

## Effects of Shear Stress and Subcritical Water on Devulcanization of Styrene–Butadiene Rubber Based Ground Tire Rubber in a Twin-Screw Extruder

Xiaojun Wang, Changping Shi, Ling Zhang, Yuncan Zhang

College of Materials Science and Engineering, Nanjing University of Technology, Nanjing, China

Correspondence to: Y. Zhang (E-mail: zhangyc@njut.edu.cn).

**ABSTRACT:** The devulcanization reaction of styrene–butadiene rubber (SBR) based ground tire rubber (GTR) in GTR/ethylene–propylene–diene monomer rubber (EPDM) blend was investigated through a compound-induced reaction by increasing screw rotation speed and being in the presence of subcritical water. The effects of temperature, pressure, screw rotation speed, or promoting agents on the gel content, Mooney viscosity, and Fourier transform infrared spectra of the sol of the devulcanized blends (devulcanized ground tire rubber (DGTR)/EPDM) were measured, and the mechanical properties and microstructures of the devulcanized blend ((DGTR/EPDM)/SBR) were characterized. The results show that subcritical water as a swelling agent and reaction medium promotes the devulcanization reaction, increases the selectivity of the crosslink breakage, keeps the extrusion material from oxidative degradation, reduces the gel particle size of the devulcanized blends, and significantly improves the mechanical properties of the devulcanized SBR/(DGTR/EPDM) blends. In subcritical water, the suitable promoting agents (alkylphenol polysulfide 450, hydrogen peroxide  $\text{H}_2\text{O}_2$ , or 450/ $\text{H}_2\text{O}_2$ ) accelerate the devulcanization reaction, keep the double bond content, and lead to further decrease of the gel content and Mooney viscosity of the devulcanized blends and further increase of the mechanical properties of the devulcanized SBR/(DGTR/EPDM) blends. Especially the compound promoting agent (450/ $\text{H}_2\text{O}_2$ ) improves the selectivity of the crosslink breakage in devulcanization of SBR-based GTR. When 450/ $\text{H}_2\text{O}_2$  is added as a compound promoting agent at the best reaction condition in subcritical water (200°C, 1.6 MPa and 1000 rpm), the tensile strength and elongation at break of the devulcanized SBR/(DGTR/EPDM) blends reach to 85.4% and 201% of vulcanized SBR (24.0 MPa, 356%), respectively. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1845–1854, 2013

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### INTRODUCTION

The process of rubber vulcanization by sulfur is essential for the manufacture of suitable tires for automobiles and aircrafts, which are indispensable to our modern society. Sulfur bridge formation between rubber molecules generated by this process affords an elastic three-dimensional network. However, the sulfur bridges cannot be naturally removed or decomposed upon disposal of the rubber waste.<sup>1</sup> Recycling of the scrap rubber poses one of the most difficult problems because of the presence of a three-dimensional crosslinked network. Most of the scrap rubber is buried in landfills, burned as fuels, used as a modifier, or devulcanized as reclaimed rubber.<sup>2</sup> Among them, the most desirable method is devulcanization. In general, the devulcanization of rubber waste is carried out through physical, chemical, or biotechnological processes. In the physical process, rubber wastes are devulcanized with the help of external energy, for example, mechanical,<sup>3,4</sup> thermomechanical,<sup>5</sup> cryomechanical,<sup>6,7</sup>

microwave,<sup>8,9</sup> or ultrasonic energies.<sup>10–20</sup> In the chemical reclaiming process, organic disulfides (such as dibenzyl disulfide, diamyl disulfide,<sup>21,22</sup> and bis(alkoxy aryl) disulfides<sup>23</sup>) and mercaptans (such as butyl mercaptan, thiophenols,<sup>24–26</sup> and xylene thiols<sup>25–27</sup>) were exclusively used as chemical reclaiming agents for the manufacture of reclaim rubber. Among them, phenol sulfide and disulfides<sup>28–33</sup> have been developed. In the biotechnological process, bacteria such as chemolithotropic microorganisms<sup>34</sup> and *Nocardia* species<sup>35–37</sup> were used for the devulcanization of scrap rubber.

During last decades, Isayev and coworkers<sup>13–20</sup> reported the devulcanization of waste tire rubber, natural rubber (NR), styrene–butadiene rubber (SBR), EPDM, and silicone rubber in a single screw extruder equipped with an ultrasound on the die. It was shown that during extrusion the high-intensity ultrasonic waves broke down the molecular chains, which 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. Recently, Zhang and coworkers<sup>38,39</sup> reported that the devulcanization process of ground tire rubber (GTR) can be performed through a high shear stress-induced reaction by increasing screw rotation speed of a twin-screw extruder. It was shown that during melt extrusion the high shear stress can effectively break up the molecular chains or three-dimensional network in the presence of polysulfide as a devulcanizing agent and thermoplastic elastomer as a swelling agent and a fluid phase of transmitting shear stress. And this way is rather convenient, efficient, and promising in the industrial application. However, during these reclaiming reactions in the above processes, the main chains were partially broken down, which led to the decreased mechanical properties of the revulcanized material. Meanwhile, the hazardous emission was also a serious problem in the experimental process.

In 1980s, the method that organic materials were oxidized in supercritical water was proposed by Modell and coworkers.<sup>40–44</sup> They investigated the oxidation of conventional and unconventional organic materials (especially toxic organic material) in a wide variety of heating and power cycles. The reaction was often preferably carried out at the near-critical density of water which means that at least the critical temperature and the critical pressure of water were achieved. This is an environmentally friendly process, which is free of hazardous emissions.

Supercritical fluids are described as “fluids in the temperature and pressure state of over the critical point,”<sup>45</sup> and fluids are termed as subcritical when they are brought between the boiling point temperature and the critical point temperature, and sufficient pressure is applied to prevent its transition to the gaseous state. Sub- and supercritical fluids such as water and alcohol are excellent reaction media and swelling solvent. The pyrolysis, liquefaction, extraction, and depolymerization of waste plastics and rubber had been reported by Goto,<sup>46</sup> Savage,<sup>47</sup> and Nishida.<sup>48</sup> Sub- and supercritical fluids showed unique physicochemical properties: low viscosity and dielectric constant, high diffusivity, and increased ion.

Nakagawa et al.<sup>49</sup> developed a smart recycling technology for the fiber reinforced plastic (FRP) using subcritical water. With this technology, thermosetting resin in FRP can be recycled at a recycling rate of 70%. Components of unsaturated polyester resin, such as glycols and fumaric acid copolymer, were separated from the aqueous reaction liquid to be reused for new unsaturated polyester preparation as raw materials. Reuse had also been made of recovered styrene–fumaric acid copolymer obtained in the aqueous phase, along with its inorganic components, for new FRP production as a low-profile additive and inorganic filler, respectively.

Goto et al.<sup>50–55</sup> reported that silane-crosslinked polyethylene used as a cable insulation material was recyclable as a thermoplastic polyethylene (PE) by treating with supercritical alcohol. The recycling process required treatment conditions of 270–320°C and 5–12 MPa for the supercritical fluid treatment. It was more efficiently achieved in an extruder rather than using conventional reactor methods, which resulted in less energy consumption than the production process for virgin PE.

**Table I.** Composition of GTR (mass%)

Volatilization	Rubber	Carbon black	Ash
5.6	46.7	37.2	10.5

Kojima et al.<sup>56–58</sup> decrosslinked a sulfur-cured natural rubber by using diphenyl disulfide in supercritical CO<sub>2</sub>. The diphenyl disulfide as the devulcanizing reagent fractionated the vulcanized rubber into a sol component having high molecular weight. The decrease in tensile strength was only around 10% at up to 40 phr of the devulcanized rubber content.

In recent years, a patent<sup>59</sup> reported that cured rubber can be devulcanized by heating it to a temperature of at least about 150°C under a pressure of at least about  $3.4 \times 10^6$  Pa in the presence of a solvent selected from the group consisting of alcohols and ketones having a critical temperature within the range of about 200°C to about 350°C. The molecular weight of the rubber can be maintained at a relatively high level if the devulcanization is carried out at a temperature of no more than about 300°C. This devulcanization technique does not significantly change the microstructure of the rubber.

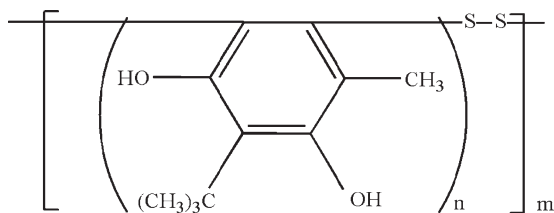
Among several subcritical fluids, water is the most advantageous for the current purpose because it is nontoxic and nonflammable. Residual water in the polymer matrix is easily and rapidly removed by releasing pressure. Water has a high critical points (374.2°C, 22.1 MPa), so much attention has been given to the subcritical water. In this study, Zhang et al. developed a continuous and environment friendly devulcanized process<sup>60</sup> that subcritical water is utilized as a devulcanization reaction medium and swelling solvent in a two-screw extruder. In a specific screw configuration, the water vapor pressure was adjusted by the rate of injecting water in order to make water in the subcritical state at a certain temperature. The combination of subcritical water, shear stress, and some devulcanizing reagent (the alkylphenol polysulfide 450, etc.) could improve the selectivity of the crosslink breakage in SBR-based GTR. In the presence of subcritical water, the effects of the temperature, pressure, screw rotation speed, or the promoting agents on the devulcanization reaction and mechanical properties of the revulcanized blends were researched. Fourier transform infrared (FT-IR) spectra of the sol of the devulcanized blend and the morphology of the fractured surface of the revulcanized blends ((DGTR/EPDM)/SBR) were also investigated.

## EXPERIMENTAL

### Materials

SBR-based GTR (particle size  $t \approx 30$  meshes) was supplied by Yangzhou Lvhuang Rubber Reclamation Co. (Yangzhou, China). The composition was examined by using the thermal gravity analysis (Netzsch STA449C/6/F) under nitrogen gas in a scanning rate of 10°C min<sup>-1</sup> and temperature range of 40–500°C and under air gas in range of 500–600°C. The results are shown in Table I.

Thermoplastic polymer, off-grade ethylene–propylene–diene monomer rubber (EPDM) 4770 (Mooney viscosity = 60



Scheme 1. Promoting agent 450 ( $n$ : 10–20;  $m$ : 20–50).

measured at 100°C), was purchased from American Dupont-Dow Co. SBR 1502 (Mooney viscosity = 61 measured at 100°C) was purchased from Shengyang Petrochemical Co. (Shengyang, China). Carbon black N330 was purchased from Wuxishi Suxin Jingxi Carbon Black Manufacture Co. (Wuxi, China). Calcium stearate, 2-mercaptobenzothiazole (Accelerant M), *N*-cyclohexylbenzothiazole-2-sulfenamide (Accelerant CBS), zinc oxide, stearic acid, sulfur, antioxidant D, and antioxidant 4010 were of industrial grade. The solvents for characterization were of reagent grade and were used without further purification.

The promoting agents of hydrogen peroxide water solution (content of 30% H<sub>2</sub>O<sub>2</sub>) and *n*-butylamine were purchased from Shanghai Lingfeng Chemical Reagent Co. China. The promoting agent of alkylphenol polysulfide 450 was purchased from Shanghai Ligao Chemical Industrial Co., China, and its structure formulation is shown in Scheme 1.

#### Devulcanization Process of GTR During Melt Extrusion

The devulcanization process was done in a corotating twin-screw extruder (TE-35, Coperion Keya Machinery Co., China). The screw diameter is 35 mm, and its length to diameter is 44; the screw configuration is shown in Figure 1. The extruder barrel has nine heating/cooling zones from hopper to die, in which the 1–3 zone's temperatures increase in order, and the 4–8 zone's temperatures were set as reaction temperature, and the die temperature was maintained 5–10°C lower than the reaction temperature. GTR (80%), EPDM (20%), and promoting agent (0.5% 450 or 3% hydrogen peroxide water solution (content of 5% H<sub>2</sub>O<sub>2</sub>) or 1.5% *n*-butylamine) were premixed. Then, the mixture was fed into the hopper of the extruder. In Figure 1, a pressure manometer and a metering pump were connected to the inlet B. In a specific screw configuration, the water vapor pressure was adjusted by the rate of injecting water to make water in the subcritical state at a certain temperature. The screw

rotation speed of the extruder was controlled between 400 and 1200 rpm, and the reaction temperature was adjusted between 180°C and 220°C, respectively. The extruded blends, which were called as the devulcanized blends (DGTR/EPDM), were cooled in water and collected.

#### Characterization of the Properties of the Devulcanized Blends (DGTR/EPDM)

The gel content ( $\omega$ ) of the devulcanized blends (DGTR/EPDM) was measured by the Soxhlet extraction method, in which the devulcanized blends were packaged with 150-mesh stainless steel cloth and extracted in boiling xylene for 24 h. The residual products were dried under vacuum and reweighed and calculated by the formulation as follows:

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

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

The Mooney viscosity of the devulcanized blends (DGTR/EPDM) was measured at 100°C by a Mooney viscometer (MZ4012B, Jiangsu Mingzhu Testing Machinery Co.) according to Chinese standard GB/T1232.1–2000.

The soluble fraction of the extracted sample was centrifuged at a speed of 3000 rpm via a centrifuge (Anke TDL-40B, China) in order to remove the carbon black. The clear solution was deposited by acetone and then dried in a vacuum oven. The dry sol was pressed into thin film at about 100°C from which infrared spectra were taken using a Nicolet 670 SXB FT-IR spectrometer.

#### Measurement of the Mechanical Properties of SBR/(DGTR/EPDM) Revulcanized Blends

In order to examine the mechanical properties of the revulcanized material, SBR and the devulcanized blends (DGTR/EPDM) were compounded on a laboratory size two roll mill according to the 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, China). The sample were cured at 160°C, and an applied pressure of 10 MPa for the respective optimum cure time ( $t = t_{90}$ ) was obtained from rheographs (MDR

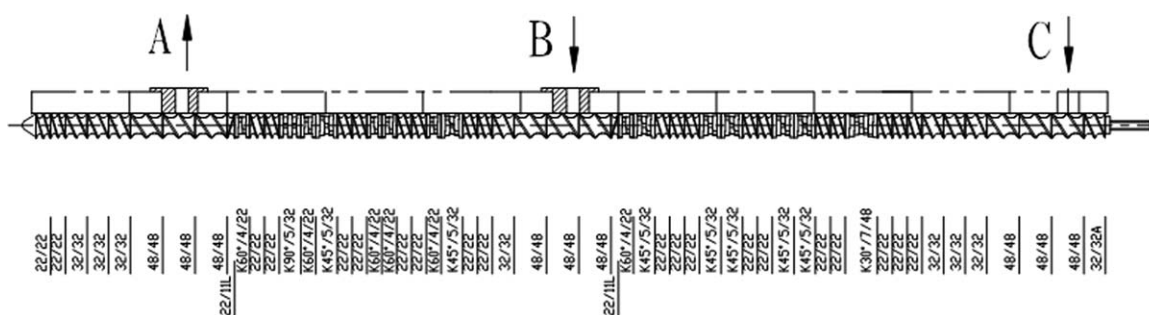
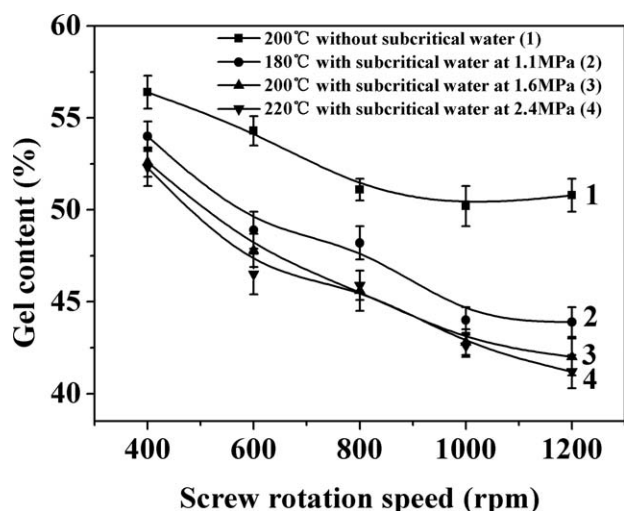


Figure 1. Screw configuration of the corotating twin-screw extruder (TE-35): A—the vent; B—the water inlet; C—feeder.



**Figure 2.** Effect of screw rotation speed on the gel content of the devulcanized blends of DGTR/EPDM in subcritical water.

2000, China). After curing, the sheet was taken out of the mold. The dumbbell shaped tensile specimens were punched out from the vulcanized sheet after 24 h of storage by a cutter. Tensile strength and elongation at break were measured following Chinese standard GB/T528–2009 in a universal testing machine (Model CMT5254, SANS Group Company, China) at  $23 \pm 2^\circ\text{C}$  and a speed of  $500 \text{ mm min}^{-1}$ .

#### Scanning Electron Microscopy (SEM) Observation

The devulcanized blends SBR/(DGTR/EDPM) (70/30) were fractured in liquid nitrogen in advance. Then the phase morphology was observed in a SEM instrument (Model JSM-5900LV, Japan).

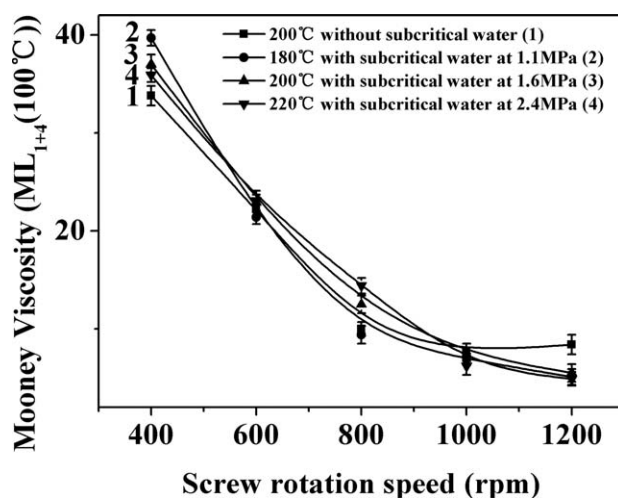
## RESULTS AND DISCUSSION

### Effect of Screw Rotation Speed on the Devulcanization Reaction in Subcritical Water

Figures 2 and 3 show that the gel content and the Mooney viscosity of the devulcanized blend (DGTR/EPDM) decreased with the increase of screw rotation speed. It was attributed to the shear stress and thermal energy which induced the crosslink breakage and/or chain scission and broke up the network of GTR. Figure 2 (curves 1 and 3) shows that the gel contents of curve 1 were higher than those of curve 3. When the temperature was  $200^\circ\text{C}$  and the pressure of water was 1.6 MPa (above saturated vapor pressure 1.58 MPa), water was at subcritical state. Under this condition, the water as a reaction media was helpful to the devulcanization. Figure 2 (curves 2–4) shows that

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

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

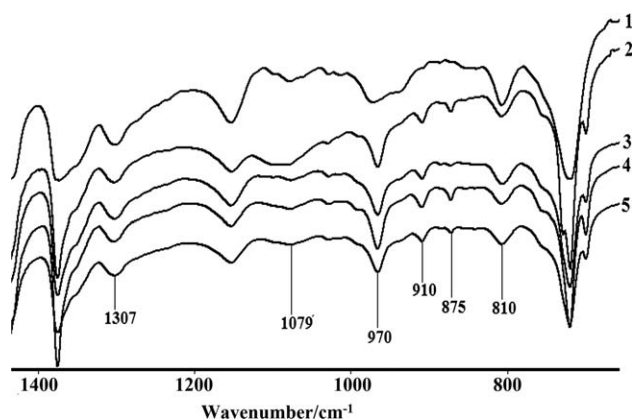


**Figure 3.** Effect of screw rotation speed on the Mooney viscosity of the devulcanized blends of DGTR/EPDM in subcritical water.

when water was at subcritical state, the higher the temperature and the pressure, the lower the gel content is, which means the amount of  $\text{H}^+$  and  $\text{OH}^-$  ions probably reacted with the intermolecular carbon–sulfur and/or sulfur–sulfur bonds increased, leading to the crosslink breakage and/or chain scission and broke up the network of GTR. So the gel content decreased significantly.

Figure 3 (curves 1–4) shows the similar Mooney viscosities at the same screw rotation speed. It means the molecular weight of main chain of the devulcanized blends is similar at same screw rotation speed. But the gel content of devulcanized blends in the presence of subcritical water (curves 2–4) was significantly lower than that of devulcanized blends without subcritical water (curve 1), which demonstrates that the solvent effect of the subcritical water significantly increases the selectivity of the crosslink breakage.

Figure 4 and Table III show that the peaks at  $1307 \text{ cm}^{-1}$  ( $>\text{CH}-$ ) and  $810 \text{ cm}^{-1}$  ( $>\text{C}=\text{CH}-$ ) were approximately identical in curves 1–5; curves 2 and 4 show some new absorption



**Figure 4.** FT-IR spectra of sol of DGTR/EPDM (1000 rpm): 1—EPDM 4770; 2— $200^\circ\text{C}$  without subcritical water; 3— $180^\circ\text{C}$  with subcritical water at 1.1 MPa; 4— $200^\circ\text{C}$  with subcritical water at 1.6 MPa; 5— $220^\circ\text{C}$  with subcritical water at 2.4 MPa.

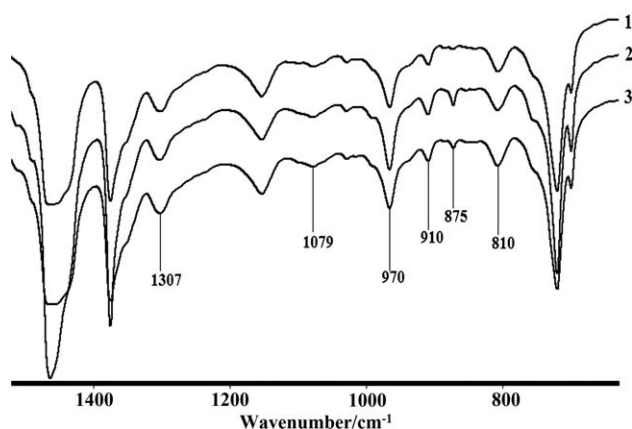
**Table III.** Area Ratio of Characteristic Peak/Reference Peak of the FT-IR Spectra (Figure 4)

Sample number <sup>a</sup>	$A_{\text{characteristic peak}}/A_{\text{reference peak}}$			
	$A_{1079}/A_{1307}$	$A_{970}/A_{1307}$	$A_{910}/A_{1307}$	$A_{875}/A_{1307}$
1	0.524	1.257		
2	0.415	1.689	0.375	0.379
3	0.284	2.041	0.576	0.122
4	0.383	2.590	0.805	0.452
5	0.356	2.191	0.622	0.206

<sup>a</sup>Sample numbers refer to Figure 4.

peaks at  $875\text{ cm}^{-1}$  ( $>\text{C}=\text{CH}_2$ ) and  $910\text{ cm}^{-1}$  ( $-\text{C}=\text{CH}_2$ ). The absorption peaks at  $875\text{ cm}^{-1}$ ,  $910\text{ cm}^{-1}$ , and  $970\text{ cm}^{-1}$  ( $-\text{CH}=\text{CH}-$  trans) were strengthened significantly, and the corresponding area ratio of characteristic peak/reference peak increased obviously. Meanwhile, the absorption peak at  $1079\text{ cm}^{-1}$  ( $\geq\text{C}-\text{O}-\text{C}-$ ) was weakened, and the corresponding area ratio of characteristic peak/reference peak decreased. This phenomenon demonstrated that subcritical water can promote the devulcanization reaction and keep the extrusion material from oxidative degradation. Curves 3–5 show that the absorption peaks at  $875\text{ cm}^{-1}$ ,  $910\text{ cm}^{-1}$ , and  $970\text{ cm}^{-1}$  ( $-\text{CH}=\text{CH}-$  trans) were strengthened firstly and then decreased, and the corresponding area ratio of characteristic peak/reference peak increased firstly and then decreased, reaching a maximum under the condition of  $200^\circ\text{C}$  with subcritical water at 1.6 MPa. It was demonstrated that subcritical water at a moderate temperature and pressure could further promote the devulcanization effectively, but it could destroy the active double bond in the chains at a higher temperature and pressure.

Figure 5 (curves 1 and 2) and Table IV show that with the increasing screw rotation speed, the absorption peaks at  $875\text{ cm}^{-1}$ ,  $910\text{ cm}^{-1}$ , and  $970\text{ cm}^{-1}$  ( $-\text{CH}=\text{CH}-$  trans) were strengthened significantly, and the corresponding area ratio of characteristic peak/reference peak increased obviously, because



**Figure 5.** FT-IR spectra of sol of DGTR/EPDM at different screw speeds ( $200^\circ\text{C}$  with subcritical water at 1.6 MPa): 1—800 rpm; 2—1000 rpm; 3—1200 rpm.

**Table IV.** Area Ratio of Characteristic Peak/Reference Peak of the FT-IR Spectra (Figure 5)

Sample number <sup>a</sup>	$A_{\text{characteristic peak}}/A_{\text{reference peak}}$			
	$A_{1079}/A_{1307}$	$A_{970}/A_{1307}$	$A_{910}/A_{1307}$	$A_{875}/A_{1307}$
1	0.347	1.578	0.346	0.125
2	0.383	2.590	0.805	0.452
3	0.626	2.255	0.599	0.472

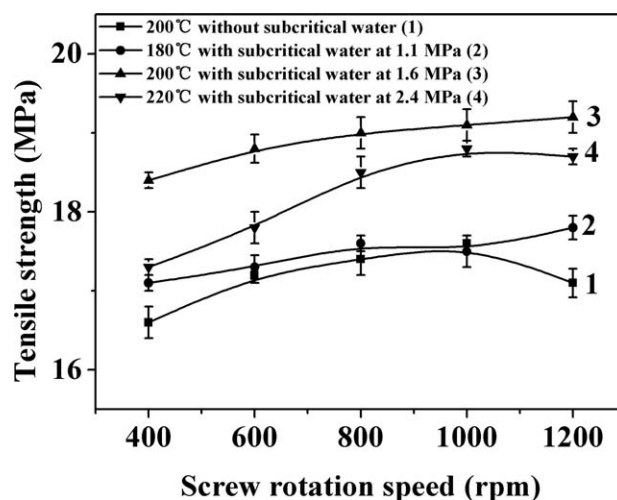
<sup>a</sup>Sample numbers refer to Figure 5.

the high shear stress induced the crosslink break and/or the chain scission of the GTR. However, curves 2 and 3 indicate that the absorption peaks at  $875\text{ cm}^{-1}$ ,  $910\text{ cm}^{-1}$ , and  $970\text{ cm}^{-1}$  ( $-\text{CH}=\text{CH}-$  trans) were weakened significantly, and the corresponding area ratio of characteristic peak/reference peak decreased obviously. This decrease could be attributed to the additive reaction of the excessive macroradicals with the double bond structure in the chains at the higher screw rotation speed, which leads to the decreased strength of the absorption peaks.

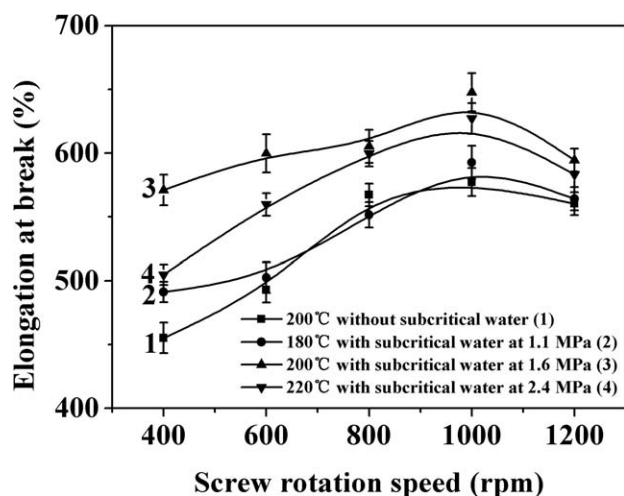
Figures 6 and 7 show that the tensile strength and elongation at break of the revulcanized SBR/(DGTR/EPDM) blends increased with the increasing screw rotation speed, and the optimum value was obtained at 1000 rpm. Curve 3 in Figures 6 and 7 was significantly higher than the others, and curve 1 was the lowest. It demonstrated that the devulcanization was much more effective in subcritical water than the devulcanization without subcritical water, and the best condition in subcritical water was 1000 rpm,  $200^\circ\text{C}$ , and 1.6 MPa.

#### Effect of Promoting Agent on the Devulcanization Reaction in Subcritical Water

Figures 8 and 9 show that in subcritical water, the gel content and Mooney viscosity of the devulcanized blends decreased with the increase of the screw rotation speed under the condition of  $200^\circ\text{C}$  with subcritical water at 1.6 MPa, because the high shear

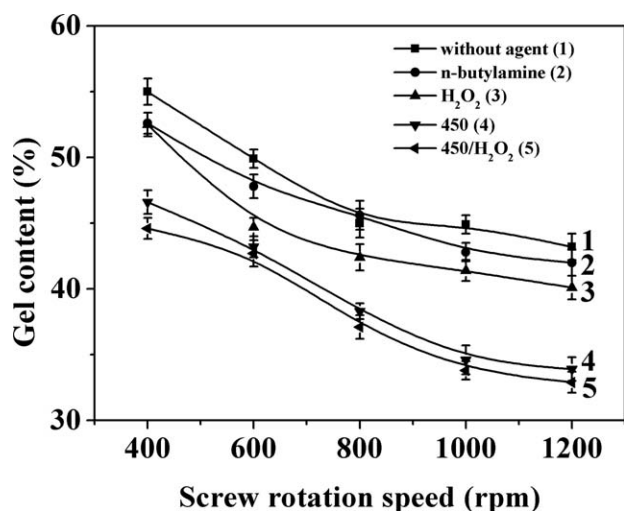


**Figure 6.** Effect of screw rotation speed on the tensile strength of revulcanized blends of SBR/(DGTR/EPDM) in subcritical water.

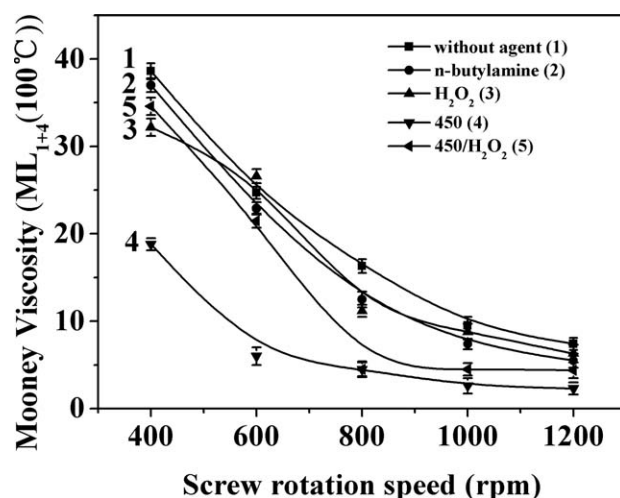


**Figure 7.** Effect of screw rotation speed on the elongation at break of revulcanized blends of SBR/(DGTR/EPDM) in subcritical water.

stress and thermal energy induced crosslink breakage and/or chain scission and broke up the network of GTR. When the reaction mixture contained a promoting agent, alkylphenol polysulfide 450, hydrogen peroxide  $H_2O_2$ , or the compound promoting agent 450/ $H_2O_2$ , the gel content of the devulcanized blend decreased significantly, especially that of the compound promoting agent, alkylphenol polysulfide 450/hydrogen peroxide  $H_2O_2$ . This phenomenon demonstrated that polysulfide 450 and/or hydrogen peroxide  $H_2O_2$  can accelerate the devulcanization reaction, especially the compound promoting agent, alkylphenol polysulfide 450/hydrogen peroxide  $H_2O_2$ . Under this condition (200°C with subcritical water at 1.6 MPa), SBR-based GTR was swollen and relaxed by the subcritical water, thus creating free space in the crosslink network to hold more promoting agent before the swelling. As a result, more promoting agent molecules could penetrate and disperse into the crosslink network with the help of subcritical water, resulting in an increase in the rate of devulcanization.



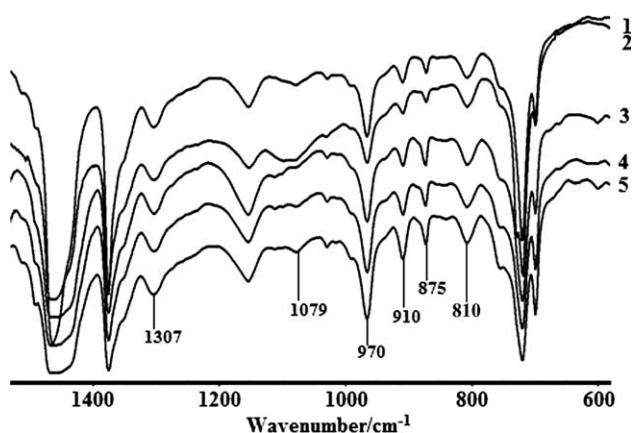
**Figure 8.** Effect of screw rotation speed on the gel content of the devulcanized blends of DGTR/EPDM in subcritical water (200°C, 1.6 MPa).



**Figure 9.** Effect of screw rotation speed on the Mooney viscosity of the devulcanized blends of DGTR/EPDM in subcritical water (200°C, 1.6 MPa).

Figures 8 and 9 show that the gel content of curve 5 was the lowest, but its Mooney viscosity was similar with that of curves 1–3. Compared with curve 4, curve 5 shows lower gel content and higher Mooney viscosity. This phenomenon demonstrated that the compound promoting agent, alkylphenol polysulfide 450/hydrogen peroxide  $H_2O_2$ , could improve the selectivity of the crosslink breakage in SBR-based GTR. There was a synergistic effect between alkylphenol polysulfide 450 and hydrogen peroxide  $H_2O_2$  on devulcanization reaction. These results suggested that the compound promoting agent 450/ $H_2O_2$  is much more effective in subcritical water.

Figure 10 and Table V show that the peaks at  $1307\text{ cm}^{-1}$  ( $>CH-$ ) and  $810\text{ cm}^{-1}$  ( $>C=CH-$ ) were approximately identical in curves 1–5; the absorption peaks at  $875\text{ cm}^{-1}$ ,  $910\text{ cm}^{-1}$ , and  $970\text{ cm}^{-1}$  ( $-CH=CH-$  trans) in curves 3–5 were strengthened significantly, and the corresponding area ratio of characteristic peak/reference peak increased obviously, especially that in curve 5. The absorption peak at  $1079\text{ cm}^{-1}$  ( $\geq C-O-C-$ ) was weakened slightly, and the corresponding area ratio of



**Figure 10.** FT-IR spectra of sol of DGTR/EPDM in the presence of different promoting agents in subcritical water (200°C, 1.6 MPa, 1000 rpm): 1—without agent; 2—*n*-butylamine; 3— $H_2O_2$ ; 4—450; 5—450/ $H_2O_2$ .

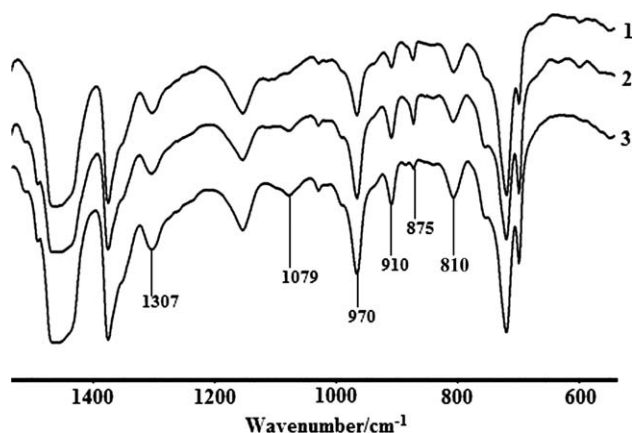
**Table V.** Area Ratio of Characteristic Peak/Reference Peak of the FT-IR Spectra (Figure 10)

Sample number <sup>a</sup>	$A_{\text{characteristic peak}}/A_{\text{reference peak}}$			
	$A_{1079}/A_{1307}$	$A_{970}/A_{1307}$	$A_{910}/A_{1307}$	$A_{875}/A_{1307}$
1	0.383	2.590	0.805	0.452
2	0.712	2.368	0.756	0.421
3	0.382	3.483	1.785	0.088
4	0.225	3.106	1.070	0.867
5	0.347	3.469	1.498	0.949

<sup>a</sup>Sample numbers refer to Figure 10.

characteristic peak/reference peak decreased a little. This phenomenon demonstrated that in subcritical water, the polysulfide 450, hydrogen peroxide  $H_2O_2$ , or the compound promoting agent 450/ $H_2O_2$  could accelerate the devulcanization reaction and prevent the crosslinking of side reaction. And the compound promoting agent 450/ $H_2O_2$  could also further keep the double content in the chains, which leads to significant increase of the double bond structure in the chains of the devulcanized blends.

Figure 11 and Table VI show that in the presence of compound promoting agents (450/ $H_2O_2$ ) in subcritical water (200°C, 1.6 MPa), the peaks at 1307  $cm^{-1}$  ( $>CH-$ ) and 810  $cm^{-1}$  ( $>C=CH-$ ) were approximately identical in curves 1–3. Compared with curve 1, the absorption peaks at 875  $cm^{-1}$ , 910  $cm^{-1}$ , and 970  $cm^{-1}$  ( $-CH=CH-$  trans) in curve 2 were strengthened significantly, and the corresponding area ratio of characteristic peak/reference peak increased obviously. This phenomenon demonstrates that with the increase of screw rotation speed, SBR content in the sol or the content of double bond structures in the chains increased, because the high shear stress induced the crosslink breakage and/or the chain scission and broke up crosslinking network of the GTR. However, compared with curve 2, the double bond area ratio of characteristic



**Figure 11.** FT-IR spectra of sol of DGTR/EPDM in the presence of 450/ $H_2O_2$  compounded promoting agents in subcritical water (200°C, 1.6 MPa): 1—800 rpm; 2—1000 rpm; 3—1200 rpm.

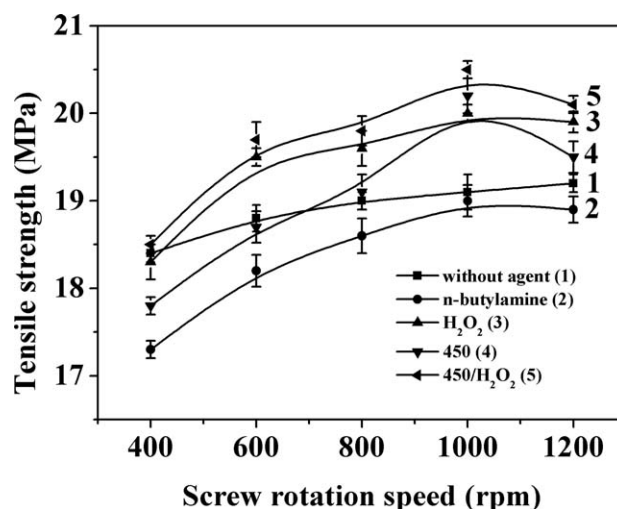
**Table VI.** Area Ratio of Characteristic Peak/Reference Peak of the FT-IR Spectra (Figure 11)

Sample number <sup>a</sup>	$A_{\text{characteristic peak}}/A_{\text{reference peak}}$			
	$A_{1079}/A_{1307}$	$A_{970}/A_{1307}$	$A_{910}/A_{1307}$	$A_{875}/A_{1307}$
1	0.189	2.335	0.782	0.679
2	0.347	3.469	1.498	0.949
3	0.435	3.029	1.163	0.190

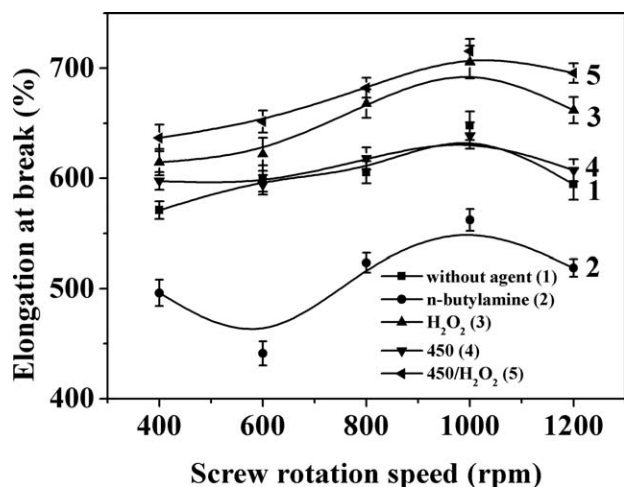
<sup>a</sup>Sample numbers refer to Figure 11.

peak/reference peak of curve 3 decreased obviously. This decrease could be attributed to the additive reaction of the excessive macroradicals with the double bond structure in the chains at the higher screw rotation speed, which led to the decrease of the absorption peak strength at this condition. The absorption peak at 1079  $cm^{-1}$  ( $\geq C-O-C-$ ) was strengthened slightly, and the corresponding area ratio of characteristic peak/reference peak increased a little, which was attributed to the oxidative reaction of rubber chain that taken place at the condition of higher shear stress.

Figures 12 and 13 show that in subcritical water (200°C and 1.6 MPa), the tensile strength and elongation at break of the revulcanized blend of (DGTR/EPDM)/SBR increased with the increase of screw rotation speed and reached to optimum values at 1000 rpm. The tensile strength and elongation at break of curve 5 (with 450/ $H_2O_2$ ) at the condition of 1000 rpm and 200°C were slightly higher than those of curves 3 ( $H_2O_2$ ) and 4 (450) and significantly higher than that of curve 1 (without promoting agent). This phenomenon demonstrated that polysulfide 450, hydrogen peroxide  $H_2O_2$ , or 450/ $H_2O_2$  could accelerate the devulcanization reaction, prevent the crosslinking reaction, and further keep the double content in the chains, especially the compound promoting agent 450/ $H_2O_2$ , which led



**Figure 12.** Effect of screw rotation speed on the tensile strength of revulcanized blends of SBR/(DGTR/EPDM) in subcritical water (200°C, 1.6 MPa).

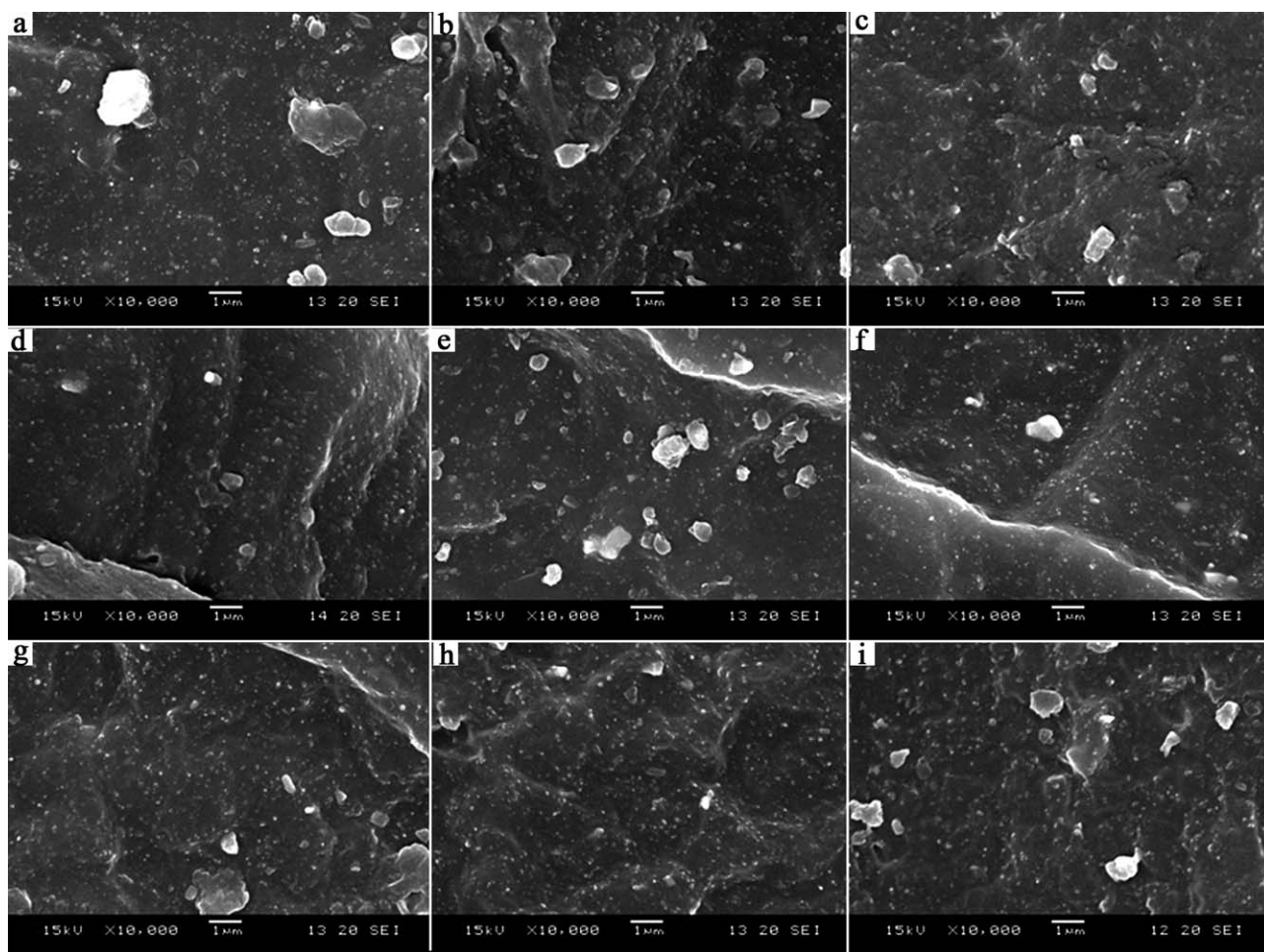


**Figure 13.** Effect of screw rotation speed on the elongation at break of revulcanized blends of SBR/(DGTR/EPDM) in subcritical water (200°C, 1.6 MPa).

to significant increase of the mechanical properties of the revulcanized blend SBR/(DGTR/EPDM). However, the tensile strength and elongation at break of curve 2 (with *n*-butylamine) at the condition of 1000 rpm and 200°C were slightly lower than those of curve 1 (without agent). This was attributed that *n*-butylamine was harmful to devulcanization reaction. When 450/H<sub>2</sub>O<sub>2</sub> was added as a compound promoting agent at the best reaction condition (200°C, 1.6 MPa, and 1000 rpm) in subcritical water, the tensile strength and elongation at break of the revulcanized blends SBR/(DGTR/EPDM) could reach to 20.5 MPa and 715.6%, respectively, which attained to 85.4% and 201% of vulcanized SBR (24.0 MPa, 356%), respectively.

#### Analysis of Fractured Surfaces of Revulcanized SBR/(DGTR/EPDM) Blend

Figure 14(a–d) shows that the size of the unfused gel particles in the revulcanized SBR/(DGTR/EPDM) blend prepared in subcritical water was obviously smaller than that without the subcritical water. The higher the temperature and the pressure, the smaller the size of the unfused gel particles was. This



**Figure 14.** SEM photographs of fractured surfaces of revulcanized SBR/(DGTR/EPDM) blends prepared under different devulcanization conditions: (a) 200°C, 1000 rpm, and without subcritical water and agent; (b) 180°C, 1.1 MPa, 1000 rpm, and without agent; (c) 200°C, 1.6 MPa, 1000 rpm, and without agent; (d) 220°C, 2.4 MPa, 1000 rpm, and without agent; (e) 200°C, 1.6 MPa, 1000 rpm, and with *n*-butylamine; (f) 200°C, 1.6 MPa, 1000 rpm, and with H<sub>2</sub>O<sub>2</sub>; (g) 200°C, 1.6 MPa, 1000 rpm, and with 450; (h) 200°C, 1.6 MPa, 1000 rpm, and with 450/H<sub>2</sub>O<sub>2</sub>; (i) 200°C, 1.6 MPa, 400 rpm, and with 450/H<sub>2</sub>O<sub>2</sub>.



phenomenon was attributed to that the subcritical water could promote the devulcanization reaction. This led to a decrease in the size of the unfused gel particles.

Figure 14(c,f,g,h) shows that the size of the unfused gel particles in the revulcanized SBR/(DGTR/EPDM) blends prepared with  $H_2O_2$ , 450, or 450/ $H_2O_2$  was smaller than those without agent, and the interface of the unfused gel particles was indistinct. The phenomenon was attributed to that  $H_2O_2$ , 450, and the compound agent 450/ $H_2O_2$  that could accelerate the devulcanization reaction and prevent the crosslinking reaction, especially the compound agent 450/ $H_2O_2$ , which led to fuse the gel particles, decreased the size of the unfused gel particles, and reinforced the interface binding strength of the revulcanized blends.

Figure 14(c,e) shows that the size of the unfused gel particles in the revulcanized SBR/(DGTR/EPDM) blends prepared with *n*-butylamine was bigger than those without the agent. This demonstrated that *n*-butylamine was harmful to devulcanization reaction.

Figure 14(h,i) shows that in the presence of compound promoting agents 450/ $H_2O_2$  and subcritical water (200°C, 1.6 MPa), with the increase of screw rotation speed, the size of the unfused gel particles in the revulcanized SBR/(DGTR/EPDM) blend significantly decreased, which means that the higher the shear stress acting on the reaction mixture, the more significantly was the breakup of the crosslinking network of the GTR. This led to a decrease of the unfused gel particle size in the revulcanized blend.

## CONCLUSION

During melt extrusion of the mixture of GTR and thermoplastic elastomer (EPDM) in the presence of subcritical water, the high shear stress coming from a twin-screw extruder induces the crosslink breakage and/or the chain scission and breaks up the crosslinking network of the GTR, leading to the decreases of the gel content and Mooney viscosity of the devulcanized blends. The subcritical water promotes the devulcanization reaction, increases the selectivity of the crosslink breakage, keeps the extrusion material from oxidative degradation, reduces the gel particle size of the devulcanized blends, and significantly improves the mechanical properties of the revulcanized SBR/(DGTR/EPDM) blends. In subcritical water, the screw speed, temperature, and pressure, respectively, exist the best value (1000 rpm, 200°C, and 1.6 MPa).

In subcritical water, the suitable promoting agents (450,  $H_2O_2$ , or 450/ $H_2O_2$ ) accelerate the devulcanization reaction and protect double bond contents, leading to further decrease of the gel content and Mooney viscosity of the devulcanized blends and further increase of the mechanical properties of the revulcanized SBR/(DGTR/EPDM) blends. Especially the compound promoting agent, alkylphenol polysulfide 450/hydrogen peroxide  $H_2O_2$ , improves the selectivity of the crosslink breakage in devulcanization of SBR-based GTR and shows a synergistic effect between alkylphenol polysulfide 450 and hydrogen peroxide  $H_2O_2$  on devulcanization reaction. When 450/ $H_2O_2$  is added as a compound promoting agent at the best reaction condition in subcritical water (200°C, 1.6 MPa and 1000 rpm), the tensile

strength and elongation at break of the revulcanized SBR/(DGTR/EPDM) blends reach to 20.5 MPa and 715.6%, respectively, which attain to 85.4% and 201% of vulcanized SBR (24.0 MPa, 356%), respectively.

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