

Effects of High Shear Stress on the Devulcanization of Ground Tire Rubber in a Twin-Screw Extruder

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ABSTRACT: The devulcanization reactions of ground tire rubber (GTR) and thermoplastic elastomer (TPE) mixtures performed during the melt-extrusion process through the induction of high shear stress by increases in the screw rotation speeds and reaction temperatures were investigated in this study. The results show that the high shear stress induced crosslink breakage and/or chain scission of GTR; this led to decreases in the gel contents and Mooney viscosities of the devulcanized GTR/(DGTR)/TPE blend and decreases in the sizes of the unfused gel particles in the revulcanized blends of styrene-butadiene rubber [SBR/(DGTR)/TPE]. When the main composition of GTR was natural rubber, its allylic unit structures in the main chains were susceptible to degradation. Although the main composition of GTR was SBR, its main chains contained lower contents of double bonds and were more stable; this led to significant changes in the gel contents and Mooney viscosities of the devulcanized blend and in the mechanical properties of the revulcanized SBR/(DGTR)/TPE blend. The ethylene-propylene-diene monomer (EPDM4770) rubber had better compatibility with GTR than the ethylene/1-octene copolymer and also had a higher molecular weight than that of EPDM3745. This led to a lower gel content and a higher Mooney viscosity in the devulcanized blend and higher mechanical properties in the revulcanized SBR/(DGTR)/EPDM4770 blend. The alkylphenol polysulfide 420 and 450 accelerated the devulcanization reaction and prevented the crosslinking reaction; this led to significant increases in the mechanical properties of the revulcanized SBR/(DGTR)/TPE blend. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Since the discovery of rubber vulcanization, from both economic and environmental views, the recycling of scrap rubber has been widely considered. The pyrolysis, pulverization, incineration, and devulcanization of scrap rubber have been reported in comprehensive reviews written by Adhikari et al.,¹ Myhre and Mackillop,² Isayev,³ and others.⁴ Among these methods, devulcanization is very viable. During this process, the rubber network is broken down, and the product can be revulcanized to produce new rubber articles. The most common devulcanization methods are reclamation by thermal,^{5,6} mechanochemical,^{7–11} thermomechanical,^{12–14} microwave,^{15,16} ultrasonic,^{17–27} and biotechnological^{28,29} methods. Solid-state shear pulverization^{30,31} and twin-screw-extruder continuous devulcanization (a thermomechanical process) have also been reported.^{32–37}

In recent decades, Isayev and coworkers^{20–28} have developed a polymer processing technology that uses high-power ultrasonic waves. They have investigated the devulcanization of waste tire rubber, natural rubber (NR), styrene-butadiene rubber (SBR),

ethylene-propylene-diene monomer (EPDM) rubber, and silicone rubber in a single-screw extruder equipped with an ultrasound source on the die. It was shown that during extrusion, the high-intensity ultrasonic waves broke down the molecular chains; this permanently reduced the viscosity of the original polymer melt or rapidly broke up the three-dimensional network in vulcanized rubbers through the scission of C–S, S–S, and C–C bonds.

Some studies^{38–51} have also shown that ultrasonic oscillations degrade the polymer melt and greatly enhance the compatibility and mechanical properties of high-density polyethylene (HDPE)/EPDM, HDPE/polystyrene (PS), polypropylene (PP)/EPDM, and PP/NR blends through the chain scission of the blends and the coupling of the long-chain radicals and effectively initiate the functionalization reaction of HDPE and EPDM with maleic anhydride to prevent the crosslinking reaction.

In recent years, Zhang, Li, and coworkers^{52–55} have found that there is a similarity of the effects between the ultrasonic

intensity and the screw rotation speed of a corotating twin-screw extruder on the functionalization reaction of HDPE and EPDM. It was reported that the functionalization reactions of HDPE and EPDM with maleic anhydride were realized by increases in the screw rotation speed in a twin-screw extruder because of the reaction between stress-induced macroradicals and maleic anhydride, and the crosslinking reaction was significantly suppressed. Recently, Zhang et al.⁵⁶ also reported that the devulcanization reaction of ground tire rubber (GTR) and thermoplastic elastomer (TPE) mixtures were performed through the induction of high shear stress in a twin-screw extruder. It was found that the gel content of the DGTR/TPE blend decreased with increasing screw rotation speed. When the screw rotation speed was 1000 rpm, the gel content of the devulcanized blend decreased to 35%. When 30 wt % of the devulcanized blend was added, the tensile strength and elongation at break of the revulcanized SBR/(DGTR/TPE) blend were 88.6 and 98%, respectively, of those of the vulcanized SBR (whose values were 22.0 MPa and 391%, respectively), and the mechanical properties of dynamically vulcanized PP/(DGTR/EPDM) and HDPE/(DGTR/EPDM) elastomers were significantly improved.

With the development of the twin-screw extruder, the screw rotation speed can reach 1000–3000 rpm and provide strong shear stress on an extruded material; this offers another possibility for the devulcanization of waste tire rubber. This method is rather convenient, efficient, and promising for industrial applications. Therefore, the study of the effect of high shear stress in a twin-screw extruder on the devulcanization process is very interesting. In this article, the devulcanization process of GTR in a twin-screw extruder is described. The effects of high shear stress on the gel content and Mooney viscosity of a devulcanized DGTR/TPE blend, Fourier transform infrared (FTIR) spectra of the sol, and morphology of the fractured surface of a revulcanized SBR/(DGTR/TPE) blend were investigated. The devulcanization efficiencies of the types of TPEs acting as swelling agents and the fluid phases transmitting shear stress in the reaction mixtures were compared. The effects of alkylphenol polysulfide promoting agents on the devulcanization reaction and the mechanical properties of the revulcanized SBR/(DGTR/TPE) blend were studied.

EXPERIMENTAL

Materials

Ground tire rubber A (GTR A; particle size \approx 30 mesh) was supplied by Yangzhou Lvhuang Rubber Reclamation Co., Ltd. (Yangzhou, China), and ground tire rubber C (GTR C; particle size \approx 20 mesh) was supplied by Nantong Tongjiang Plastic Material Co., Ltd. (Nantong, China). Their compositions were examined with thermogravimetric analysis (Netzsch STA449C/6/F, Selb, Germany) at a scanning rate of 10°C/min under nitrogen gas in the range 40–500°C and under air gas in the range of 500–600°C, respectively. The results are shown in Table I.

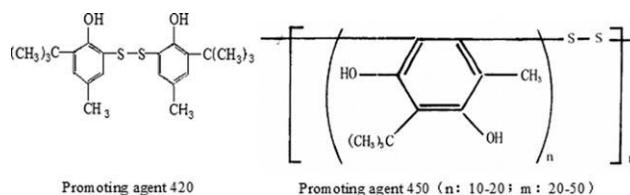
EPDM3745 (Mooney viscosity = 45, measured at 100°C), EPDM4770 (Mooney viscosity = 70), and ethylene/1-octene copolymer (POE8150; Mooney viscosity = 35) were purchased from DuPont-Dow Co. (Newark, DE, USA) SBR1502 was purchased from Shengyang Petrochemical Co., Ltd. (Shengyang, China). Carbon black N330 was purchased from Wuxishi Suxin Jingxi

Table I. Composition of GTR (mass %)

Type of GTR	Volatilization	Rubber	Carbon black	Ash
GTR A	5.6	46.7	37.2	10.5
GTR C	4.3	55.5	36.1	4.1

Carbon Black Manufacture Co., Ltd. (Wuxi, China). Antioxidant 1010, calcium stearate, 2-mercaptobenzothiazole (Accelerant M), *N*-cyclohexylbenzothiazole-2-sulfenamide (Accelerant CBS), zinc oxide, stearic acid, sulfur, antioxidant D, and antioxidant 4010 were industrial grade. The solvents for the characterization were reagent grade and were used without further purification.

The alkylphenol polysulfide 420 and 450 promoting agents were purchased from Nanjing Haibo Science and Technology Co., Ltd. (Nanjing, China), and Shanghai Ligao Chemical Industrial Co., Ltd. (Shanghai, China), respectively, and their structural formulas are shown:



Devulcanization Process of GTR During Melt Extrusion

The devulcanization process was carried out in a corotating twin-screw extruder (TE-35, Coperion Keya Machinery Co., Ltd., Nanjing, China) at different screw rotation speeds and different extrusion temperatures. The screw diameter was 35 mm, and the length-to-diameter ratio was 45. The screw configuration is shown in Figure 1. There were nine heating/cooling zones from the hopper to the die, in which the temperatures in zones 1, 2, and 3 zone increased in increments of 10°C, and the temperatures in zones 4, 5, 6, 7, and 8 were set as the reaction temperature. The die temperature was maintained at 5–10°C lower than the reaction temperature. GTR (80%), EPDM (20%) or POE (20%), and a small amount of stabilizing ingredients (0.15% antioxidant 1010 and 0.15% calcium stearate) or promoting agent (0.5% alkylphenol polysulfide 420 or 0.5% 450) were premixed. Then, the mixture was fed into the hopper of the extruder. The screw rotation speed was controlled between 400 and 1200 rpm, and the reaction temperature was adjusted between 180 and 270°C. The extruded blends, which were called the *devulcanized blends* (DGTR/TPE), were cooled in a water flume and collected.

Characterization of the Properties of the Devulcanized Blends (DGTR/TPE)

The gel content (W) of the devulcanized blends (DGTR/TPE) was measured by the Soxhlet extraction method, in which the devulcanized blends were packaged with 150-mesh stainless steel cloth, and were extracted in boiling xylene for 24 h. The residual products were dried *in vacuo* and were then reweighed and calculated by the following formula:

$$\omega = \left(1 - \frac{m_1 - m_2}{m_0} \right) \times 100\%$$

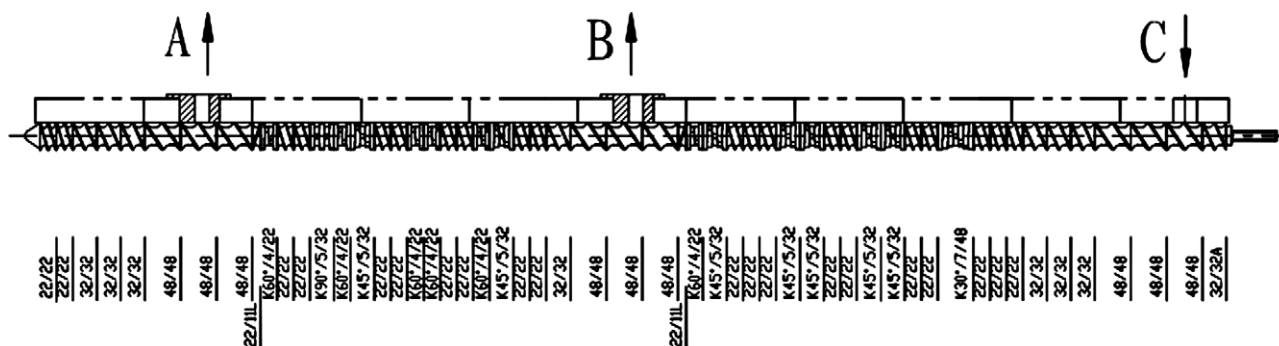


Figure 1. Screw configuration of the corotating twin-screw extruder (TE-35): (A) second vent, (B) first vent, and (C) feeder.

where m_0 is the mass of devulcanized blend (g), m_1 is the mass of the devulcanized blend and stainless steel cloth package before extraction (g), and m_2 is the mass of the devulcanized blend and stainless steel cloth package after extraction (g).

The Mooney viscosity of the devulcanized blends (DGTR/TPE) was measured at 100°C with a Mooney viscometer (MZ4012B, Jiangsu Mingzhu Laboratory Mechanical Manufacture, Jiangdu, China) according to Chinese standard GB/T1232.1-2000.

The soluble fraction of the extracted sample was centrifuged at a speed of 3000 rpm in a centrifuge (Anke TDL-40B, Shanghai Lontuo Instrument Equipment Co., Ltd., Shanghai, China) to remove carbon black. The clear solution was deposited with acetone and then dried in a vacuum oven. The obtained sol was pressed into a thin film at about 100°C; the film was used for infrared spectral characterization (Nicolet 670 SXB FTIR spectrometer, Madison, MI, USA).

Mechanical Measurements of the Revulcanized SBR/(DGTR/TPE) Blends

To examine mechanical properties of the revulcanized material, SBR and the devulcanized blends (DGTR/TPE) were compounded on a laboratory two-roll mill [S(X)K-160A, Shanghai Rubber Machinery Co., Ltd., Shanghai, China] according to the compounding formulations listed in Table II. The mixing time was 10 min. The compounded rubber stocks after 24 h of storage were placed in a mold and pressed between the platens of a hydraulic press (QLB-350X350X2-25t, Shanghai Rubber Machinery Co., Ltd., Shanghai, China). The samples were cured at 160°C and with an applied pressure of 10 MPa for the respective optimum cure times ($t = t_{90}$, the time to achieve 90% cure) obtained from rheographs (MDR 2000, Wuxi Liyuan Chemical Industry Equipment Co., Ltd., Wuxi, China). After curing, the hot mold was cooled in another hydraulic press, and then, the sheet was taken out of the mold. The dumbbell-shaped test specimens were punched out from the vulcanized

sheets after 24 h of storage with a tensile specimen cutter. The tensile strength and elongation at break were measured according to Chinese standard GB/T528-2009 in a universal testing machine (model CMT5254, SANS Group Co., Shenzhen, China) at $23 \pm 2^\circ\text{C}$ at a speed of 500 mm/min.

Scanning Electron Microscopy (SEM) Observations

The revulcanized SBR/(DGTR/TPE) (70/30) blends were fractured in liquid nitrogen, and then, the phase morphologies were observed in an SEM instrument (JSM-5900LV, JEOL, Tokyo, Japan).

RESULTS AND DISCUSSION

Effect of the Type of GTR on the Devulcanization Reaction

Figure 2 shows that the gel content of the devulcanized blend (DGTR/EPDM) decreased with increasing screw rotation speed at a constant reaction temperature (240°C), and it reached the minimum at 1000 rpm and then slightly increased at 1200 rpm. This was attributed to the slight crosslinking reaction under high shear stress conditions. The gel contents of GTR A were higher than those of GTR C.

Figure 3 shows that the gel contents of the devulcanized blend (DGTR/EPDM) decreased continuously with increasing reaction temperature at a constant screw rotation speed (1000 rpm), and it reached the minimum at 240°C and then slightly increased at 260°C. The gel contents of GTR A were higher than those of GTR

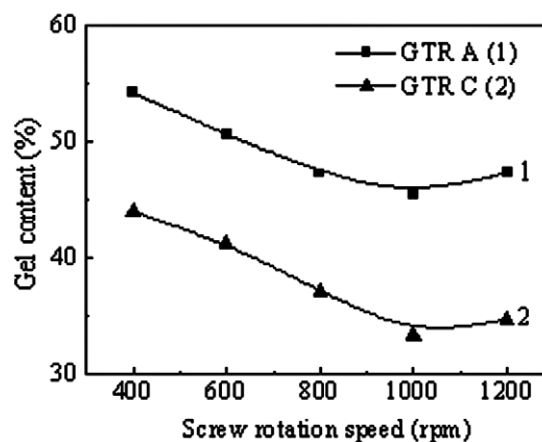


Figure 2. Effect of the screw rotation speed on the gel content of the devulcanized blends (DGTR/EPDM4770). The extrusion temperature was 240°C.

Table II. Compounding Formulation of the SBR/DGTR/TPE Blends (phr)

SBR	70	Accelerant CBS	0.8
DGTR/TPE	30	ZnO	5
N330	35	Stearic acid	2
S	2	Antioxidant D	1
Accelerant M	0.5	Antioxidant 4010	1

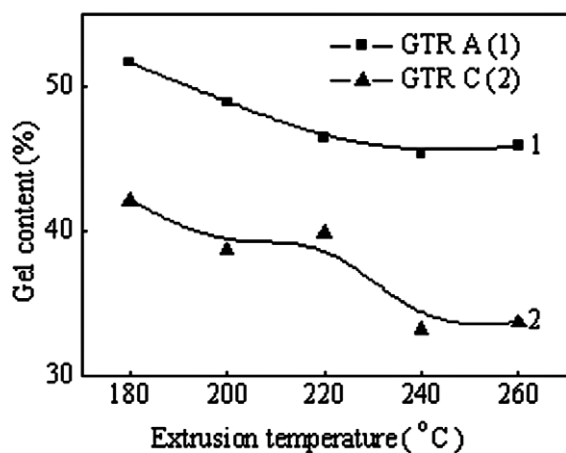


Figure 3. Effect of the extrusion temperature on the gel content of the devulcanized blends (DGTR/EPDM4770). The screw rotation speed was 1000 rpm.

C. Compared with the gel contents of the undevulcanized GTR A and C (which were measured as 80 and 93%, respectively), the gel contents of the devulcanized blends (GTR 80%/EPDM 20%) decreased significantly to 64 and 74.4%, respectively.

Figure 4 shows that Mooney viscosities of the devulcanized blends (DGTR/EPDM) obtained at a lower screw rotation speed or a lower reaction temperature were higher than those obtained at a higher screw rotation speed or a higher reaction temperature. The Mooney viscosity of the devulcanized blend of GTR A was significantly higher than that of GTR C.

Combined with the reported results,^{51–55} it was demonstrated that the shear stress acting on the reaction mixture increased with increasing screw rotation speed. A higher shear stress induced crosslink breakage and/or chain scission and broke up the network of GTR. This led to decreases in the gel contents and Mooney viscosities of the devulcanized blends. The higher the screw rotation speed and the reaction temperature were, the more obvious the effects were. Figures 2–4 also show that the gel content and Mooney viscosity of the devulcanized blends of GTR A were noticeably higher than those of GTR C; this demonstrated that the crosslinking network in GTR A was more stable than that in GTR C.

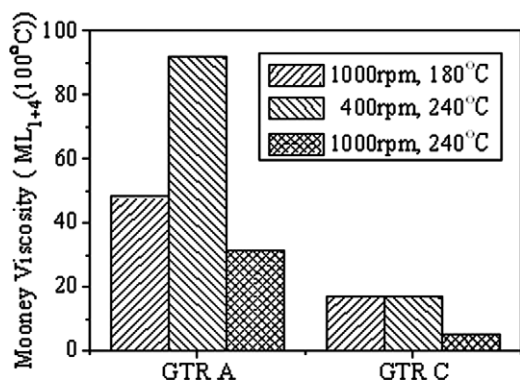


Figure 4. Mooney viscosity of the devulcanized blends (DGTR/EPDM4770).

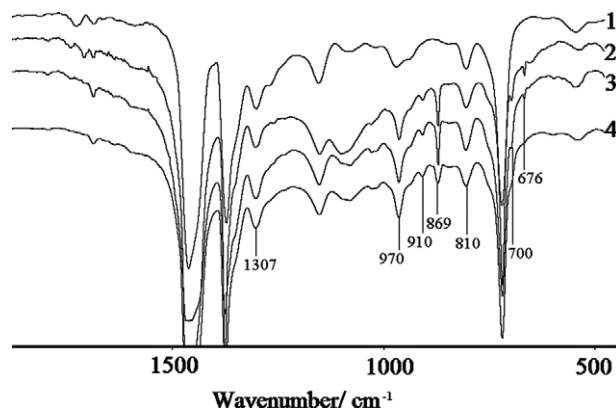


Figure 5. FTIR spectra of the sol of the devulcanized blends (DGTR A/EPDM4770): (1) EPDM, (2) 400 rpm and 240°C, (3) 1000 rpm and 180°C, and (4) 1000 rpm and 240°C.

Figure 5 shows that the peaks at 1307 cm^{-1} ($>\text{CH}-$) and 810 cm^{-1} ($>\text{C}=\text{CH}-$) were approximately identical in curves 1–4; some new absorption peaks at 910 cm^{-1} ($-\text{CH}=\text{CH}_2$), 869 cm^{-1} ($>\text{C}=\text{CH}_2$), and 676 cm^{-1} (aromatic substituent) appeared, and the absorption peaks at 970 cm^{-1} ($-\text{CH}=\text{CH}-$ trans) were strengthened with increases in the reaction temperature and/or screw rotation speed. This phenomenon demonstrated that the SBR content in the sol or the content of double-bond structures in the chains increased with increasing reaction temperature and/or screw rotation speed because the high shear stress induced crosslink breakage and/or chain scission and broke up the network of GTR.

Figure 6 shows that some new absorption peaks at 1233 cm^{-1} ($\geq\text{C}-\text{O}-\text{C}-$), 1090 cm^{-1} ($\geq\text{C}-\text{O}-\text{C}-$), 890 cm^{-1} ($>\text{C}=\text{CH}_2$), and 838 cm^{-1} ($>\text{C}=\text{CH}-$) appeared, and the absorption peaks at 970 cm^{-1} ($-\text{CH}=\text{CH}-$ trans) and 838 cm^{-1} ($>\text{C}=\text{CH}-$) of curves 2 and 3 were strengthened with increasing reaction temperature and/or screw rotation speed. This phenomenon also demonstrated that the NR content in the sol or the content of double-bond structures in the chains increased with increasing reaction temperature or screw rotation

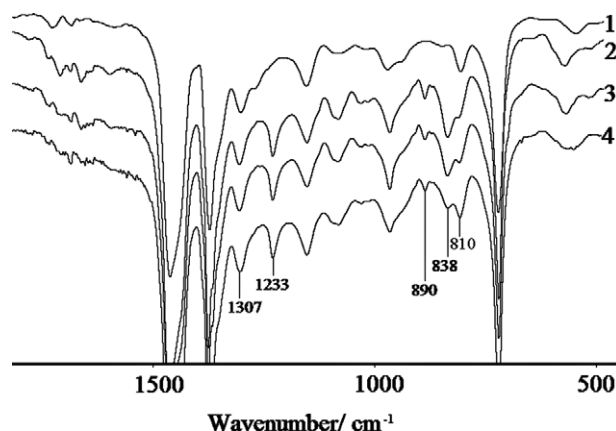


Figure 6. FTIR spectra of sol of the devulcanized blends (DGTR C/EPDM4770): (1) EPDM, (2) 400 rpm and 240°C, (3) 1000 rpm and 180°C, and (4) 1000 rpm and 240°C.

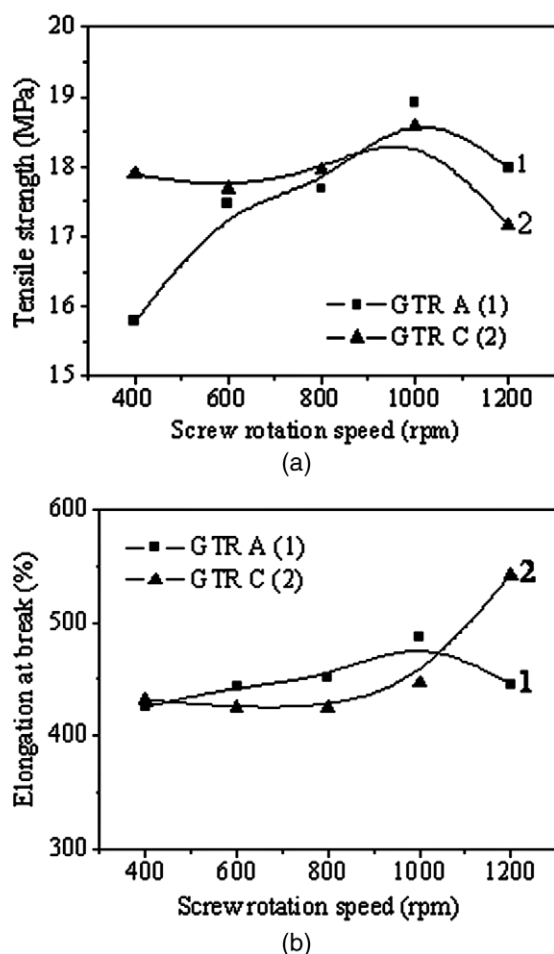


Figure 7. Effect of the screw rotation speed on the (a) tensile strength and (b) elongation at break of the revulcanized SBR/(DGTR/EPDM4770) blends. The extrusion temperature was 240°C.

speed because the high shear stress induced crosslink breakage and/or chain scission and broke up the network of GTR. However, the absorption peaks at 970 cm^{-1} ($-\text{CH}=\text{CH}-$ trans) and 838 cm^{-1} ($>\text{C}=\text{CH}-$) slightly decreased in curve 4 in Figure 6. This was attributed to the additional reaction of the excessive macroradicals with double bonds in the chains at a higher reaction temperature and a higher screw rotation speed; this led to a decrease in the absorption peaks. In addition, the peaks at 1233 cm^{-1} ($\geq\text{C}-\text{O}-\text{C}-$) and 1090 cm^{-1} ($\geq\text{C}-\text{O}-\text{C}-$) in curves 2–4 in Figure 6 indicated that the oxidative reaction of rubber chains took place during the devulcanization process.

Figures 7 and 8 show that the tensile strength and elongation at break of the revulcanized SBR/(DGTR/EPDM) blends increased with increasing screw rotation speed or reaction temperature, and the maximum value or a better value was obtained at 1000 rpm or at 220°C. The tensile strength and elongation at break of the revulcanized SBR/(DGTR A/EPDM) blend were significantly higher than those of the revulcanized SBR/(DGTR C/EPDM) blend under the conditions of 1000 rpm and 220°C.

The main composition of GTR C was NR, which contained allylic unit structure in the main chains and could easily be

degraded. Also, its crosslinking network could easily be broken; this led to a lower gel content and Mooney viscosity of the devulcanized blend and lower mechanical properties in the revulcanized SBR/(DGTR C/EPDM) blend. On the contrary, the main composition of GTR A was SBR, which contained a low content of double bonds in the main chains and was more stable than GTR C. This led to a higher gel content and Mooney viscosity in the devulcanized blend and higher mechanical properties in the revulcanized SBR/(DGTR A/EPDM) blend under the same devulcanization conditions.

Effect of the Type of TPE on the Devulcanization Reaction

In the devulcanization process, the compatibility and molecular weight of TPE, which acted as a swelling agent and a fluid phase for transmitting shear stress in the reaction mixture, were very important to the devulcanization reaction. Figures 9 and 10 show that the gel content of the devulcanized blend decreased with increasing screw rotation speed or reaction temperature. Curve 1 decreased slowly, curve 2 decreased significantly, and curve 3 was between them; this was attributed to the compatibility between the elastomer and the devulcanized

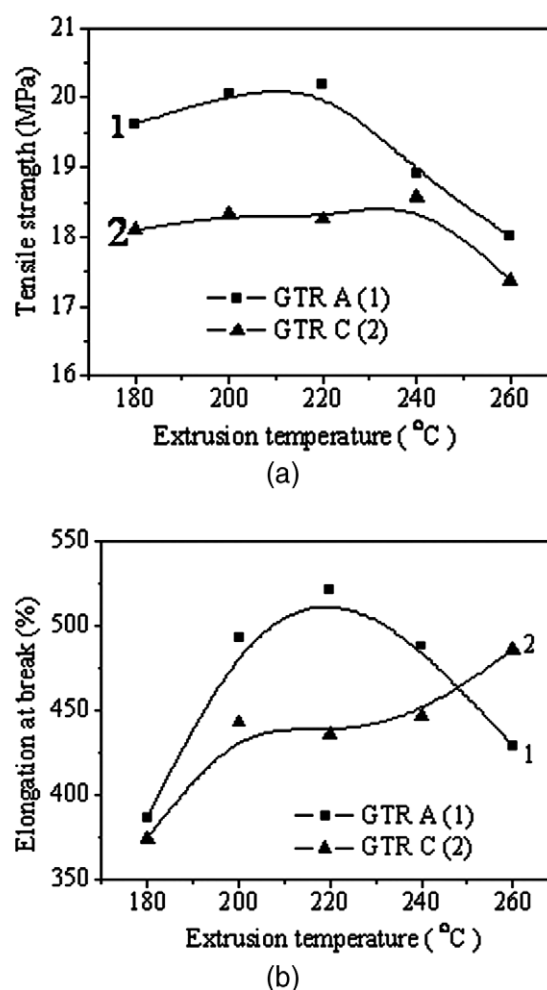


Figure 8. Effect of the extrusion temperature on the (a) tensile strength and (b) elongation at break of the revulcanized of the SBR/(DGTR/EPDM4770) blends. The screw rotation speed was 1000 rpm.

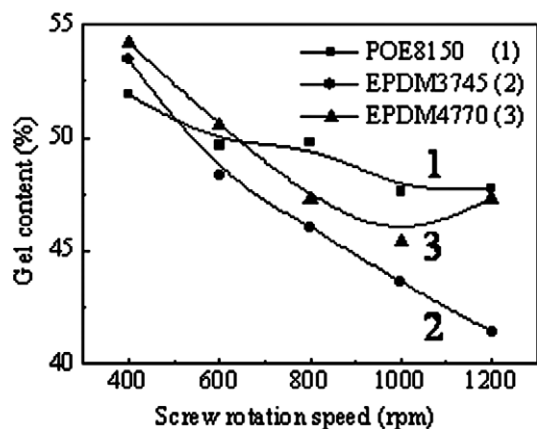


Figure 9. Effect of the screw rotation speed on the gel content of the devulcanized blend (DGTR A/TPE). The extrusion temperature was 240°C.

rubber. According to the general principle that a blend with better compatibility usually comes from better similarity between their molecular structures, the compatibility between POE8150 and the devulcanized rubber was poor, and the shear stress transmittance was poor, but the compatibility between EPDM3745 and the devulcanized rubber was better, and the shear stress could be transmitted effectively. Although the compatibility between EPDM4770 and the devulcanized rubber and the stress transmittance were between those of the POE8150/devulcanized rubber and EPDM3745/devulcanized rubber blends, because of its molecular weight, it was higher than that of EPDM3745, and this led to a change of the gel content of the devulcanized blend.

Figure 11 shows that Mooney viscosity of the devulcanized blends decreased with increasing screw rotation speed. The slopes of the curves were consistent with the compatibility and Mooney viscosities of the elastomers; this meant that the better the compatibility was and the higher the Mooney viscosity of the elastomer was, the more effective the shear stress transmittance was, and the more obvious the decrease of Mooney viscosity of the devulcanized blend was.

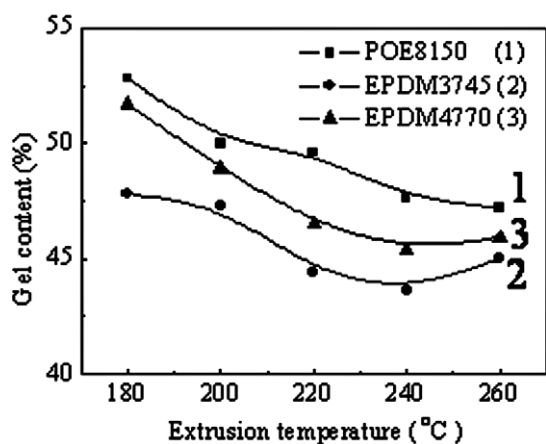


Figure 10. Effect of the extrusion temperature on the gel content of the devulcanized blends (DGTR A/TPE). The screw rotation speed was 1000 rpm.

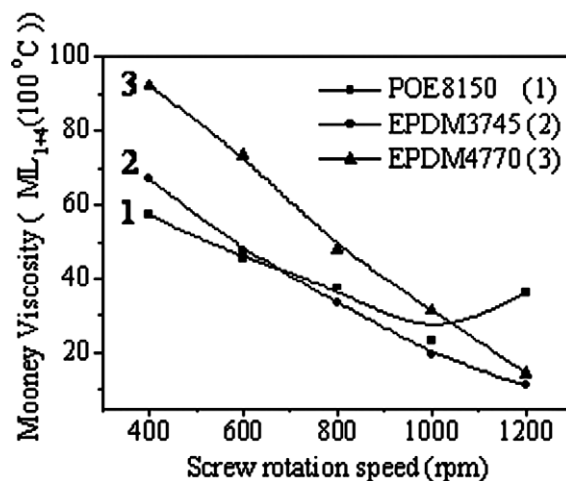


Figure 11. Effect of the screw rotation speed on the Mooney viscosity of the devulcanized blends (DGTR A/TPE). The extrusion temperature was 240°C.

Figure 12 shows that new absorption peaks at 970 cm^{-1} ($-\text{CH}=\text{CH}-$ trans) and 910 cm^{-1} ($-\text{HC}=\text{CH}_2$) appeared for the sols of the devulcanized blends, and the absorption peaks were strengthened with increasing reaction temperature and/or screw rotation speed. This meant that the SBR content in the sol or the content of double-bond structures in the chains increased because the high shear stress induced crosslink breakage and/or chain scission and broke up the network of GTR.

Figure 13 shows that some new absorption peaks at 1000 cm^{-1} ($-\text{HC}=\text{CH}_2$), 970 cm^{-1} ($-\text{CH}=\text{CH}-$ trans), 910 cm^{-1} ($-\text{HC}=\text{CH}_2$), 869 cm^{-1} ($>\text{C}=\text{CH}_2$), and 840 cm^{-1} ($>\text{C}=\text{CH}-$) appeared for the sols of the devulcanized blends, and these absorption peaks were strengthened with increasing reaction temperature and/or screw rotation speed. This meant that the SBR content and NR content (in a small ratio) in the sol or the content of double-bond structures in the chains increased because the high shear stress induced crosslink breakage and/or chain scission and broke up the network of GTR.

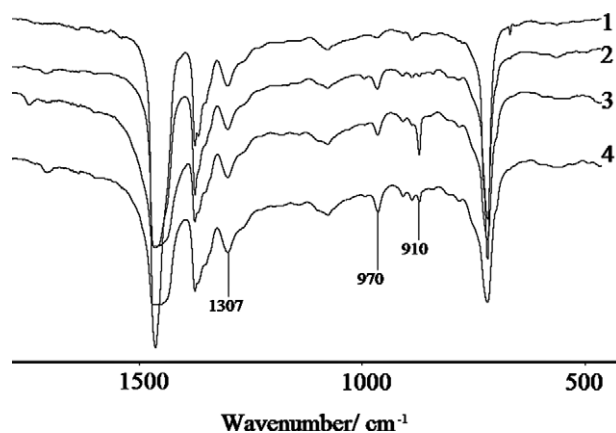


Figure 12. FTIR spectra of the sol of the DGTR A/POE8150 blends: (1) POE, (2) 400 rpm and 240°C, (3) 1000 rpm and 180°C, and (4) 1000 rpm and 240°C.

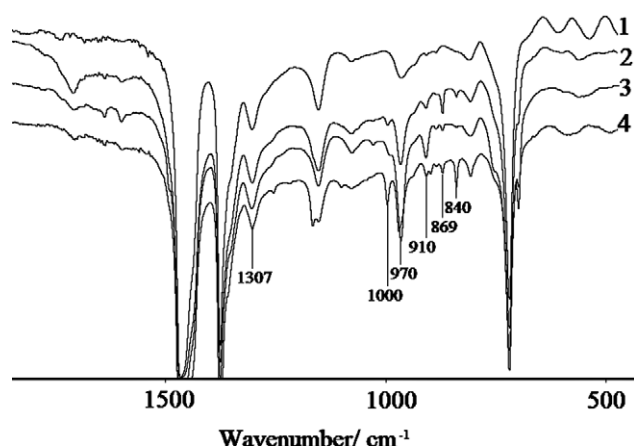


Figure 13. FTIR spectra of the sol of the DGTR A/EPDM3745 blends: (1) EPDM3745, (2) 400 rpm and 240°C, (3) 1000 rpm and 180°C, and (4) 1000 rpm and 240°C.

It was shown that the absorption peaks strength in Figure 13 were significantly higher than those in Figures 12 and 5; this meant that the devulcanization degree of the EPDM3745 blend

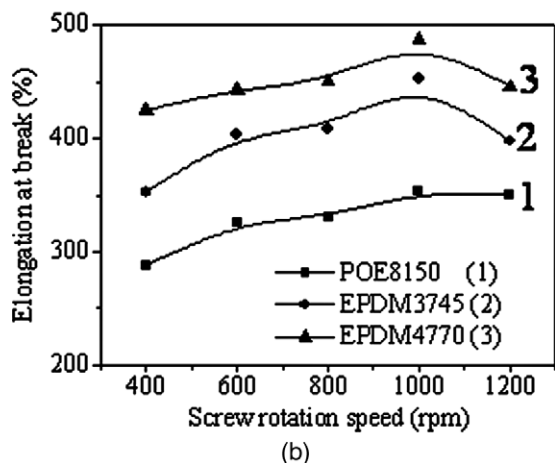
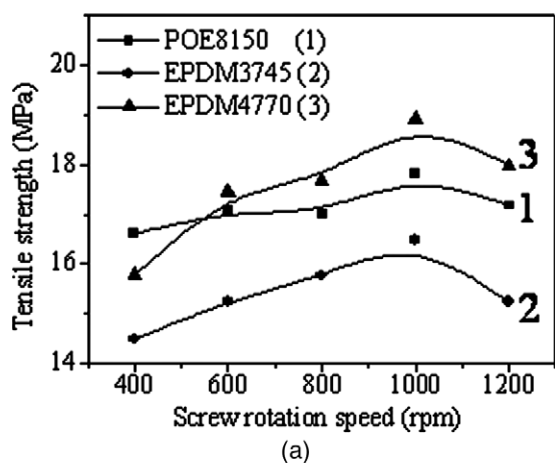


Figure 14. Effect of the screw rotation speed on the (a) tensile strength and (b) elongation at break of the revulcanized SBR/(DGTR A/TPE) blend. Extrusion temperature is 240°C.

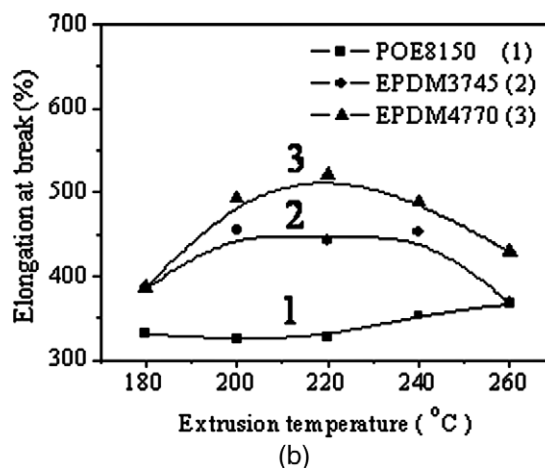
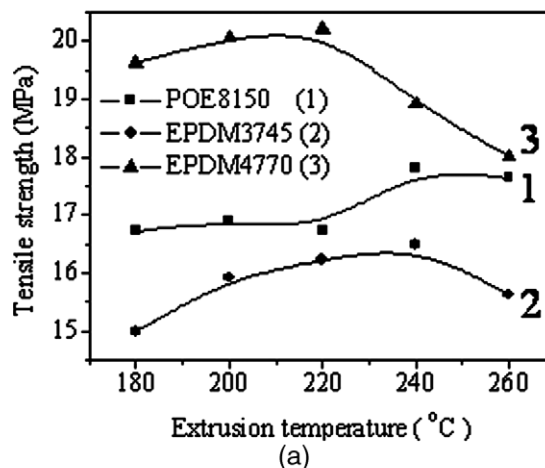


Figure 15. Effect of the extrusion temperature on the (a) tensile strength and (b) elongation at break of the revulcanized SBR/(DGTR A/TPE) blend. The screw rotation speed was 1000 rpm.

was higher than that of the POE8150 blend or EPDM4770 blend. Acting as a swelling agent and a fluid phase of transmitting shear stress in the reaction mixture, EPDM3745 had good

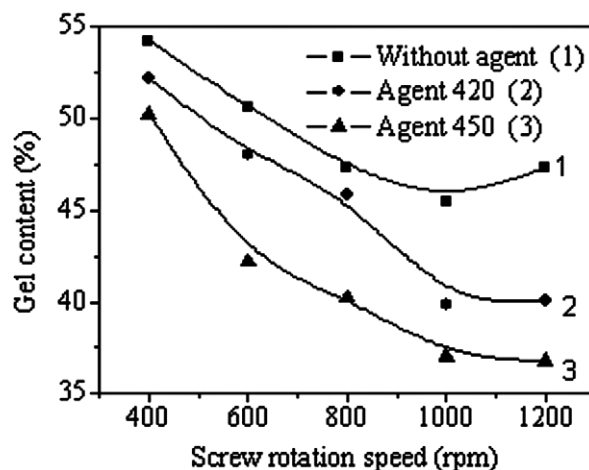


Figure 16. Effect of the screw rotation speed on the gel content of the devulcanized blends (DGTR A/EPDM4770). The extrusion temperature was 240°C.

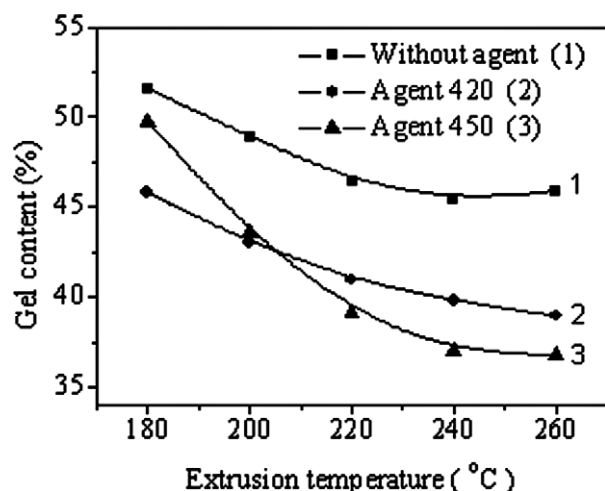


Figure 17. Effect of the extrusion temperature on the gel content of the devulcanized blends (DGTR A/EPDM4770). The screw rotation speed was 1000 rpm.

compatibility and stress transmission ability, and this leads to the increase in the sol content of the devulcanized blend.

Figures 14 and 15 show that the tensile strength and elongation at break of the revulcanized (DGTR A/TPE)/SBR blend increased with increasing screw rotation speed or reaction temperature and reached the maximum or a better value at 1000 rpm or at 220°C. It was also shown that the tensile strength and elongation at break of the revulcanized SBR/(DGTR A/EPDM4770) blends (curve 3) were significantly higher than those of the revulcanized SBR/(DGTR A/POE8150) (curve 2) and SBR/(DGTR A/EPDM3745) (curve 1) blends under conditions of 1000 rpm and 220°C. This phenomenon demonstrated that EPDM4770 had better compatibility than POE8150 and had a higher molecular weight than that of EPDM3745; this led to a lower gel content and a higher Mooney viscosity in the devulcanized blend and higher mechanical properties in the revulcanized SBR/(DGTR A/EPDM4770) blend.

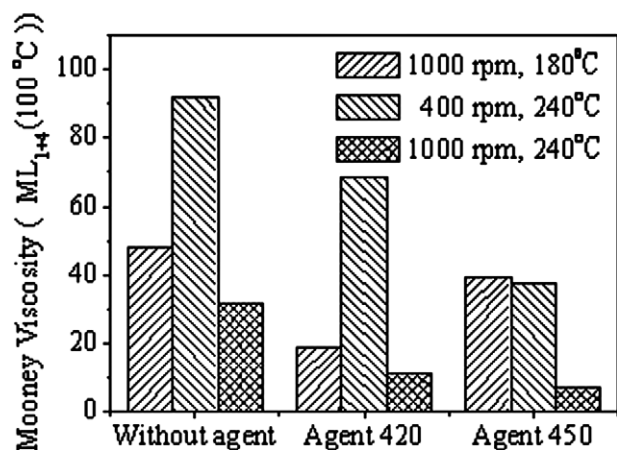


Figure 18. Mooney viscosity of the devulcanized blend (DGTR A/EPDM4770).

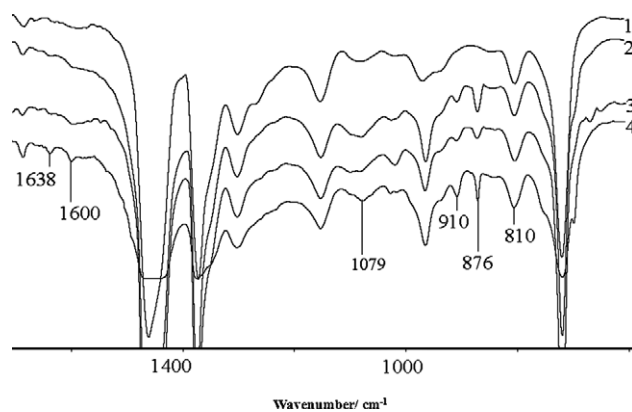


Figure 19. FTIR spectra of the sol of the devulcanized blends (DGTR A/EPDM4770) prepared at 220°C and 1000 rpm: (1) EPDM4770, (2) without agent, (3) with agent 420, and (4) with agent 450.

Effect of the Polysulfide Promoting Agents on the Devulcanization Reaction

Figures 16 and 17 show that the gel content of the devulcanized blend decreases with increasing screw rotation speed or with the reaction temperature, and when the reaction mixture contained a promoting agent, alkylphenol polysulfide 420 or 450, the gel content of the devulcanized blend decreased significantly, especially that of the promoting agent alkylphenol polysulfide 450.

Figure 18 shows that the Mooney viscosity of the devulcanized blend (DGTR/EPDM) containing a promoting agent, alkylphenol polysulfide 420 or 450, was significantly lower than that of the blend without a promoting agent.

Figure 19 shows that some new absorption peaks at 1079 cm^{-1} ($\geq\text{C}-\text{O}-\text{C}-$), 910 cm^{-1} ($-\text{HC}=\text{CH}_2$), and 876 cm^{-1} ($>\text{C}=\text{CH}_2$) appeared, and the absorption peak strength at 970 cm^{-1} ($-\text{CH}=\text{CH}-$ trans) increased slightly with increasing screw rotation speed and reaction temperature. Compared with the curve 2, the absorption peaks strength in the curve 3 decreased, but those in curve 4 increased.

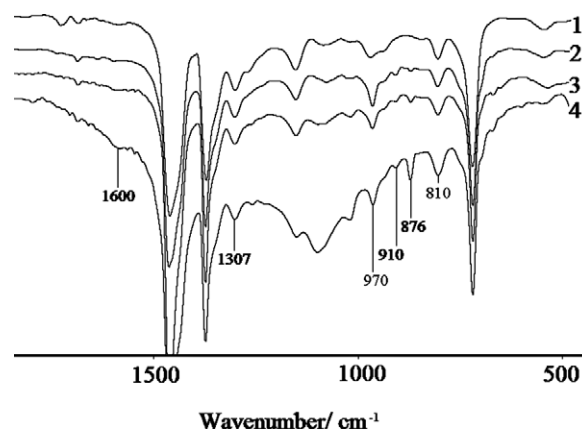


Figure 20. FTIR spectra of the sol of the devulcanized blends (DGTR A/EPDM4770) prepared with promoting agent 420: (1) EPDM, (2) 400 rpm and 240°C, (3) 1000 rpm and 180°C, and (4) 1000 rpm and 240°C.

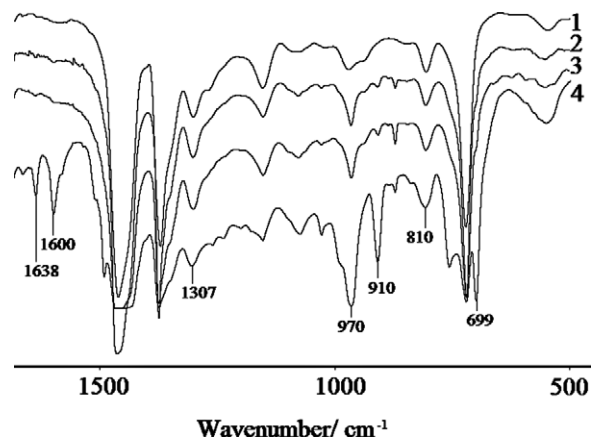


Figure 21. FTIR spectra of the sol of the devulcanized blends (DGTR A/EPDM4770) prepared with promoting agent 450: (1) EPDM, (2) 400 rpm and 240°C, (3) 1000 rpm and 180°C, and (4) 1000 rpm and 240°C.

Figure 20 shows that the absorption peak strengths at 970 cm^{-1} ($-\text{CH}=\text{CH}-$ trans), 910 cm^{-1} ($-\text{HC}=\text{CH}_2$), and 876 cm^{-1} ($>\text{C}=\text{CH}_2$) did not change obviously with increasing screw

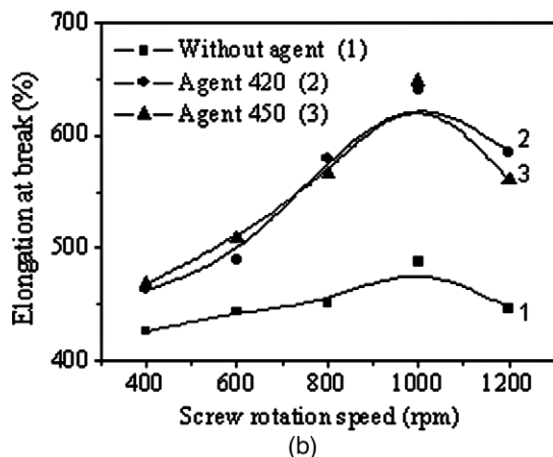
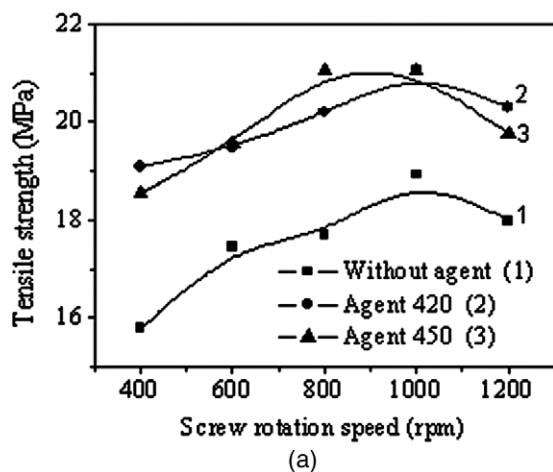


Figure 22. Effect of the screw rotation speed on the (a) tensile strength and (b) elongation at break of revulcanized blends SBR/(DGTR A/EPDM4770). The extrusion temperature was 240°C.

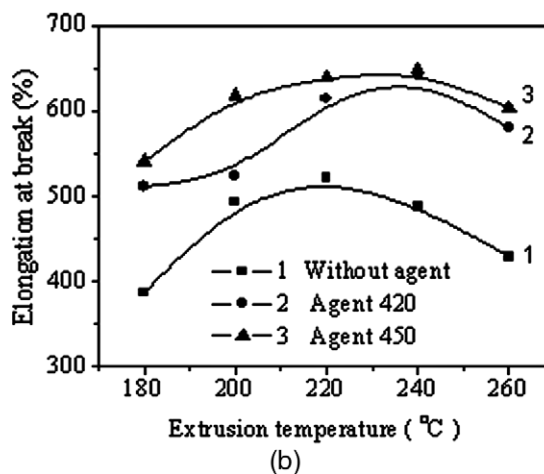
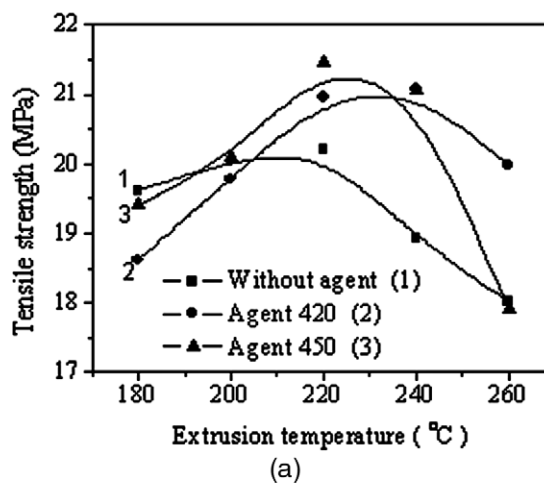


Figure 23. Effect of the extrusion temperature on the (a) tensile strength and (b) elongation at break of the revulcanized SBR/(DGTR A/EPDM4770) blends. The screw rotation speed was 1000 rpm.

rotation speed and/or reaction temperature. Figure 21 shows that the absorption peak strengths at 970 cm^{-1} ($-\text{CH}=\text{CH}-$ trans), 910 cm^{-1} ($-\text{HC}=\text{CH}_2$), and 876 cm^{-1} ($>\text{C}=\text{CH}_2$) increased significantly with increasing screw rotation speed and/or reaction temperature.

Although polysulfide 420 accelerated the devulcanization reaction, it led to the additional reaction of the produced radicals with double bonds in the chains, so the double-bond content of the sol decreased. In contrast, polysulfide 450 not only accelerated the devulcanization reaction but also prevented the cross-linking reaction and the additional reaction; as a result, the double-bond content of the sol increased significantly.

Figures 22 and 23 show that the tensile strength and elongation at break of the revulcanized SBR/(DGTR A/EPDM4770) blend increased with increasing screw rotation speed or reaction temperature and reached a maximum or better value at 1000 rpm or at 220°C. It was shown that the tensile strength and elongation at break of the revulcanized SBR/(DGTR A/EPDM4770) blends (curve 3, with polysulfide 450) were slightly higher than those of the revulcanized SBR/(DGTR A/EPDM4770) blends

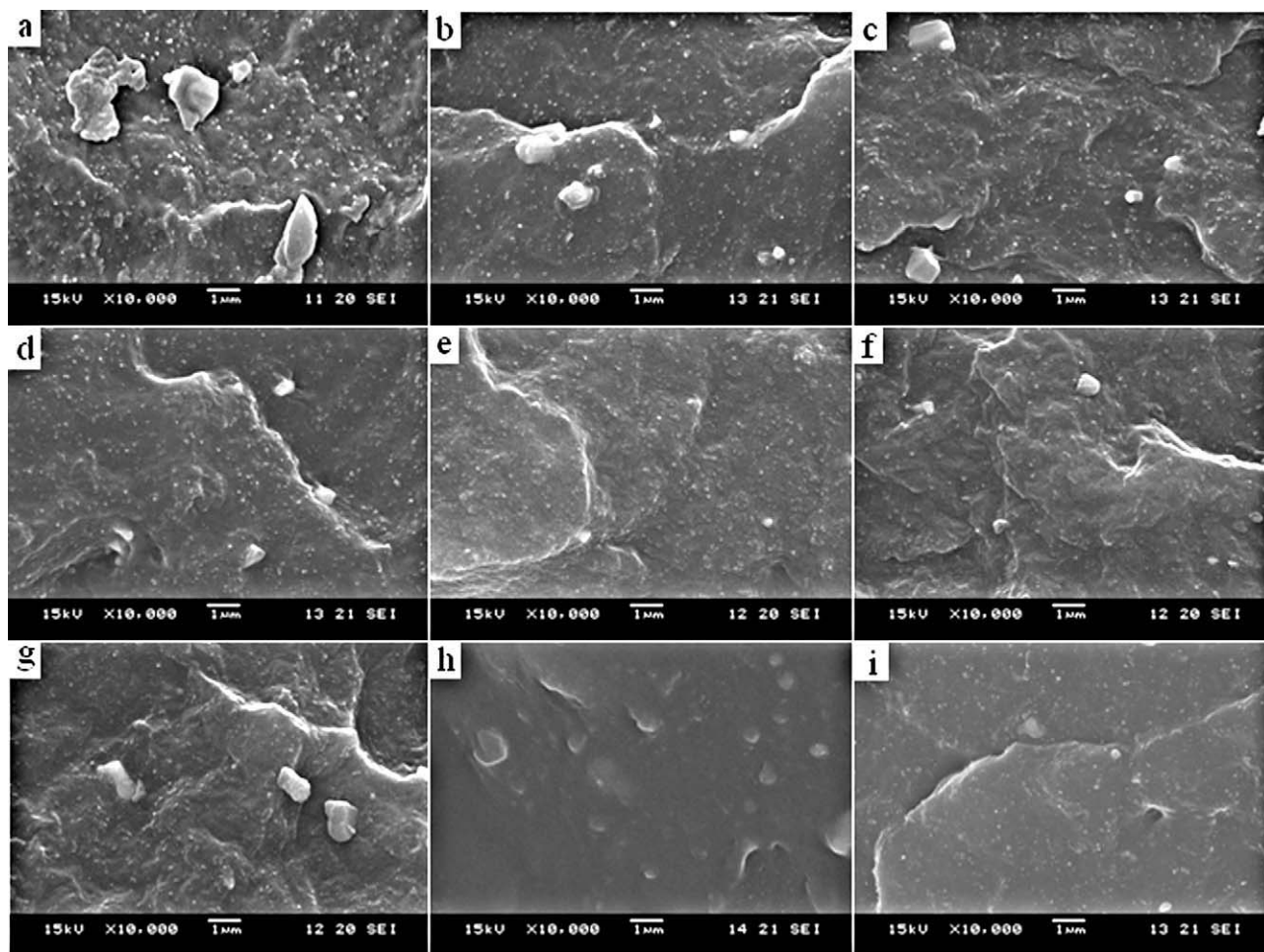


Figure 24. SEM photographs of the fractured surface of the revulcanized SBR/(DGTR/TPE) blends prepared under different devulcanization conditions: (a) GTR A/EPDM4770, undeveloped; (b) DGTR A/EPDM4770 at 240°C and 400 rpm; (c) DGTR A/EPDM4770 at 180°C and 1000 rpm; (d) DGTR A/EPDM4770 at 240°C and 1000 rpm; (e) GTR C/EPDM4770 at 240°C and 1000 rpm; (f) DGTR A/EPDM3745 at 240°C and 1000 rpm; (g) DGTR A/POE8150 at 240°C and 1000 rpm; (h) DGTR A/EPDM4770 at 240°C and 1000 rpm and with alkylphenol polysulfide 420; and (i) DGTR A/EPDM4770 at 240°C and 1000 rpm and with alkylphenol polysulfide 450.

(curve 2, with polysulfide 420) and were significantly higher than those of the revulcanized SBR/(DGTR A/EPDM4770) blends (curve 1, without promoting agent) under conditions of 1000 rpm and 220°C. This phenomenon demonstrated that polysulfides 420 and 450 could accelerate the devulcanization reaction and prevent the crosslinking reaction. Particularly, polysulfide 450 could also protect the double bonds in the chains; this led to a significant increase in the mechanical properties of the revulcanized SBR/(DGTR A/EPDM4770) blend.

In the presence of polysulfide 450 and at 220°C and 1000 rpm, the tensile strength and elongation at break of the revulcanized SBR/(DGTR A/EPDM4770) (70/30) blend reached 21.5 MPa and 639%; these values were 89.6 and 179% of those of the vulcanized SBR (with values of 24.0 MPa and 356%), respectively.

Analysis of the Fractured Surfaces of the Revulcanized SBR/(DGTR/TPE) Blend

Figure 24(a–d) shows that the size of the unfused gel particles in the revulcanized SBR/(DGTR/TPE) blend decreased signifi-

cantly with increasing screw rotation speed or reaction temperature; this meant that the higher the shear stress was and the stronger the heat energy acting on the reaction mixture was, the more significant the breakup of the crosslinking network of GTR was. This led to a decrease in the unfused gel particle size in the revulcanized SBR/(DGTR/TPE) blend.

Figure 24(d,e) shows that the size of the unfused gel particles in the revulcanized SBR/(DGTR C/EPDM4770) blend was obviously smaller than those in the revulcanized SBR/(DGTR A/EPDM4770) blend. This phenomenon was attributed to the fact that the main composition of GTR C was NR, which contained allylic unit structures in the main chains and was easily degradable. Also, the crosslinking networks were easily broken, and this led to the size decrease in the unfused gel particles in the revulcanized SBR/(DGTR C/EPDM) blend.

Figure 24(d,f,g) shows that the sizes of unfused gel particles in the revulcanized blends of SBR/(DGTR A/EPDM3745) and SBR/(DGTR A/EPDM4770) were significantly smaller than

those in the revulcanized SBR/(DGTR A/POE8150) blend. This phenomenon was attributed to the fact that the compatibility between POE8150 and the devulcanized rubber was worse than those of EPDM4770 and EPDM3745. This led to poor stress transmission ability and some bigger unfused gel particles in the revulcanized SBR/(DGTR A/POE8150) blend.

Figure 24(d,h,i) shows that the sizes of the unfused gel particles in the revulcanized SBR/(DGTR A/EPDM4770) blends with polysulfide 420 or 450 were smaller than those in the revulcanized SBR/(DGTR A/EPDM4770) blend, and the interface of the unfused gel particles was indistinct. The phenomenon was attributed to the fact that polysulfide 420 and 450 accelerated the devulcanization reaction and prevented the crosslinking reaction; this led to a decrease in the size of the unfused gel particles and the reinforcement of the interfacial binding strength of the revulcanized SBR/(DGTR A/EPDM4770) blends with polysulfide 420 or 450.

CONCLUSIONS

During the melt extrusion of a mixture of GTR and thermoplastic elastomer, the high shear stress coming from a twin-screw extruder induced crosslink breakage and/or chain scission and broke up the crosslinking network of GTR; this led to decreases in the gel content and Mooney viscosity of the devulcanized blends. The higher the screw rotation speed and the reaction temperature were, the stronger the mechanical energy and heat energy acting on the reaction mixture were, and the more obvious the crosslink breakage and/or chain scission and the breakup of the crosslinking network were. This led to a significant decrease in the gel content and Mooney viscosity of the devulcanized blend and a decrease in the unfused gel particle sizes in the revulcanized SBR/(DGTR/TPE) blend.

When the main composition of GTR was NR, its allylic unit structure in the main chains was susceptible to degradation, and the crosslinking network could easily be broken. This led to a lower gel content and Mooney viscosity in the devulcanized blend and lower mechanical properties in the revulcanized SBR/(DGTR/TPE) blend. When the main composition of GTR was SBR, its main chains contained a low content of double bonds and were more stable; this led to a higher gel content and Mooney viscosity of the devulcanized blend and higher mechanical properties in the revulcanized SBR/(DGTR/TPE) blend.

EPDM4770 had better compatibility with GTR than POE8150 and had a higher molecular weight than EPDM3745; this led to a lower gel content and a higher Mooney viscosity in the devulcanized blend and higher mechanical properties in the revulcanized SBR/(DGTR A/EPDM4770) blend.

Polysulfides 420 and 450 accelerated the devulcanization reaction and prevented the crosslinking reaction. Particularly, polysulfide 450 also protected the double bonds in the chains; this led to a significant increase in the mechanical properties of the revulcanized SBR/(DGTR A/EPDM4770) blend. In the presence of polysulfide 450 and at 220°C and 1000 rpm, the tensile strength and elongation at break of the revulcanized SBR/(DGTR A/EPDM4770) (70/30) blend reached 21.5 MPa and 639%, respectively, which were 89.6 and 179%, respectively, of

those of the vulcanized SBR (with values of 24.0 MPa and 356%). Meanwhile, the sizes of the unfused gel particles in the revulcanized blend reached a minimum.

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