

## Independent Investigation on the Influences of the Processing Conditions on the Reclamation of Crosslinked Isoprene Rubber After the Impregnation of a Reclaiming Reagent

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**ABSTRACT:** In this study, the reclamation of sulfur (S)-cured isoprene rubber (IR) was investigated independently after the impregnation process of the reclaiming reagent diphenyl disulfide (DD) into the crosslinked IR matrix with supercritical carbon dioxide (scCO<sub>2</sub>) as the transmission medium. According to the mass uptake of DD into IR and scanning electron microscopy–energy-dispersive X-ray spectrometry measurements, DD was highly impregnated and homogeneously dispersed in the network under 12 MPa at 80°C for 11 h in scCO<sub>2</sub>. During the impregnation process, almost no reclaiming reaction occurred. Then, through three different reclaiming methods, a mechanochemical method, a chemical method with oxygen, and a chemical method without oxygen, the influences of the shear force, reclaiming atmosphere, reaction time, and amounts of reclaiming reagent on the reclamation with crosslinked IR with pre-impregnated DD were independently investigated and compared with those of the reaction without pre-impregnated DD. The sol fraction of the reclaimed rubber and molecular weight of the sol were measured. The results show that the reclaiming speed greatly depended on the amount of reclaiming reagent and that the reclaiming reaction was dramatically accelerated when the reclaiming reagents were pre-impregnated into the crosslinked IR under the same processing conditions. This indicated that the impregnation time of the reclaiming reagent into the crosslinked network constituted a large proportion of the reclaiming time. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40298.

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### INTRODUCTION

Because vulcanized rubbers having a three-dimensional cross-linked structure cannot be reprocessed easily, the question of how to reuse waste rubbers is a great challenge in the rubber industry. In China, according to government data, about 283 million waste tires, the weight of which is more than 10 million tons, were generated in 2012. To solve this problem, many methods for recycling the waste rubber products, such as pulverization,<sup>1,2</sup> pyrolysis,<sup>3,4</sup> and reclamation,<sup>5,6</sup> have been used. From the viewpoints of energy saving and environmental protection, the reclamation of the waste is preferable to other recycling methods.<sup>7</sup> Reclamation of rubber vulcanizates is the result of the scission of crosslinking bonds introduced by vulcaniza-

tion (called *devulcanization*) combined with the main-chain scission (called *degradation*). A considerable number of reclamation methods, including mechanical,<sup>8</sup> mechanochemical,<sup>9–11</sup> ultrasonic,<sup>12</sup> microwave,<sup>13</sup> and chemical methods,<sup>14–18</sup> have been reported so far for crosslinked rubbers.

Most of the methods mentioned previously have been carried out with the aid of reclaiming reagents to speed up the reclaiming reaction. However, it is essential to introduce the reclaiming reagents into the rubber network, and this introduction is also one of the most difficult problems in reclaiming waste rubber; otherwise, the reclaiming reactions just occur on the surface of the rubber vulcanizate. Generally, organic solvents are used to swell the rubber vulcanizate and then transfer the reclaiming

reagents into the network. However, the removal of these solvents after devulcanization not only requires complex purification processes but also brings environmental problems. Recently, supercritical fluids have been reported as excellent media for swelling the polymeric matrix and transferring the low-molar-mass materials into the swollen matrix.<sup>19,20</sup> Among these supercritical fluids, supercritical carbon dioxide (scCO<sub>2</sub>) is chemically inactive, nontoxic, nonflammable, and inexpensive. Furthermore, CO<sub>2</sub> has an easily accessible critical point (the critical temperature and pressure are 31.1°C and 7.38 MPa, respectively).<sup>21</sup> The removal of this swelling solvent is very easy because CO<sub>2</sub> is gaseous at room temperature. As reported by Kojima et al.,<sup>22,23</sup> scCO<sub>2</sub> is much more effective than other supercritical fluids for the impregnation of reclaiming reagents, such as diphenyl disulfide (DD), into the rubber network. Thus, scCO<sub>2</sub> has its own advantages in playing the role of a transmission medium.

With the excellent properties of scCO<sub>2</sub>, people can effectively reclaim crosslinked rubbers with the aid of reclaiming reagents. Kojima et al.<sup>22</sup> obtained a 100% sol fraction when sulfur (S)-cured isoprene rubber (IR) was reclaimed with either DD or PhSH/*n*-BuNH<sub>2</sub> as the reclaiming agent at 180°C and 10 MPa for 60 min. In our previous study,<sup>24</sup> sulfur-cured butyl rubber was completely devulcanized with scCO<sub>2</sub> as the transmission medium and DD as the reclaiming agent at 180°C and 14.1 MPa for about 120 min. Although vulcanized rubber can be highly reclaimed by scCO<sub>2</sub>, the molecular weight of the sol fraction of reclaimed rubber is very low because of the unselective scission of crosslinking bonds and main-chain bonds. What is more, the reaction time analyzed by former researchers was actually composed of the impregnation time of the reclaiming reagents and the reclaiming reaction time. Thus, it is still impossible to determine the role of the impregnation process of reclaiming reagents on the reclamation and the exact reclaiming reaction time for obtaining a 100% sol fraction.

On the other hand, through the mechanochemical reclaiming method (MCR) and chemical reclaiming methods, the influences of the shear force, reclaiming atmosphere, temperature, time, amount of reclaiming reagent, and dumping conditions on the reclaiming results, such as the sol fraction, crosslinking density of the gel, and number-average molecular weight ( $M_n$ ) of the sol have been thoroughly studied by our team<sup>25</sup> and some others.<sup>26–28</sup> However, none of these influencing factors on the reclamation were observed separately from the impregnation process. Thus, it is impossible to clarify the effects of these influencing factors on the reclamation unless the reclaiming reagents have been dispersed in the crosslinked rubber network in advance.

In this study, to independently investigate the effects of the processing conditions on the reclaiming reaction, the reclaiming reagent DD was first transferred into the crosslinked IR network with scCO<sub>2</sub> as the transmission medium. In the impregnation step, the effects of the pressure and impregnation time on the impregnation and dispersion of DD in the network were investigated at 80°C. In the reclaiming step, the sulfur-cured IR with pre-impregnated DD was reclaimed by three different reclaiming

methods: MCR, a chemical reclaiming method with oxygen (CR-1), and a chemical reclaiming method without oxygen (CR-2). The effects of the shear force, reclaiming atmosphere, reaction time, and amount of reclaiming reagent on the sol fraction of the reclaimed samples and  $M_n$  of the sol were measured to compare with those of traditional reclaiming methods.

## EXPERIMENTAL

### Materials

The IR was provided by Qingdao Yi Ke Si New Material Co. (China). The  $M_n$  and polydispersity index (PDI) of the IR were 401,500 g/mol and 3.47, respectively. The DD was bought from Acros Organics, Inc. Other compounding ingredients, such as sulfur, dicumyl peroxide (DCP), zinc oxide (ZnO), stearic acid (SA), accelerator N-cyclohexyl-2-benzothiazole-sulfenamide (CZ/CBS), and accelerator NOBS, were bought locally. The solid carbon dioxide was obtained from Beijing Tiangang Co. (China).

### Impregnation and Dispersion Measurements

To exclude the effect of sulfur used in the sulfur-cured vulcanizate and to quantify the impregnation of DD containing sulfur into the vulcanizates, we cured the IR with 1 part per hundred parts of rubber (phr) by weight of DCP at 160°C after mixing on the two-roll mill. The optimum cure time was determined by a nonrotor rheometer. A cylinder of the crosslinked IR (diameter = 25 mm, height = 12 mm) was molded for use in the impregnation experiment. The sample was hung in a high-pressure reactor [GSH (2), inner volume = 1800 mL]<sup>24</sup> made by Weihai Hangyu Chemical Industry Co., Ltd. (China). During the impregnation experiment, the temperature was fixed at 80°C, and the pressure and soaking time were varied from 6.3 to 14.6 MPa and from 1 to 12 h, respectively. After the impregnation, the sample was taken out after a quick decompression and dried completely to a constant weight. The mass uptake of DD into the IR was calculated by eq. (1):

$$\text{Mass Uptake} = (m_2 - m_1) / m_0, \quad (1)$$

where  $m_1$  and  $m_2$  are the masses of the crosslinked IR before and after the impregnation, respectively, and  $m_0$  is the mass of DD used (1.0 g in this experiment). The diffusion coefficient of DD in the crosslinked IR under scCO<sub>2</sub> was estimated by Fick's law, as described in eq. (2):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2}, \quad (2)$$

where  $C$  is the concentration of the solute,  $t$  is the time,  $X$  is the distance, and  $D$  is the diffusion coefficient. The decrosslinking reagent DD (solute) was considered to be distributed between the crosslinked IR (rubber phase) and the solvent phase at equilibrium under the experimental impregnation conditions, and the distribution coefficient ( $K_c$ ) of the solute was defined by eq. (3):

$$K_c = \frac{C_{\text{rubber}}}{C_{\text{solvent}}}, \quad (3)$$

where  $C_{\text{rubber}}$  and  $C_{\text{solvent}}$  are the concentrations of the solute in the rubber phase and the solvent phase at equilibrium, respectively.

After we determined the impregnation of DD into crosslinked IR, the dispersion of DD in the IR matrix was investigated by

**Table I.** Curing Recipe of the IR Compounds

| Ingredient    | IR  | ZnO | SA  | S   | CZ  | NOBS |
|---------------|-----|-----|-----|-----|-----|------|
| Content (phr) | 100 | 6.0 | 2.5 | 2.5 | 0.5 | 0.5  |

means of scanning electron microscopy (SEM) in combination with an energy-dispersive X-ray spectrometry (EDX). Herein, the content of sulfur elements measured by SEM–EDX stood for the content of DD at different positions. Thus, to eliminate the disturbance of sulfur from other chemicals, the IR was cured by DCP rather than sulfur. The DCP-cured sheet ( $20 \times 2 \times 2 \text{ mm}^3$ ) and 1.0 g of DD were hung in the reactor at  $80^\circ\text{C}$  and 12 MPa, with the conditions determined by the previous impregnation experiment, and the soaking time was varied from 7 to 11 h. After the impregnation, the sample was taken out and dried to a constant weight. After a cross section of the sheet was cut in liquid nitrogen, the sulfur contents at three different positions of the cross section from the edge to the center (the edge, 0.5 mm away from the edge, and the center) were measured. By comparing the sulfur content averaged over three specimens at different positions, we determined the dispersion of DD in the IR matrix.

### Reclaiming Process

In step 1, the sulfur-cured IR (the curing recipe is shown in Table I) was cut into small pieces ( $20 \times 20 \times 2 \text{ mm}^3$ ) and then put into the reactor at  $80^\circ\text{C}$  and 12 MPa for 11 h together with different amounts of DD.

In step 2, to clarify the influences of the shear force, reclaiming atmosphere, reaction time, and amounts of reclaiming reagent on the reclamation, the crosslinked IR with pre-impregnated DD was then reclaimed by three different reclaiming methods: MCR, CR-1, and CR-2.

MCR was carried out on a two-roll mill (diameter = 160 mm) with a roller spacing of 0.5 mm. The crosslinked IR pre-impregnated with 10 wt % DD was milled to compare with the traditional conventional method, where DD was added during the shear reclaiming process. During the reclaiming process, cooling water was circulated to maintain a low reclaiming temperature ( $<40^\circ\text{C}$ ), and the effect of the shearing time (5, 10, 20, and 30 min) was observed.

CR-1 was carried out by an electrothermal drying oven ( $750 \times 600 \times 500 \text{ mm}^3$ ) with the temperature ranging from room temperature to  $300^\circ\text{C}$ . A watch glass was put into the oven, and preheated to  $165^\circ\text{C}$ . Then, the samples were put onto the watch glass for different reclaiming reaction times. After a given time, the samples were immediately put into cold water to terminate the reclaiming process. The amount of DD pre-impregnated was also 10 wt % of IR.

CR-2 was carried out by a vacuum-pressing machine. The top and bottom plates of the machine and specific mold with nine circular holes (diameter = 25 mm, height = 2 mm) for placing the samples were preheated to  $165^\circ\text{C}$ . The pressure of the hot-press chamber was immediately vacuumed to  $-0.1 \text{ MPa}$  after

about 0.90 g of the IR vulcanizates pre-impregnated with different amounts of DD into were placed the hole, corresponding to the reaction starting time. By controlling the reaction time, we obtained the reclaimed samples after cooling the mold down immediately. The amounts of pre-impregnated DD were 0, 1, 4, and 10 wt % of the crosslinked IR used.

Furthermore, the traditional reclaiming method (TCR) with  $\text{scCO}_2$  as the transmission medium was used for comparison. After some dry ice was preloaded into the reactor to expel the existing air, we added the preweighed IR, DD (10 wt %), and some more dry ice. The reactor was immediately sealed off, heated up to a prefixed temperature ( $165^\circ\text{C}$ ) at a heating rate of  $3^\circ\text{C}/\text{min}$ , maintained at this temperature and 12 MPa for different reaction times, cooled down to  $80^\circ\text{C}$ , and decompressed. The reclaimed rubber was then taken out of the reactor.

### Characterization

**Extraction in Acetone and Sol Fraction Measurement.** After reclamation, the sol and gel components of the product (with weight  $W_1$ ) were separated with the Soxhlet extraction method. First, the low-molecular-weight compounds, such as the unreacted DD and the curing agents that had not reacted with the polymer chains during the curing process, were removed by Soxhlet extraction with acetone as the solvent for 48 h, and the residue was dried to a constant weight ( $W_2$ ) *in vacuo*. Then, the sol and gel components of the residue were separated with toluene as a solvent for 72 h, and the insoluble gel fraction was dried *in vacuo* at room temperature to another constant weight ( $W_3$ ). Acetone extraction (Ac-ex) and sol fraction were calculated by eqs. (4) and (5), respectively:

$$\text{Ac-ex fraction (\%)} = (W_1 - W_2) / W_1 \times 100\% \quad (4)$$

$$\text{Sol fraction (\%)} = (W_2 - W_3) / W_2 \times 100\% \quad (5)$$

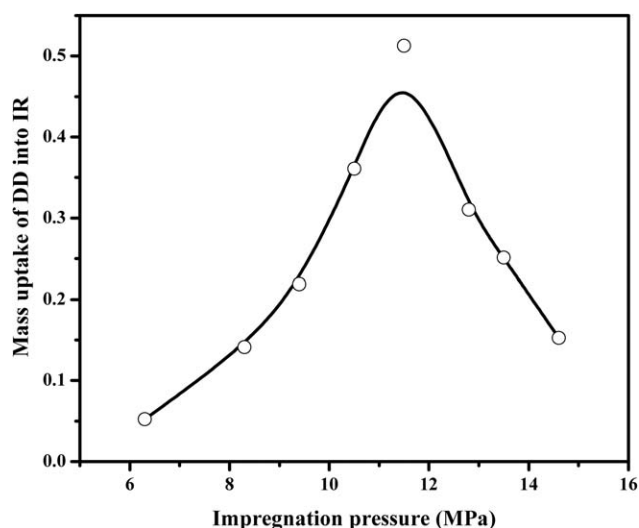
**Gel Permeation Chromatography (GPC) Measurement.** The molecular weight and molecular weight distribution of the sol component of the reclaims were determined with GPC (GPC515-2410 System, Waters Co., Ltd.). The GPC analyses were performed at a tetrahydrofuran flow rate of 1.0 mL/min at  $35^\circ\text{C}$ . Polystyrene was used as the standard.

**Crosslinking Density Measurement.** The crosslinking density of the sulfur-cured IR before and after the impregnation process was measured by the swelling technique with toluene as the solvent. Small pieces of samples were immersed in toluene for 72 h at  $30^\circ\text{C}$ . The crosslinking density was calculated with the Flory–Rehner equation<sup>29</sup> with an interaction parameter of 0.393 for toluene.

## RESULTS AND DISCUSSION

### Determination of the Impregnating Conditions

We investigated the effect of the pressure on the impregnation of DD into the IR vulcanizate at  $80^\circ\text{C}$  for 2 h by controlling the addition of dry ice, as shown in Figure 1. The mass uptake of DD was very low at pressures lower than the critical pressure of  $\text{CO}_2$  (7.38 MPa) but increased rapidly with increasing pressure at pressures higher than 8.0 MPa, reached a maximum at about 12.0 MPa, and then decreased with pressure at pressures higher than 12.0 MPa. The abrupt increase in the mass uptake of DD



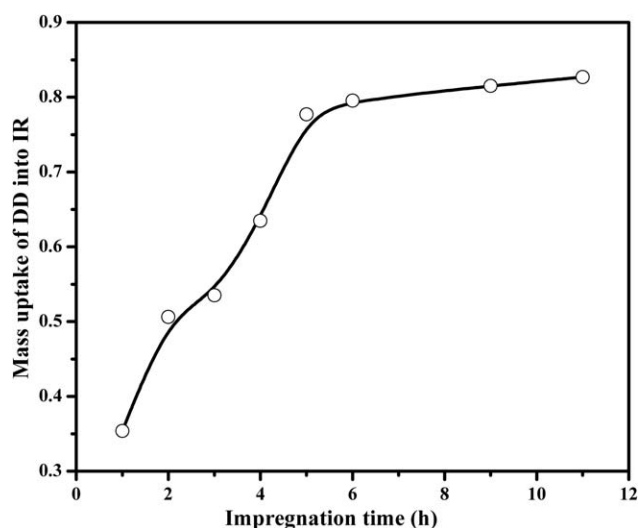
**Figure 1.** Effect of the impregnation pressure on the mass uptake of DD into IR at 80°C after 2 h of soaking in CO<sub>2</sub>.

was mainly due to the function of the scCO<sub>2</sub> in accelerating DD permeation into the rubbery matrix, and the consistently high mass uptake was due to the modest solubility of DD in scCO<sub>2</sub> and the high affinity of DD for IR. However, an unexpected decrease in the mass uptake of DD was discovered when the pressure was higher than about 12.0 MPa. The conventional view is that the solubility of scCO<sub>2</sub> increases with increasing pressure, and the increase in solubility should lead to an increase in the DD mass uptake. However, the increase in pressure reduced the free volume of the polymer matrix and impeded the impregnation of DD into the rubbery matrix. Thus, the impregnation of DD into the vulcanizate was the result of competition between the acceleration effect of scCO<sub>2</sub> and the impediment of volume reduction with increasing pressure. At pressures lower than about 12 MPa, with increasing pressure, especially pressures higher than the critical pressure, the acceleration effect of scCO<sub>2</sub> increased dramatically, whereas the effect of the pressure on the volume reduction was relatively low. Thus, the impregnation of DD into the vulcanizate increased rapidly. However, at pressures higher than about 12 MPa, the impeditive effect of the free volume reduction of the vulcanizate increased significantly, although it was still less than the accelerating effect and, thus, decreased the mass uptake of DD. We picked 12 MPa as the impregnation pressure for the next experiment to investigate the mass uptake of DD into IR with the impregnation time.

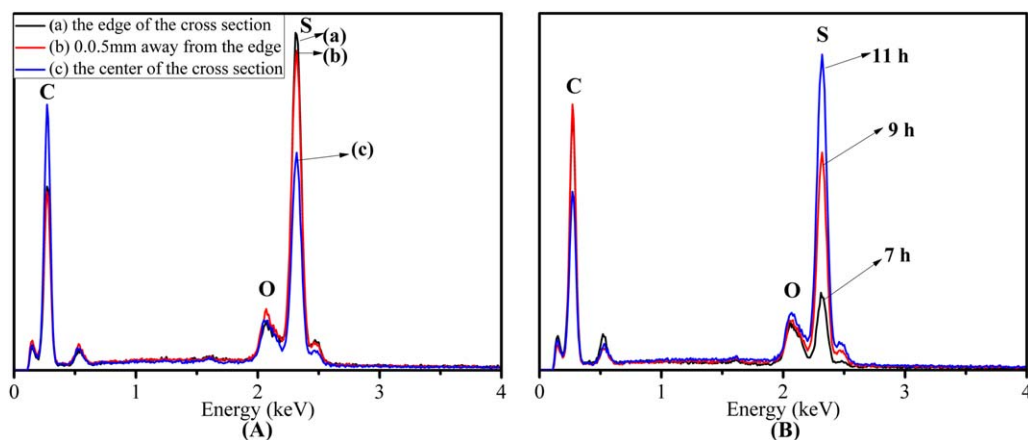
The effect of the impregnation time on the mass uptake of DD into the IR vulcanizate at 80°C and 12 MPa in scCO<sub>2</sub> is shown in Figure 2. With increasing impregnation time, the mass uptake of DD increased and reached equilibrium at about 7 h. Thereafter, the mass uptake of DD remained constant at about 0.84. The high-mass DD transferring into the IR matrix indicated that the affinity of DD for IR was much higher than that for scCO<sub>2</sub>. The diffusion coefficient of DD in the IR vulcanizate under scCO<sub>2</sub> was estimated to be  $7.1 \times 10^{-11} \text{ m}^2/\text{s}$  with eq. (2); this value was similar to the value of  $3.2 \times 10^{-11} \text{ m}^2/\text{s}$  at 40°C and 10 MPa obtained by Kojima et al.<sup>23</sup>

Furthermore,  $K_c$  of DD in the IR matrix under scCO<sub>2</sub> was calculated with eq. (3). The degree of swelling of the crosslinked IR was 1.15, as measured by Kojima et al.,<sup>23</sup> and the volume of the IR vulcanizate was just about 0.327% that of the reactor (1800 mL). As a result, the equilibrium  $K_c$  value was calculated to be 4184 for scCO<sub>2</sub> at 80°C and 12 MPa. This value was about four times as high as that obtained by Kojima et al.<sup>23</sup> It is possible that the different experimental conditions, such as the higher temperature and pressure and the much larger volume of the reactor used in this study, resulted in the different value. Our calculated value further strengthened the view that it was the modest solubility of DD in scCO<sub>2</sub> and the high affinity of DD for IR that resulted in the high mass uptake of DD in the IR network.

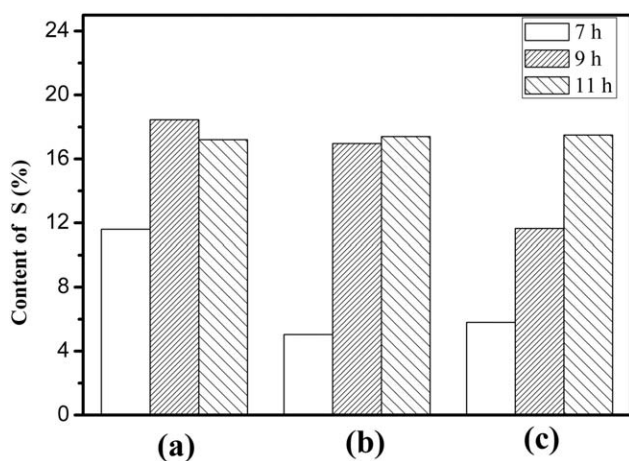
Because the reclaiming reagent DD could highly impregnate the IR vulcanizate under scCO<sub>2</sub>, the dispersion of DD in IR is also very important for the next reclaiming step. The quantitative analysis of the dispersion of DD in the IR matrix was investigated by SEM–EDX, and the sulfur content determined by SEM–EDX stood for the mass of DD. The EDX spectra of different positions impregnated for 9 h and of the center for different impregnation times are shown in Figure 3(A,B), respectively. The EDX analysis of the constituent elements showed that the elements were carbon, oxygen, and sulfur. Then, the content of sulfur was calculated through the proportion of its peak area, and the results are depicted in Figure 4. We can clearly see from Figure 4 that the content of sulfur increased with increasing impregnation time from 7 to 9 h and remained almost constant after 9 h; this indicated the osmotic equilibrium of DD. Furthermore, the content of sulfur gradually decreased from the edge to the center of the IR at 7 and 9 h but remained consistent at 11 h. This phenomenon suggested that the dispersion of DD in the IR matrix was related to the impregnation time, and the DD could disperse in the IR matrix homogeneously after it reached osmotic equilibrium at about 11 h in this study. Thus, DD could highly impregnate and be homogeneously dispersed in the IR network with scCO<sub>2</sub> at



**Figure 2.** Effect of the impregnation time on the mass uptake of DD into IR at 80°C and 12 MPa in scCO<sub>2</sub>.



**Figure 3.** EDX spectra for (A) different positions of the cross section of the DCP-cured IR vulcanizate impregnated with DD for 9 h and (B) center of the cross section of the DCP-cured IR vulcanizate at different impregnation times. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4.** Dispersion of DD in the IR vulcanizate from (a) the edge to (c) the center of the cross section at 80°C and 12 MPa for different soaking times.

80°C and 12 MPa for more than 11 h, and these conditions were adopted in the impregnation step of our reclaiming method.

#### Characterization of the Structure of the IR Vulcanizate Before and After Impregnation

In the impregnation step, a certain amount of DD was used to impregnate the sulfur-cured IR under  $\text{sCO}_2$  at 80°C and 12.0 MPa for 11 h according to the results previous. After the impregnation process, it was of great importance to determine whether the reclaiming reactions actually occurred or not. Thus, the crosslinking density and sol fraction of the IR vulcanizates

before and after impregnation were measured, and the results are shown in Table II for the case in which 3 g of DD and 30 g of IR were used. The measurements of the crosslinking density and sol fraction of the IR vulcanizates before and after impregnation showed no change within the experimental errors; this indicated that almost no reclaiming reaction occurred during the impregnation step. Furthermore, the Ac-ex method was used to calculate the amount of unreacted DD, which was the difference value between the amount of the Ac-ex before and after the impregnation. The amount of DD calculated from the experimental data shown in Table II was 2.43 g. This value was close to the total osmotic amount of DD (2.46 g) from eq. (4). This result further confirmed that almost no reclaiming reaction occurred during the impregnation step.

#### Reclaiming Process

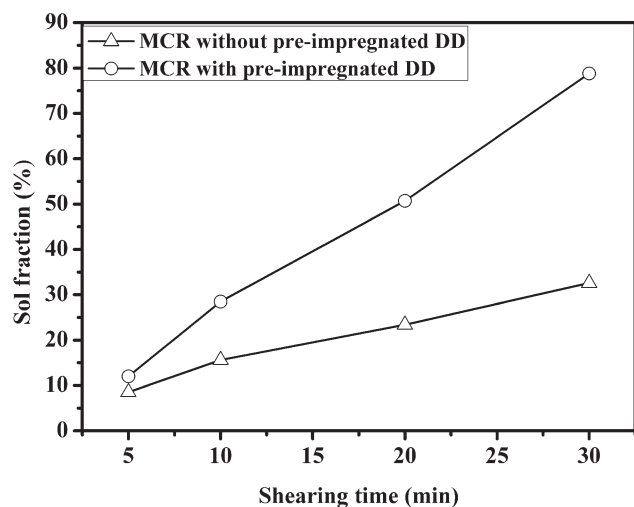
To investigate the influences of the shear force, reclaiming atmosphere, reaction time, and amounts of reclaiming reagent on the reclamation. MCR and the chemical reclaiming methods were used to reclaim the obtained sulfur-cured IR with homogeneously dispersed and unreacted DD.

#### MCR

MCR was used to determine the effect of the shear force and shearing time on the reclamation. The reclaiming results for the IR vulcanizates with and without pre-impregnated DD are shown in Figure 5 and Table III. We can clearly see from Figure 5 that the sol fraction of the reclaimed rubber increased with increasing shearing time, and the sol fraction the reclaimed rubber obtained from the IR vulcanizate pre-impregnated by DD was much higher than that obtained from the IR vulcanizate not impregnated by DD under the same reclaiming conditions.

**Table II.** Structure Characterizations of the IR Vulcanizate Before and After Impregnation Under  $\text{sCO}_2$  at 80°C and 12.0 MPa for 11 h

|                     | Mass uptake of DD (g) | Ac-ex fraction (%) | Sol fraction (%) | Crosslink density ( $\times 10^{-4}$ mol/cm <sup>3</sup> ) |
|---------------------|-----------------------|--------------------|------------------|--|
| Before impregnation | —                     | 5.51               | 0                | 2.49   |
| After impregnation  | 2.46                  | 12.20              | 0                | 2.20   |

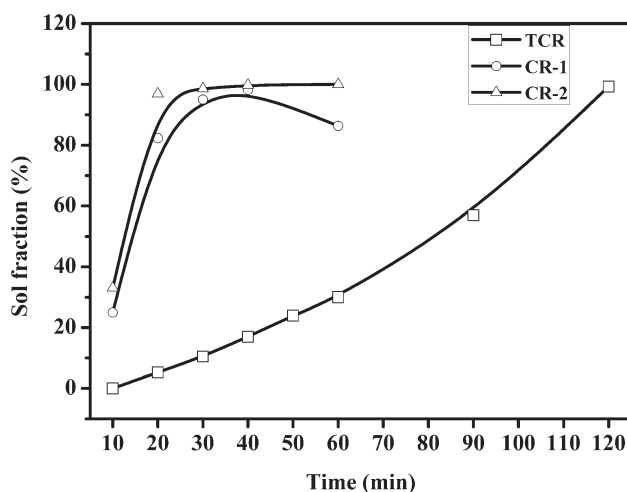


**Figure 5.** Effect of the shearing time on the sol fraction of IR with and without pre-impregnated DD by MCR.

As the milling of the vulcanizates progressed, IR with pre-impregnated DD became much stickier than that without pre-impregnated DD at the same shearing time. After 30 min, the IR with pre-impregnated DD was too sticky to be operated for a longer time, and we obtained a reclaimed rubber with a sol fraction of 78.8%. During milling, the vulcanized rubber samples underwent tremendous mechanical shearing, and this resulted in random scission of the crosslinking bonds and main-chain bonds. The DD also broke into radicals as the temperature rose because of mechanical shearing.<sup>30</sup> These DD molecular radicals combined with the radicals from the broken polymer chains, and this prevented the recombination of polymer radicals and, thereby, formed the sol fraction. For the impregnated sample, the free radicals generated by DD were homogeneously dispersed in the network, and they quickly combined with the broken polymer chain radicals from the edge to the center of the vulcanizates. On the contrary, DD could not get inside the crosslinking network of the unimpregnated sample simply by the shear-squeeze effect and mostly gathered at the surface of the vulcanizates. Thus, the polymer radicals could not effectively combine with the DD free radicals throughout the network, and this resulted in a lower sol fraction of the reclaimed IR than that obtained from the impregnated sample at the same shearing time. Furthermore, Table III shows that the  $M_n$  of the sol dropped significantly below that of the raw IR; this indicated an excessive main-chain degradation

**Table III.** Comparison of the Reclaiming Results Obtained by MCR

| Shearing time (min) | MCR without pre-impregnated DD |      | MCR with pre-impregnated DD |      |
|---------------------|--------------------------------|------|-----------------------------|------|
|                     | $M_n$                          | PDI  | $M_n$                       | PDI  |
| 10                  | 18,430                         | 1.88 | 22,750                      | 1.77 |
| 20                  | 16,853                         | 2.18 | 19,454                      | 2.37 |
| 30                  | 11,941                         | 2.54 | 14,714                      | 2.58 |



**Figure 6.** Sol fraction of the reclaimed rubber as a function of the reaction time for CR-1, CR-2, and TCR.

caused by the strong mechanical shear force. However, the  $M_n$  of the sol from the unimpregnated sample was a little lower than that of the sol from the impregnated sample because the unimpregnated sample had a higher concentration of DD at the surface. This led to more severe main-chain degradation. Thus, the IR vulcanizates with pre-impregnated reclaiming reagents underwent a much faster and more homogeneous reclaiming reaction than those without pre-impregnated reclaiming reagents under the condition of shear force.

#### Chemical Reclaiming (CR) Methods

The sol fractions of the reclaimed rubber from CR-1, CR-2, and TCR are depicted in Figure 6 as a function of the reaction time. We can clearly see that the sol fractions of CR-1 and CR-2 were much higher than that of TR at the same reaction time and that CR-1 and CR-2 reached complete reclamation in just 40 min, whereas TR took more than 120 min to reach complete reclamation. This result implies that the reclaiming reaction rate of the IR vulcanizates with pre-impregnated DD was much higher than that of the IR vulcanizates without pre-impregnated DD.

It is suspected that the formation of the sol fraction was the result of the combination of the DD molecular radicals and polymer molecular radicals<sup>7</sup> or the hydrogen abstraction of DD radicals from IR to form benzene thiol and IR vulcanizate radicals; this led to the main-chain scission and/or crosslinking scission.<sup>31</sup> During the reclaiming process of the TCR, although the efficiency of  $\text{scCO}_2$  for transferring DD was very high at 160°C, DD could not penetrate into and be dispersed in the three-dimensional network at the same time but did so gradually over a period of time. Therefore, the reclamation of the vulcanizates by TCR was a process in which the reclamation took place from the outer sides to the inner sides of the vulcanizates with the impregnation process of DD from the outside to the inside. On the contrary, for the vulcanizates with pre-impregnated DD, the DD radicals homogeneously dispersed in the network could directly combine with the polymer radicals because the impregnation of DD was accomplished in the first impregnation step

**Table IV.** Comparison of the Molecular Weights and Molecular Weight Distributions of the Sol Components Obtained by CR-1, CR-2, and TCR

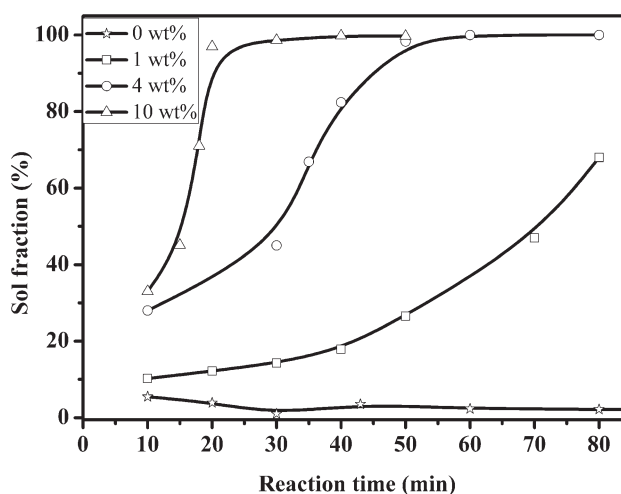
| Reaction time (min) | CR-1   |      | CR-2   |      | TCR    |      |
|---------------------|--------|------|--------|------|--------|------|
|                     | $M_n$  | PDI  | $M_n$  | PDI  | $M_n$  | PDI  |
| 10                  | 28,435 | 3.20 | 22,440 | 1.88 | —      | —    |
| 20                  | 27,536 | 4.09 | 20,750 | 2.57 | 20,434 | 3.02 |
| 30                  | 22,724 | 3.75 | 19,243 | 2.87 | 17,540 | 3.19 |
| 40                  | 21,832 | 4.82 | 17,329 | 2.65 | 15,689 | 4.15 |
| 60                  | 23,287 | 5.04 | 17,899 | 2.74 | 15,580 | 3.69 |

at 80°C; this resulted in a rapid increase in the formation of the sol fraction. Through the comparison of the reclaiming mechanism and the reclaiming results between TCR and CR-1/CR-2, we believe that the impregnation time of the reclaiming reagents into the crosslinked network constituted a large proportion of the reclaiming time in the traditional reclaiming method. Thus, it was crucial to accelerate the impregnation speed of the reclaiming reagents into the network to achieve effective and rapid reclamation.

Additionally, CR-1 led to a slightly higher sol fraction than CR-2 under the same conditions, as shown in Figure 6. In other words, the exclusion of oxygen increased the rate of reclamation. The presence of oxygen had a two-sided effect during reclamation: the oxygen radicals increased the reclaiming rate through combination with the polymer chain radicals, but they also triggered some complex chemical transformations, such as the formation of new intramolecular and intermolecular bonds, and this resulted in a decrease in the rubber sol fraction. As the curve in Figure 6 shows, the sol fraction of the reclaimed rubber obtained by CR-2 increased with the reaction time and remained consistent after 20 min with a 100% sol fraction, whereas that obtained by CR-1 first increased, reached a 100% sol fraction at 40 min, and then decreased with increasing reaction time. Thus, CR-2 led to the suppression of the generation of reactive radicals, followed by the reduction of complex chemical transformations, and further enhanced the importance of the oxygen-free atmosphere in the reclaiming process.<sup>32</sup>

Because a high molecular weight of the sol is essential for the high quality of the reclaimed rubber, the  $M_n$  and PDI values of the sol components obtained by CR-1, CR-2, and TCR were measured, and the results are shown in Table IV. The molecular weight of the sol component decreased sharply below that of the raw IR; this indicated that significant main-chain scission occurred during the reclamation along with crosslinking scission. In addition, a higher sol fraction combined with a longer reaction time usually led to a lower  $M_n$  and a higher PDI; these were indications that more severe main-chain scission occurred during the process of gaining higher sol contents.

As discussed previously, 10 wt % DD highly impregnated and was homogeneously dispersed in the network, and then, the rate of reclamation was greatly promoted. On the other hand, the effect of the amount of DD impregnated into the matrix

**Figure 7.** Sol fraction as a function of the reaction time for the reclaimed rubber obtained by CR-2 with different amounts of impregnated DD.

on the rate of reclamation was also worthy of investigation. Figure 7 shows the sol fractions obtained by the impregnation of different amounts of DD (0, 1, 4, and 10 wt %) as a function of the reaction time. The slope of the curve reflects the rate of the reclamation, and it is obvious that the greater the amount of DD was impregnated, the higher the rate of reclamation was. If no reclaiming reagents (0 wt % DD) were impregnated into the network, almost no sol fraction was produced over the reaction time at 165°C and with an oxygen-free atmosphere. This indicated that the use of the reclaiming reagent was essential for the chemical reclamation of the vulcanizates. As discussed previously, the combination of DD molecular radicals and polymer radicals was the main reason for the formation of the sol fraction. Furthermore, excess amounts of DD may have led to main-chain scission, which was also responsible for the fast generation of the sol fraction.<sup>16,24</sup> Thus, the greater the amount of DD was dispersed in the network, the higher was the chance of DD molecular radicals combining with polymer molecular radicals; this resulted in the acceleration of reclamation and a higher sol fraction of the reclaimed rubber.

## CONCLUSIONS

The sulfur-cured IR was reclaimed after the impregnation process of the reclaiming reagents (DD) into the crosslinked IR matrix with  $\text{scCO}_2$  as the transmission medium. DD highly impregnated the rubber and was homogeneously dispersed in the network under 12 MPa at 80°C for 11 h, and almost no reclaiming reaction occurred after the impregnation process. Then, through MCR and the chemical reclaiming methods, the influences of the shear force, reclaiming atmosphere, reaction time, and amounts of reclaiming reagent on the reclamation with crosslinked IR with pre-impregnated DD were independently investigated and compared with that without pre-impregnated DD. As a result, the IR vulcanizates with the pre-impregnated reclaiming reagents underwent a much faster and more homogeneous reclaiming reaction than those without pre-impregnated reclaiming reagents under the same processing conditions; this indicated that the impregnation time of the

reclaiming reagents into the crosslinked network constituted a large proportion of the reclaiming time in TCR. The reclaiming speed greatly depended on the amount of reclaiming reagent, and the accurate reclaiming reaction times for completely reclaiming the crosslinked IR pre-impregnated with 10 wt % DD were just 20 min under an oxygen-free atmosphere and 40 min under air at 165°C.

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