process [31–34]. Continuous devulcanization in a twin-screw extruder is one of the modern methods in this field that benefits from continuous operation, environmental protection, high speed, high efficiency and energy

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http://dx.doi.org/10.1016/j.polymdegradstab.2016.04.002

saving of the reclaiming process, compared to the traditional methods [35–38].

Sutanto et al. used a kinetic model to describe EPDM devulcanization in an extrusion process [39]. They used two types of EPDM, i.e. efficient vulcanized (EV) and a semi-efficient vulcanized (SEV), to produce devulcanized rubber in a co-rotating twin-screw extruder. The revulcanized blends of devulcanized with virgin material have shown that at least 25% of the devulcanized rubber can be added to the virgin material without making significant change in the final mechanical properties [40]. Shi and co-workers devoted an effort on the reclamation of ground tire rubber (GTR) by using different methods including twin-screw extruder. Finally, they recommended an optimum reclaiming method with an oxygen-free medium, without high shear force, and at relatively low temperature [28]. Mangili et al. studied and optimized the ultrasonic devulcanization of a ground tire rubber in a co-rotating twin-screw extruder using the response surface methodology based on an experimental design. They intend to evaluate the influence of process variables including ultrasonic amplitude, temperature, screw speed and flow rate on devulcanization. Their results showed the ultrasonic amplitude is the most effective parameter [41]. Maridass and Gupta have used counter rotating twin-screw extruder to devulcanize the ground NR powder [42]. Jalilvand et al. produced devulcanized EPDM using diphenyl disulfide as a devulcanizing agent in a laboratory intermeshing co-rotating twin-screw extruder. According to their results, shear stress is an important factor for increasing percent of devulcanization and the temperature is the most important factor determining the sol fraction [43]. Many industries prefer to use chemical reclaiming agents, generally organic disulfides or mercaptans, for the reclaiming processes. These chemicals are used for natural and synthetic rubbers including diphenyl disulfide, dibenzyl disulfide, diamyl disulfide, bis(alkoxy aryl) disulfides, butyl mercaptan, phenol sulfides and other disulfides [44]. There are many reports in the literature on the effect of disulfides as a chemical agent on the reclaiming of natural and synthetic rubbers [45–50].

The main objective of this study is to introduce a novel chemical agent for reclaiming of waste automotive EPDM rubber using the extrusion technology. This chemical, which is produced in gas refineries, is called disulfide oil (DSO). Since this byproduct is odorous, flammable and incapable to be burnt because of the presence of excessive sulfur leading to environmental pollution, its conservation and safe disposal is one of the main problems of gas refineries [51]. The DSO is generally rich in small chain lengths alkyl disulfides, but the exact chemical composition can vary depending on types of sulfur contaminants in the treated feedstock.

This paper is organized as follows ….

2. Experimental

2.1. Materials

Waste EPDM rubber used in this study was kindly supplied by Part Lastik Group Company, Mashhad, Iran. The exact composition of the rubber was unclear. However, based on the thermogravimetric analysis (TGA-50, Shimadzu, Japan), it has a general composition according to Table 1 and Fig. 1. Virgin EPDM (KEP 270, Kumho Polychem, Korea), carbon black (N330, Pars Co., Saveh, Iran), process oil (oil 840, Behran Co., Tehran, Iran), ZnO (Pars Rangineh Co., Tehran, Iran), stearic acid (Uni Chemical, Malaysia), antioxidant (NA 4010), MBTS, TMTD, zinc dibutyl dithio carbamate (Perkacit ZDBC) and elemental sulfur (Bayer Co., Germany) were used in this study. DSO as a devulcanizing agent was supplied by South Pars Oil and Gas Company, Iran. The solvents (toluene and acetone) used in characterization of the devulcanized samples were supplied by Shazand Petrochemical Co. (Arak, Iran).

Table 1
Thermogravimetric analysis results for EPDM waste rubber.

Property	Amount (%wt)
oil	5
EPDM	79
Carbon black and other fillers	16

2.2. Devulcanization method and sample preparation

Reclamation of the waste EPDM rubber was carried out using a laboratory intermeshing co-rotating twin screw extruder (Model TSE 20, Brabender Co., Germany). The extruder contained five heating/cooling zones and a screw diameter of 20 mm with L/D ratio of 40. The last three zones of extruder have been adjusted at constant temperature and reported as barrel temperature. The applied necessary reclaiming pressure is built up by combination of reversed flighted section and kneader along the screw (shown in Fig. 2). Constant feed rate was achieved by using a fixed screw speed of 120 rpm for all samples. The reclamation additives were process oil (5phr) and DSO (different concentrations). Experiments were carried out at different conditions presented in Table 2 using variable DSO concentration and temperature. Finally, the reclaimed samples were rolled by using a laboratory two roll mill.

2.3. Characterization

2.3.1. Sol-gel measurement

Soxhlet extraction method was used to separate the sol fraction of the reclaimed rubber. Small amount of the sample (5 gr) was extracted for at least 12 h, using acetone as the solvent to remove low molecular weight substances such as processing oil. The extracted sample was dried and weighed (m_1) allowed swelling by immersing in toluene (approximately 400 ml) for 72 h at room temperature. Then, specimen was taken out from toluene, weighed (m_s) and dried to a constant weight (m_2). Swelling test, which was used to analyze the network structure of the reclaimed samples, was performed according to ASTM D 6814-02, 2002, The sol fraction (wt%) was calculated according to Eq. (1):

$$Sol\,fraction\ (\%) = \frac{m_1 - m_2}{m_1} \times 100 \tag{1}$$

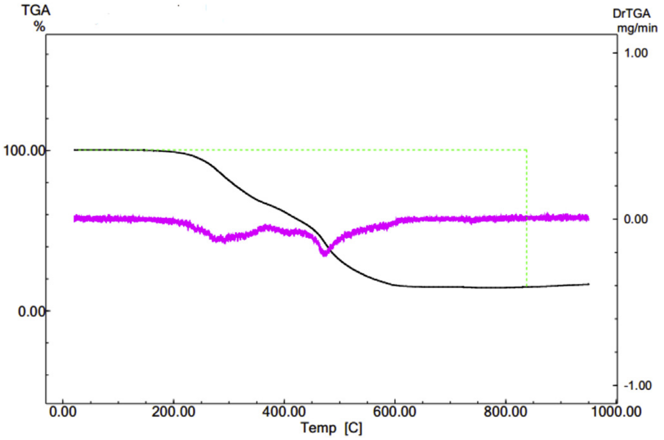

Fig. 1. TGA chart of waste EPDM rubber.

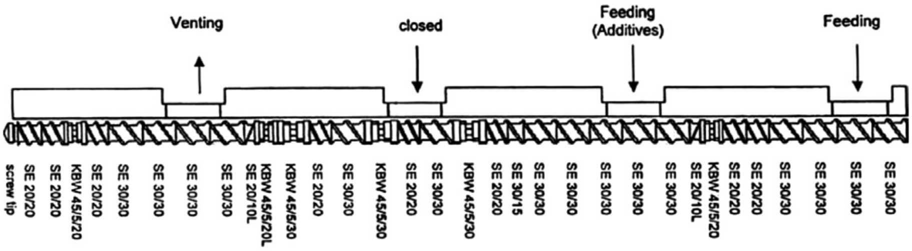

Fig. 2. Schematic view of screw profile.

Table 2
Devulcanization condition for the prepared samples.

Sample no.	DSO concentraion (phr)	T (°C)
1	5	220
2	7	220
3	5	250
4	7	250
5	5	290
6	7	290

It has been reported that the rupture of the rubber network during the process can be correlated to the sol fraction [28].

2.3.2. Crosslink density

Crosslink density of the gel part of the samples was also determined by swelling test based on the Flory-Rehner equation (Eq. (2)) [52]:

$$V_e = \frac{-\left[\ln\left(1 - V_r\right) + V_r + \chi V_r^2\right]}{\left[V_l\left(V_r^{1/3} - V_r/2\right)\right]} \tag{2}$$

where the Flory-Huggins' interaction parameter (χ) for toluene-EPDM system was adopted from Ref. [53]:

$$\chi = 0.429 + 0.218\, V_r \tag{3}$$

where V_e, V_r and V_l are crosslink density, rubber volume fraction in the swollen sample and molar volume of the solvent, respectively.

Due to the presence of filler in the waste EPDM, V_r was modified according to the following equation [54]:

$$V_r = \frac{1}{1 + \frac{d_r}{d_s}\left(\frac{1-f_{sol}}{1-f_{sol}-f_{fill}}\right)\left(\frac{m_s}{m_2} - 1\right)} \tag{4}$$

where d_r and d_s are the densities of the rubber and solvent, f_{sol} is the sol fraction of the initial sample, f_{fill} is the initial weight fraction of the filler in the sample, w_s is the weight of the swollen gel measured in Section 2.3.1, and w_0 is the weight of the dried sample. The density of the rubber was determined using digital densitometer Precisa xr-405.

2.3.3. Degree of devulcanization

The degree of devulcanization was calculated using Eq. (5):

$$Devulcanization\ (\%) = \frac{V_{e2} - V_{e1}}{V_{e1}} \times 100 \tag{5}$$

where Ve_1 and Ve_2 are the crosslink densities before and after devulcanization, respectively. Horikx's theory is an approach to track the type of degradation caused by reclamation. This theory was developed to provide deeper understanding from the performed devulcanization reaction [55]. Horikx investigated two extreme cases. (i) The first limit corresponds to the case where main chain scission occurs. In this case the relative decrease in crosslink density is calculated using the following equation:

$$1 - \frac{V_f}{V_i} = 1 - \frac{\left(1 - S_2^{1/2}\right)^2}{\left(1 - S_1^{1/2}\right)^2} \tag{6}$$

where V_i, V_f, S_1 and S_2 are the crosslink densities and sol fractions before and after devulcanization, respectively. (ii) The second limit corresponds to the case where crosslink scission occurs. The relative decrease in crosslink density is calculated using the following equations instead:

$$1 - \frac{V_f}{V_i} = 1 - \frac{\gamma_f\left(1 - S_2^{1/2}\right)^2}{\gamma_i\left(1 - S_1^{1/2}\right)^2} \tag{7}$$

where the parameters γ_f and γ_i are the crosslink indexes corresponding to the average number of crosslinks per chain in the residual gel before and after devulcanization, respectively. Horikx's theory is restricted to the mentioned cases and cannot explain the situations where there is a combination of both main chain and crosslink scission [56].

2.3.4. Mooney viscosity

Mooney viscosity of the rubber compounds was measured according to ISO 289, 2005 (ML 121 °C (1 + 4) min) using a Mooney MV2000 apparatus from Alpha Technologies. The results were expressed in Mooney Units (MU).

2.3.5. Compounding and curing characteristic measurement

The reclaimed rubber (RR) was mixed with specific fractions of the virgin rubber. Blends were compounded according to the

Table 3
Revulcanization formulations.

Ingredient	A	B	C
EPDM	100	80	60
RR	–	20	40
Carbon black	40	40	40
Oil	5	5	5
NA 4010	1	1	1
ZnO	4	4	4
Stearic acid	1.5	1.5	1.5
MBTS	0.8	0.8	0.8
TMTD	0.3	0.3	0.3
ZDBC	0.3	0.3	0.3
S	1.8	1.8	1.8

formulation presented in Table 3 on a lab-scale mill for about 15 min to obtain homogeneous EPDM compounds.

The curing characteristics of the reclaimed rubbers were measured at 160 °C for up to 20 min (ISO 3417, 2008) by means of a oscillating disk rheometer cure-meter (ODR, Gotech testing machines, model GT-M2000-F, Taiwan). The cure rate indices (CRI) were calculated as follows:

$$CRI = \frac{100}{t_{90} - t_{s2}} \tag{8}$$

The resulting compounds were then cured at 160 °C for the optimum curing time of t_{90} by compression molding at the pressure of 20 MPa.

2.3.6. Mechanical properties

Dumbbell-shaped specimens were punched out from compression molded sheets. The tensile strength, elongation at break and modulus at different elongations of the revulcanized rubber compounds were measured using a tensile testing machine (Instron machine, model 6025, England) according to ASTM D412-98a, 2002 at room temperature. The average of three replicates was reported for each sample.

The Shore A hardness was determined based on ASTM D 2240-02, 2002 with a Durometer hardness tester (Model Zwick, Germany). The reported hardness values are the average of three different measurements on the same samples, likewise.

Cylindrical samples (12.5 mm thick and 29.0 mm in diameter) were used to determine the compression set of the revulcanized compounds (cured at 180 °C for 13 min). The test was performed at 70 °C for 24 h by using a compression set testing apparatus (Taha Ghaleb Toos Co.) in accordance to ASTM D395-03, 2003. Finally, the set was calculated using the following expression:

$$\text{Compression set} = \frac{\text{Initial thickness} - \text{final thickness}}{\text{Initial thickness}} \times 100 \tag{9}$$

The resilience was measured using cylindrical samples, 12 mm thick and 50 mm in diameter. The samples were placed in a Dunlop Tripsometer (Model Zwick, Germany) according to the test method described in ASTM D2632–01, 2008, at room temperature. Measurements were repeated at three different positions on the same sample, and the average of the three readings was reported.

3. Results and discussion

3.1. Characterization of the reclaimed rubber (swelling test and mooney viscosity)

Crosslink density (CLD), sol fraction and percentage of the devulcanization were obtained from swelling test and the results are listed in Table 4, along with the results of viscosity measurements.

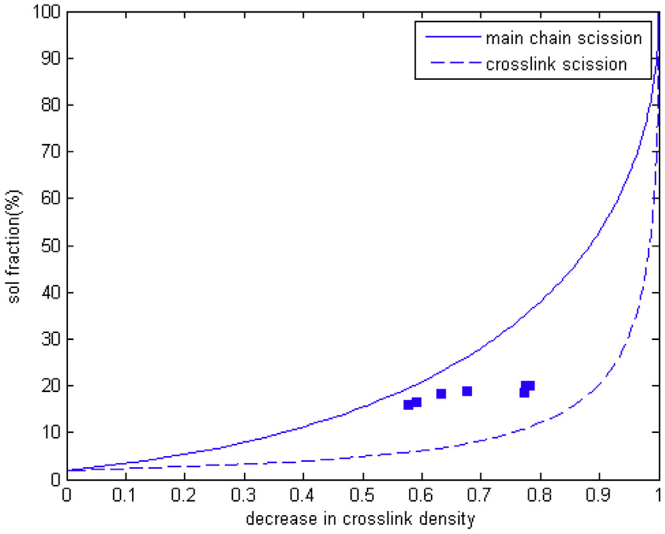

Fig. 3. Sol fraction of the reclaimed rubber versus relative decrease in crosslink density. Limits of pure main chain (solid line) and pure crosslink (dashed line) scission and the experimental data (squares).

As it can be seen in Table 4, increasing the DSO concentration at low temperature (220 °C) leads to CLD increase which in turn results in decrease of devulcanization and sol fraction (Sample No. 1 and 2). However, at higher temperature (250 and 290 °C), increasing DSO concentration favors devulcanization reaction and causes more breakage of the rubber network structure.

The results obtained for the samples prepared at lower DSO concentrations and different temperatures (Samples No. 1, 3 and 5) indicate that the highest decrease in CLD and associated highest increase in sol fraction were obtained at highest temperature of 290 °C (72% decrease and 19% increase, respectively). Horikx's theory was further utilized to provide a better perception from type of degradation reactions happened. The sol fractions of the devulcanized rubber versus decrease in crosslink density as predicted by the Horikx's theory are shown in Fig. 3. All of the experimental data obtained in this work are located between the two extreme curves confirming that the reclaiming reactions involve both crosslink and main chain scissions [55].

The mooney viscosity of the elastomeric compounds is a measure of the flow- and process-ability and is determined by the structure and composition of the reclaimed rubber. In general, low molecular weight substances such as processing oils contain higher the sol fraction and result in lower mooney viscosities. The experimental data as depicted in Table 3 clearly follow the general trend of lower mooney viscosity at higher devulcanization extends. The devulcanized rubber samples with Mooney viscosities between 45 and 70 MU are suitable for blending with virgin EPDM rubber [57].

Table 4
Characterization of the reclaimed rubber.

Sample No.	Density (g/cm^3)	CLD $\times 10^3$(mol/cm^3)	STD $\times 10^5$	Devulcanization (%)	STD	Sol fraction (%)	STD	Mooney viscosity (MU)
A	1.055	0.2999	0.12	0	–	2.0	0.003	–
1	1.156	0.1170	0.17	61	0.65	18.5	0.04	54
2	1.169	0.1316	0.2	56	0.8	18.1	0.06	58
3	1.139	0.1473	0.32	50	0.81	15.0	0.01	68
4	1.110	0.1434	0.27	52	0.63	16.0	0.09	66
5	1.151	0.0821	0.33	72	1.41	18.8	0.10	40
6	1.160	0.0814	0.0014	73	1.12	20.0	0.04	37

Table 5
Curing properties of the rubber compounds.

Compound no.	Scorch time (ts_2) (min:s)	Cure time (t_{90}) (min:s)	Δ torque (dN m)	CRI (s^{-1})
A	1:09	7:33	37.572	0.260
B1	1:07	7:59	35.224	0.243
B2	1:10	6:01	32.558	0.344
B3	1:09	9:10	37.218	0.208
B4	1:06	7:19	34.426	0.268
B5	1:04	6:41	33.142	0.297
B6	1:07	6:15	32.699	0.325
C1	1:01	5:33	27.272	0.368
C2	0:59	8:17	33.774	0.228
C3	1:01	9:15	28.951	0.202
C4	1:01	8:48	26.945	0.214
C5	1:07	6:20	29.038	0.319
C6	1:08	5:43	25.909	0.364

3.2. *Curing properties of the rubber compounds*

Three set of compounds at different levels of reclaimed rubber were prepared. Sample A contains no recycled material while B and C series correspond to the compounds containing 20 and 40 wt% of RR, respectively. B1–B6 and C1–C6 are the compounds containing 20 wt% and 40 wt% of RR produced at specific condition mentioned in Table 4. The ODR test obtained from rheometer graph are shown in Table 5.

According to the Table 5, the scorch time of the C series compounds is lower than B series compounds, indicating that the increasing RR content resulted in decrease of the scorch time. However, the optimum curing time showed different behavior and in the case of B2, B3 and B4, increased by increasing RR content as shown for samples C2, C3 and C4.

The difference between the minimum and maximum of the torque value is related to the crosslink density of the vulcanized rubber. This value has been decreased for all samples compared to the reference Sample A. Additionally, for almost all samples increasing the RR content has resulted in lower torque values.

The CRI value is a measure of the curing rate and therefore higher CRI values are favored for industrial applications. As can be observed in Table 5, the CRI values of the most of the samples show a minor increase compared to the reference compound.

3.3. *Mechanical properties*

Mechanical properties including tensile strength, elongation at break, modulus at different elongations of the vulcanized rubber, hardness, compression set and resilience of the reference compound and the revulcanized samples are shown in Table 6.

According to the results shown in Table 6, the tensile strength values have no significant difference with the reference compound A and surprisingly, even increase in tensile strengths were observed in some cases (B2, B5, B6, and C3–C6). Moreover, higher tensile strength values were achieved at 40 wt% of RR.

There was no obvious trend for the elongation at break, though; the corresponding in all samples (except B6 and B7) showed some improvement compared to the reference compound.

Generally speaking, higher DSO concentrations in the studied range had positive effects on the reclamation process and consequently on the mechanical properties of revulcanized samples and even at higher fractions of the reclaimed rubber.

The harnesses of the all revulcanized samples were higher than the reference compound more probably due to the presence of filler in the reclaimed rubber.

For the compounds, modulus at 100% elongation is near or higher than the reference compound and the improvement is more sensible for the blends containing 40 wt% of the reclaimed powder. This observation showed that the more addition of reclaimed rubber in the blends is beneficial to the modulus at different elongations (as shown in Table 6). Moreover, the addition of the reclaimed powder improve the elongation at break in most cases with the exception of compound B6 and consequently for the compounds showing the elongation at break above 300%, modulus at 300% elongation was observed unlike the reference compound. However, the compound C3 showed modulus at 300% elongation while its elongation at break was 297%. This observation is reasonable because each result in Table 6 was the average of three replicates.

Compression set is the end result of progressive stress relaxation, which is the steady decline in sealing force that results when an elastomer is compressed over a period of time [58]. The obtained results imply that in the most cases the compression set has been deteriorated for the studied conditions.

Resilience of the revulcanized rubber decreased compared to the reference compound A and this deterioration was more sensible when 40 wt% of RR was used. The values in the range of 40–50% are more typical for the majority of tested elastomers [59].

It is noted that the increase in strength and mechanical properties resulted in some compounds containing reclaimed EPDM maybe also due to the amount of carbon black that is higher for compounds B and C. In order to verify this aim, experiments (C′4 and C′5) were carried out by considering the carbon black existing in the reclaimed rubber. The results showed in Table 7.

Table 6
Mechanical properties of the rubber compounds.

Compound no.	Tensile strength (MPA)	STD	Elongation at break (%)	STD	Hardness (shore A)	STD	Modulus at 100% (MPa)	STD	Modulus at 200% (MPa)	STD	Modulus at 300% (MPa)	STD	Compression set (%)	STD	Resilience (%)	STD
A	14.3	0.99	268	16	68	0.8	3.2	1.1	9.108	0.3	-	-	13	2.1	60	1.1
B1	14.2	1.57	314	17	70	0.1	3.159	0.2	7.902	0.4	13.33	0.5	28	1.4	53	4.2
B2	14.6	0.85	361	16	70	0.4	2.717	0.04	6.687	0.04	11.359	0.1	38	1.5	50	2.6
B3	13.7	0.29	276	2	71	0.1	3.747	0.0	9.006	0.01	-	-	21	2.1	52	1.7
B4	14.2	1	308	20	70	0.0	3.22	0.07	8.115	0.1	12.201	1.9	33	1.0	52	1.5
B5	15.8	0.04	337	1	69	0.5	3.071	0.0	7.963	0.01	13.515	0.03	30	1.0	55	1.0
B6	14.6	0.46	227	7	68	0.1	4.614	0.2	12.289	0.3	-	-	31	2.6	53	5.0
C1	13.9	0.06	325	22	74	0.1	3.857	0.4	8.425	0.8	12.882	0.9	48	3.0	40	2.1
C2	14.0	0.63	277	3	75	0.9	4.277	0.3	9.833	0.4	-	-	23	1.2	44	2.1
C3	15.2	0.14	297	11	74	0.8	4.248	0.1	9.877	0.3	15.099	10.7	34	1.9	42	2.3
C4	15.0	0.35	313	5	74	0.3	3.92	0.03	9.053	0.1	14.323	0.2	38	2.4	45	1.7
C5	15.0	0.53	320	18	73	0.8	3.854	0.1	8.906	0.2	14.028	0.3	34	2.2	43	1.0
C6	16.3	0.36	243	13	72	0.7	5.79	0.4	13.39	0.6	-	-	45	2.0	44	3.0

Table 7
Mechanical properties of the rubber compounds (subtracting carbon black of reclaimed rubber).

Compound No.	Tensile strength (MPA)	STD	Elongation at break (%)	STD	Hardness	STD	Modulus at 100% (MPa)	STD	Modulus at 200% (MPa)	STD	Modulus at 300% (MPa)	STD	Compression set (%)	STD	Resilience (%)	STD
A	14.3	0.9	268	16	68	0.8	3.2	1.1	9.108	0.3	-	-	13	2.1	60	1.1
C′4	13.6	1.8	240	24	74	0.5	4.6	0.1	11	0.3	-	-	18	2.0	44	1.5
C′5	13.5	0.5	213	11	73	0.9	5.2	0.2	12.5	0.4	-	-	17	2.0	43	1.0

As results showed, the decrease in carbon black of the final compounds resulted the drop in mechanical properties lowering the reference compound. However, in the industrial application of reclaimed rubber, this consideration does not apply.

4. Conclusions

The mechanochemical reclamation of waste automotive EPDM rubber was successfully carried out by a co-rotating twin-screw extruder using a novel reclaiming agent (DSO). The results confirmed that this oily waste which is a byproduct of the gas refineries is an effective reclaiming agent. The maximum devulcanization (73%) was obtained at the specific operation condition (T = 290 °C, DSO; 7 phr and screw speed of 120 rpm). The reclaimed rubber was further blended with the virgin EPDM rubber at two different ratios (20 and 40 wt%) and the mechanical properties including tensile strength, elongation at break, modulus at different elongations, hardness, compression set and resilience of the revulcanized samples were measured. The data showed that using 40 wt% of RR at some specific operation conditions had no adverse effect on the scorch time, optimum curing time and rate of curing of the rubber compounds. Moreover, mechanical properties were not worsened and surprisingly, tensile strength and elongation at break improved in the most cases. However, the mechanical properties of final products which were compounded by subtracting the carbon black in reclaimed EPDM rubber drop compared to the reference (C′4 and C′5). In summary, the successful devulcanization of waste EPDM with the aid of DSO as a new reclaiming agent is a promising approach to resolve the problem of both DSO and the waste rubber disposal.

Acknowledgments

The authors gratefully acknowledge the financial support from South Pars Oil and Gas Company 91-208. The technical support, supply of rubber and chemicals from Baspar Sazeh Toos Co. of Part Lastic Group Co. are greatly appreciated.

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