Journal of Applied Polymer SCIENCE

Complete Devulcanization of Sulfur-Cured Butyl Rubber by Using Supercritical Carbon Dioxide

Kuan Jiang, Jinwei Shi, Youyong Ge, Rui Zou, Pengjun Yao, Xiaolin Li, Liqun Zhang

Key Laboratory of Beijing City for Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, China
Correspondence to: L. Zhang (E-mail: zhanglq@mail.buct.edu.cn)

ABSTRACT: Sulfur-cured butyl rubber was devulcanized completely in supercritical CO_2 by using diphenyl disulfide (DD) as a devulcanizing reagent. The optimum devulcanizing conditions were studied and the sol fraction of the reclaimed rubber obtained was up to 98.5%. The possible devulcanizing mechanism was investigated. Then, the sol component of reclaimed rubber was characterized by gel permeation chromatography, ^{1}H-NMR, and differential scanning calorimetry, and the reclaimed rubber was characterized by TGA. Because of the substitution of a large portion of allylic hydrogen by sulfurated functional groups during vulcanization, the signal of the olefinic proton shift. As a result of the numerous decreases in the active crosslinking sites and the remaining DD, reclaimed rubber could not be cured by sulfur. At last, the blends of virgin butyl rubber and different contents of reclaimed rubber were revulcanized and their mechanical properties investigated. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Waste rubber cannot be recycled easily because of the presence of a three-dimensional crosslinked structure. Recycling of waste rubber not only solves the waste disposal problem and maintains environmental quality, but also saves the valuable and limited resource of fossil feedstock. Reclaiming of waste rubber is, therefore, the most desirable approach to solve the disposal problem. Reclaiming of waste rubber products is the conversion of a three dimensionally interlinked, and infusible thermoset polymer to a two-dimensional, plastic, low-modulus, processable, and vulcanizable thermoplastic product having many of the properties of virgin rubber.[1] Considerable attention has been given to the reclaiming of waste rubber by physical and chemical means. Mechanical,[2–4] thermo-mechanical,[5] cryo-mechanical,[6] microwave,[7] ultrasound,[8,9] and many other physical reclaiming methods have been reported so far to reclaim waste rubber. Chemical reclaiming methods, such as organic disulfides,[10] mercaptans,[11] and alkali metals[12] have been investigated. In a recent review, Warner [13] summarized in detail the action of various chemical probes on vulcanized rubber. Nevertheless, none of the above physical and chemical reclaiming methods could reclaim waste rubber effectively. For a reclaimed product to have good quality, the sol fraction and its molecular weight should be as high as possible, and the Mooney viscosity of the reclaimed rubber should be adequate for easy processability.

Recently, many studies had been reported for the decomposition of waste plastics and rubbers by using supercritical fluids.[14,15] The objectives of these studies were to break the waste plastics and rubbers into low-molecular-weight compounds using as fuel. However, there were few reports about the reclamation of waste rubber by using supercritical fluids. In this work, we designed a green process that reclaims waste rubber using supercritical CO_2 as the devulcanization reaction media. Supercritical CO_2 fluid is chemically inactive, nontoxic, nonflammable, and inexpensive. Furthermore, CO_2 has an easily accessible critical point (the critical temperature and pressure are 31.1°C and 7.38 MPa, respectively).[16] The removal of this swelling solvent is very easy because CO_2 is gaseous at room temperature. Supercritical CO_2 as a solvent is similar to typical hydrocarbon solvents such as toluene. Kojima et al.[17,18] reported that the rubber matrix could be swollen and the low-molar mass molecules could penetrate and disperse into it with the help of supercritical CO_2. Therefore, it is expected that supercritical CO_2 can be used for swelling rubber vulcanizates involving both natural rubber (NR) and synthetic rubbers. Recently, Kojima et al.[19,20] reported that unfilled NR and polyisoprene rubber (IR) could be effectively

devulcanized in supercritical CO_2. The sol content was higher compared with other methods. Recently, Tzoganakis[21] introduced a new method to recycle waste rubber. He reported that waste rubber could be devulcanized inside an extruder by using CO_2.

Butyl rubbers are copolymers of isobutylene with isoprene, with diene included to give the rubber some reactivity during crosslinking. Generally, butyl rubber contains less than 3% diene. Because of its low unsaturation and chain linearity, and the presence of the quaternary carbon atoms substituted by the methyl groups, butyl rubber has low gas permeability, and high thermal and antioxidant stability and chemical resistance. As a consequence, butyl rubber is useful for a wide range of applications.[22] In recent years, with decrease in the oil resources and increase in the demand of butyl rubber, the price of virgin butyl rubber increased markedly. Thus, the reclaiming of waste butyl rubber is a very meaningful undertaking.

In this work, unfilled sulfur-cured butyl rubber was devulcanized in supercritical carbon dioxide by using diphenyl disulfide (DD) as the devulcanizing reagent. The effect of reaction time, temperature, pressure, and amount of DD used were studied. A possible devulcanizing reaction was proposed based on the results obtained. The sol components of the reclaimed butyl rubber were characterized by gel permeation chromatography (GPC), ^{1}H-NMR, and differential scanning calorimetry (DSC), and the reclaimed butyl rubber was characterized by thermal gravimetric analysis (TGA). Then, the blends of virgin butyl rubber with different amounts of reclaimed butyl rubber were cured using sulfur as the curing agent and their mechanical properties investigated.

EXPERIMENTAL

Materials
Butyl rubber (Polysar 301) was purchased from Bayer, Germany. The unsaturation was 1.6%. Sulfur (S) was obtained from Biaosheng Chemical, China. Stearic acid (SA) was obtained from Yanfan Chemical, China. Zinc oxide (ZnO) was obtained from Longchang Chemical, China. Tetramethylthiuram disulfide (TMTD) was purchased from Huangyan Chemical, China. The devulcanizing reagent DD (melting point 58–60°C) was purchased from Acros Organic, New Jersey, USA. Solid carbon dioxide was obtained from Beijing Tiangang, China.

High-Pressure Reactor
The high-pressure reactor (GSH (2), inner volume 1800 mL) was obtained from Weihai Hangyu Chemical Industry, China. The reactor's design pressure and working pressure were 25 MPa and 20 MPa, respectively, and the working temperature was 300°C.

Preparation of Vulcanizates
To keep the analysis simple, we used a simple formulation. The formulation (including rubber and curatives, but excluding fillers or antioxidants) is shown in Table I.

The compound (Sample A) was prepared by mixing butyl rubber with curatives in a Banbury mixer in accordance with the composition shown in Table I. The Mooney viscosity (ML_{1+4}, 100°C) of the compound was measured. Then the compound was cured at 160°C and 15 MPa for T_{90} (the optimum curing

time), which was measured by an Oscillating Disk Rheometer (Beijing Huanfeng Chemical Industry, China). The cured butyl rubber was trimmed into quadrate sheets (20 mm × 20 mm × 2 mm). The sheets were subjected to the devulcanization reaction described below.

Devulcanization Reaction
The devulcanization reaction was carried out in a high-pressure reactor. At first, 100 g of solid carbon dioxide was put into the high-pressure reactor to replace as much air as possible. Then 50 g of butyl rubber vulcanizate and prefixed weights (from 0 to 5 g) of DD and solid carbon dioxide were added. The reactor was immediately sealed off, heated up to a prefixed temperature (from 140°C to 190°C) at a heating rate of 3 °C/min, and maintained at this temperature for a definite soaking time (from 0 to 240 min). After that, the reactor was cooled down to room temperature, and CO_2 was discharged from the reactor. The product containing sol and gel components was taken out of the reactor.

Separation of Sol and Gel Components
After the devulcanization, the product (weight W_1) containing sol and gel components was separated by using the Soxhlet extraction method with cyclohexane as the solvent for 96 h. The cyclohexane solution containing the sol component and the insoluble product containing the gel component were dried *in vacuo* at room temperature to constant weight, and the weight of the sol component was designated as W_2. The sol fraction was calculated by eq. (1):

$$\text{Sol fraction} = (W_2/W_1) \times 100\% \qquad (1)$$

Revulcanization
Prior to revulcanization, the reclaimed butyl rubber with curatives were homogenized and compounded by using a two-roll mill. The revulcanization procedure was the same as that of the vulcanization given above. The compounds using sulfur as the curative were cured at 160°C.

Characterization
The Mooney viscosity of the uncured compound and the reclaimed butyl rubber was measured by a Mooney viscometer (M3810C, Beijing Huanfeng Chemical Industry, China). The molecular weights of virgin butyl rubber, uncured compound, and the sol component were determined with GPC (GPC515-2410 System, Waters, USA). GPC analyses were performed using tetrahydrofuran (THF) at a flow rate of 1.0 mL/min at 35°C. Polystyrene was used as the standard. The ^{1}H-NMR spectroscopy was carried out with a Bruker AV600 spectrometer (Germany) at 23°C. Deuterated chloroform (CDCl$_3$) was used as the solvent for the NMR measurements. The DSC thermograms were recorded in the temperature range −80°C to 100°C on a differential scanning calorimeter (Mettler-Toledo, Switzerland) at a heating or cooling rate of 10 °C/min under a nitrogen atmosphere. The glass-transition temperature (T_g) was taken as the temperature at the midpoint of the heat capacity change. Thermogravimetric analysis was performed with a TGA analyzer (Mettler-Toledo, Switzerland) at a heating rate of 10 °C/min under a nitrogen atmosphere. The tensile and tear tests were

Table I. Formulation of Butyl Rubber Compound (phr)

Sample	Butyl rubber	Reclaimed butyl rubber	ZnO	SA	S	TMTD	DD
A	100	–	3	1	1.75	1	–
B	100	–	–	–	–	–	2
C	100	–	3	1	1.75	–	2
D	100	–	3	1	1.75	1	2
E	100	–	3	1	1.75	1	8
F	–	100	3	1	1.75	1	–
G	–	100	3	1	1.75	1	–
H	70	30	3	1	1.75	1	–
I	50	50	3	1	1.75	1	–

The values are in parts per hundred rubber in weight (phr).
G: The reclaimed butyl rubber was extracted for 96 h by using acetone as the solvent.

carried out using a CTM4104 testing machine (Shenzhen SANS Testing Machine, China) according to ISO 37-1994. The hardness of the revulcanized samples was measured with a Shore A type hardness meter.

RESULTS AND DISCUSSION

Optimum Conditions for Devulcanization

Effect of Reaction Pressure on Devulcanization. The effect of reaction pressure on devulcanization was investigated by using 4 g of DD and 50 g of vulcanized butyl rubber for a reaction time of 120 min at 180°C. The pressure in the reactor was controlled by the amount of solid carbon dioxide put into the reactor. The results are shown in Figure 1.

As seen from Figure 1, with the reaction pressure increasing, the sol fraction in the reclaimed butyl rubber increases, especially around and over the critical point (7.38 MPa). The sol fraction reaches the steady-state value at 11.5 MPa. The critical pressure of carbon dioxide is 7.38 MPa. When the pressure of carbon dioxide was lower than 7.38 MPa, the carbon dioxide in the reactor was just compressed gas, which was unable to swell the vulcanizate, and DD could not penetrate into the vulcanizate and disperse in the crosslink sites. Under this condition, the sol component obtained was mainly due to the thermal degradation of butyl rubber and the devulcanization that took place on the surface of vulcanizate in the presence of DD. However, when the pressure of carbon dioxide was higher than 7.38 MPa, carbon dioxide was at the supercritical state. Under this condition, the butyl rubber matrix was swollen and relaxed by the supercritical CO_2, thus creating free space in the polymer matrix to hold more DD than before the swelling.[23] As a result, many DD molecules could penetrate and disperse into the crosslink network with the help of supercritical CO_2, resulting in an increase in the rate of devulcanization. These results suggest that devulcanization is much more effective in the supercritical CO_2 than in gaseous CO_2.

Effect of Reaction Temperature and Amount of DD on Devulcanization. The effect of reaction temperature and amount of DD on devulcanization was investigated by using 50 g of vulcanized butyl rubber for a reaction time of 120 min at 14.1 MPa. The results are shown in Figure 2.

It can be seen from Figure 2 that the sol fraction hardly changes at temperatures below 160°C. The sol fraction increases with increasing reaction temperature at temperatures above 160°C, reaching 98.5% at 180°C. With increasing reaction temperature, the reactivity of DD molecules increases and the rate of impregnation of the vulcanizate matrix with DD also increases. The chance of combination of DD molecule radicals with polymer molecular radicals is enhanced, resulting in the increase of sol fraction.

Figure 2 also shows that the sol fraction is about 15% without DD. This portion of sol component was mainly attributed to the thermal degradation of the vulcanized rubber. The sol fraction of reclaimed butyl rubber increases with increasing amount of DD, reaching 98.5% with 4 g of DD. Such a significant amount of sol component could not have come from the thermal degradation of the vulcanized rubber alone and is attributed to the devulcanization caused by DD. Under this condition, because of the finite impregnation efficiency of supercritical CO_2, the amount of DD put into the reactor did not penetrate into and disperse in the three dimensional network at the same time, but gradually over a period of time.
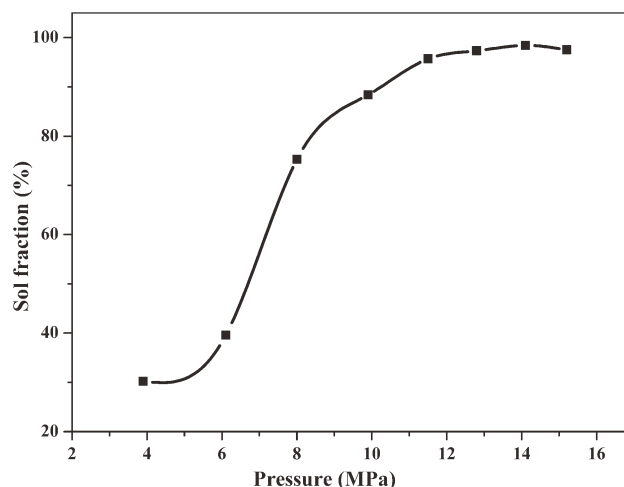

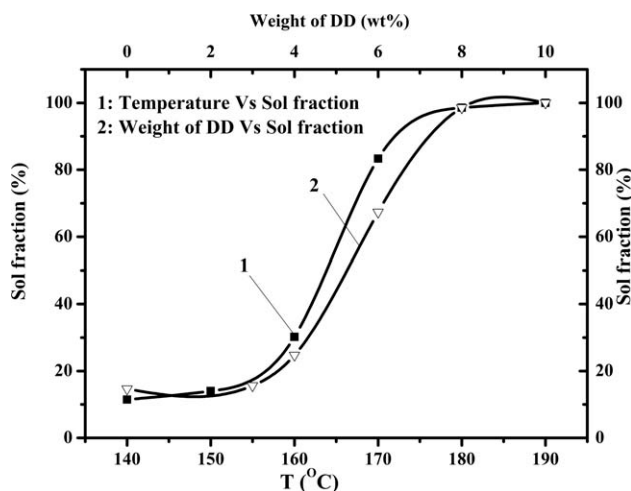**Figure 1.** Dependence of sol fraction on reaction pressure.

Figure 2. Dependence of sol fraction on reaction temperature and amount of DD.

Thus, more DD molecules could penetrate into and disperse in the network to participate in the devulcanization with increasing amount of DD, resulting in an increase in the rate of devulcanization. Further increase in the amount of DD might lead to a decrease in molecular weight of the sol component of the reclaimed butyl rubber though the sol fraction remained constant.

Effect of Reaction Time on Devulcanization. The effect of reaction time on devulcanization was investigated by using 50 g of vulcanized butyl rubber and 4 g of DD at 180°C and 14.1 MPa. Figures 3 and 4 show the sol fraction, number average molar mass (M_n), and polydispersity index (PDI) of the sol component as a function of reaction time.

Figure 3 shows that when the reaction time is 30 min, the sol fraction of the reclaimed butyl rubber is more than 20%. With the increase in reaction time, the sol content of the reclaimed butyl rubber increases almost linearly, reaching 98.5% at a reaction time of 120 min and staying there with further increase in reaction time. From Figure 4, it can be seen that the number
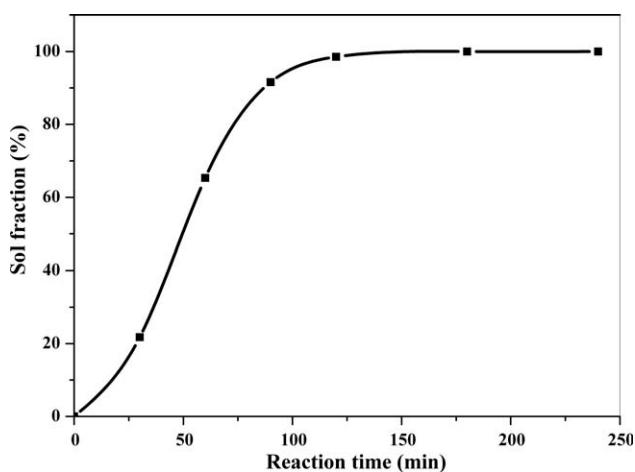

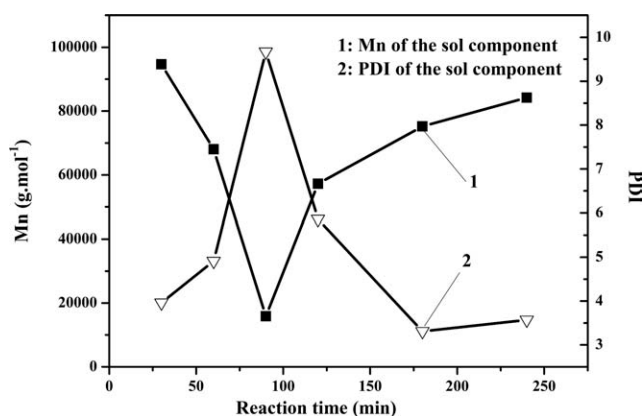**Figure 3.** Effect of reaction time on sol fraction of reclaimed butyl rubber.

Figure 4. Effect of reaction time on M_n and PDI of sol component.

average molar mass of the sol component decreases sharply with increasing reaction time, reaching a minimum at a reaction time of 90 min. The number average molar mass then increases slowly as the reaction proceeds further. The shape of the PDI versus reaction time curve is the reverse of the number average molar mass versus time curve.

When the devulcanization takes place, as seen from Scheme 1, there are two major methods to generate the sol component in the devulcanization around crosslink sites (we are planning to elaborate later). In this three-dimensional network, since the combination of DD molecule radicals with polymer radicals occurs at random and the probability that all the crosslinks in a molecular chain are cleaved at the same time is very small, the time when this crosslinked molecular chain changes into sol component corresponds to the cleavage of the last crosslink site of this molecular chain. In addition, the impregnation efficiency of supercritical CO_2 also affects the time that the sol component first appears. Therefore, we set 30 min as the onset reaction time to investigate the effect of reaction time on devulcanization. Only when the last crossklinked bond is broken up, then this sol component separates from the devulcanizing network system and dissolves in supercritical CO_2 fluid.

During the same reaction time, the fewer the number of crosslinking sites in a polymer chain, the fewer the number of crosslink bonds that required to be cleaved, and the sooner this crosslinked polymer chain converted into sol component and separated away from the devulcanizing network system. Meanwhile, there were fewer small segments that this polymer chain broke into, resulting in a relatively high molar mass and low PDI compared with the sol component generated later. This was the reason that M_n was larger and PDI was lower at the beginning of the reaction. With increasing reaction time, the polymer chains left in the network were supposed to have more crosslinking sites (such as polymer chain L_3 and L_4 in Scheme 1), according to Scheme 1, these polymer chains would probably be divided into more segments with lower molecular mass, resulting in further decrease in M_n and increase in PDI of the sol component. When the reaction time reached 90 min, the content of gel component was close to the minimum. At this time the, three-dimensional crosslink network was damaged severely. Such a network could be swollen highly and tended to form
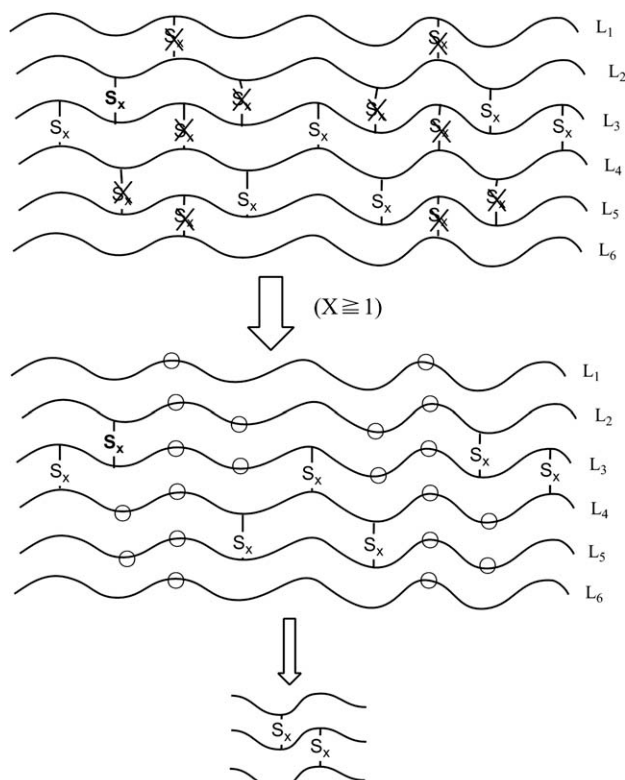
Scheme 1. Three dimensionally crosslinked butyl rubber network. The crosses indicate the locations of breakage of crosslink. The circles indicate the locations of probable breakage of main chain.

graft polymers with several main chain segments, and these graft polymers could be dissolved in supercritical CO_2. Also, the molecular mass of these graft polymers was relatively high, thus increasing the M_n of the sol component. With further increase in the reaction time, the concentration of DD molecule radicals decreased substantively. At this time, the polymer chain radicals tended to combine with each other to form block polymers according to reaction (F) in Scheme 2. The molecular mass of these block polymers was supposed to be higher than that of polymers obtained by end capping of DD molecule radicals and polymer chain radicals. Consequently, the PDI of the sol component decreased.

We considered the following to be the optimum devulcanizing condition: 50 g of vulcanized butyl rubber and 4 g of DD at 14.1 MPa and 180°C for a reaction time of 120 min. A 98.5% yield of sol component in the reclaimed butyl rubber could be obtained. This condition was used in the rest of this work unless otherwise stated.

Possible Mechanism for Butyl Rubber Devulcanization

We have found from the above experimental results that the devulcanization behavior of butyl rubber is strongly related to the devulcanizing mechanism. Before proposing a mechanism, we carried out further experiments to better understand the process.

Fifty grams of virgin butyl rubber was treated (allowed to react) at 14.1 MPa and 180°C for 120 min. Table II shows that the

molecular mass of butyl rubber decreased after reacted at 14.1 MPa and 180°C for 120 min. Besides causing thermal degradation, DD also led to the decrease in the molar mass of butyl rubber. This implied that the main chain could be broken up under this condition. Besides, this phenomenon was the same with that during devulcanization. An excess amount of DD molecule radicals would combine with butyl rubber polymer radicals. The molecular mass of sol component obtained this way was supposed to be lower than that obtained by the end capping of butyl rubber polymer radicals.

Figure 5 shows the ^{1}H-NMR spectra of the three samples. The molar fraction of isoprene unsaturation in the butyl rubber could be determined with following equation[24]:

$$\text{Isoprene unsaturation } (\text{mol}\%) = [8A/(A+B)] \times 100 \quad (2)$$

where A and B are the integral signal intensities of the 5.0–5.2 and 0.8–2.2 ppm regions in Figure 5.

The unsaturations of the three samples were 1.81 mol %, 1.89 mol %, and 1.75 mol %, respectively. Evidently, the difference
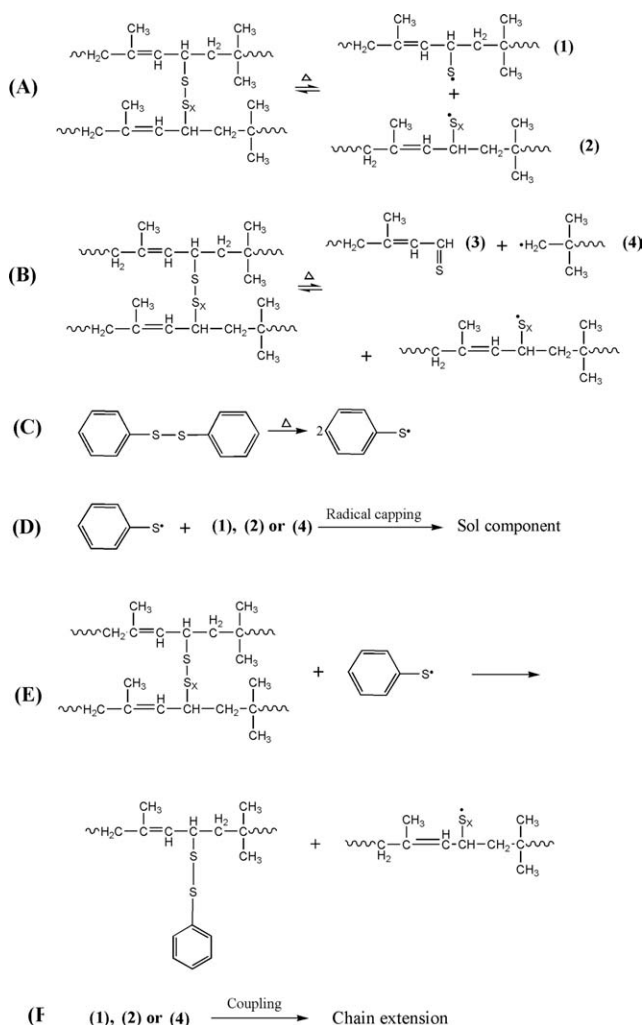
Scheme 2. Possible devulcanizing reaction with DD as devulcanizing reagent.
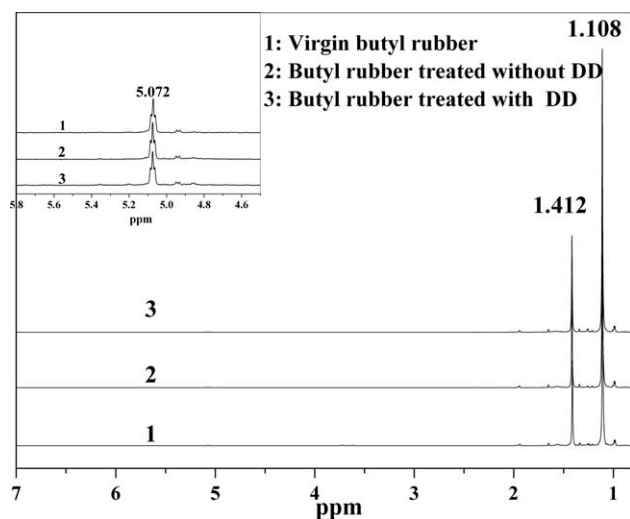
Table II. Molecular Mass and Polydispersity of Virgin Butyl Rubber and Treated Butyl Rubber

Sample	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI
A[a]	141,000	457,000	3.24
B[b]	124,000	341,000	2.76
C[c]	107,000	281,000	2.69

[a]Virgin butyl rubber, [b]50 g of butyl rubber treated at 14.1 MPa and 180°C without DD for 120 min, [c]50 g of butyl rubber treated at 14.1 MPa and 180°C with 4 g of DD for 120 min.

Table III. Bond Strength of Different Bonds in Rubber Network[28]

Type of bond	Bond dissociation energy (kJ/mol)
C—C	349
C—S—C	302
—S$_2$—	273
—S$_x$— ($x \geq 3$)	256
—S—S— (DD)	225

in these values was within the experimental uncertainty. Obviously, the signal of the olefinic proton does not shift, and the unsaturation of the three samples does not change. Figure 5 also shows that the frequency resonances at 1.108 ppm and 1.412 ppm attributed to the methyl proton and methylene proton of the polyisobutylene units of butyl rubber are not affected. That is, the structure of the main chain, especially the polyisobutylene units of butyl rubber, remained unbroken during the treatment carried out above. The polyisobutylene units of butyl rubber did not dissociate as a result of thermal degradation and the reaction involving DD molecule radicals. Thermal degradation did not destroy the double bonds. The DD molecule radicals did not add to the double bonds in butyl rubber either, but combined with butyl rubber radicals during devulcanization, leading to the decrease in the molar mass of the sol component.

As discussed above, we speculated the possible mechanism for butyl rubber devulcanization, shown in Scheme 2. It has been reported that crosslink scission and main chain scission took place during curing.[25] Although the temperature of the degradation of rubber main chain is higher than 300°C, some scission of the crosslinks and main chain might still take place at crosslink sites at 180°C,[26] such as according to reaction (A) or (B)[27] in Scheme 2. Some large molecular radicals could be generated though the dissociation energy of C—C bond is much higher[28] according to Table III. In the absence of radical terminators, the

Figure 5. ^{1}H-NMR spectra of virgin butyl rubber and treated butyl rubber at 14.1 MPa and 180°C for 120 min.

crosslinking and decrosslinking reaction were supposed to be in balance. Even so, a portion of sol component like (3) in Scheme 2 was generated, as indicated by Figure 2. In the absence of DD molecules, such sol component was supposed to be generated by thermal degradation accompanied with crosslink scission and main chain scission.

At 180°C, DD molecules also dissociated into steady radicals attributed to the lower dissociation energy of S—S bond, and these radicals did not add to the double bonds in butyl rubber as indicated by Figure 5. Because of the finite impregnation efficiency of supercritical CO_2, a large amount of polymer chain radicals had existed when the DD molecule radicals impregnated into and dispersed around the crosslink sites with the help of supercritical CO_2. When the DD molecule radicals impregnated into the three-dimensional network, the devulcanizing reaction took place according to reaction (D) and reaction (E) in Scheme 2, and some sol component was generated. On prolonged reaction time, the crosslink density of the gel component decreased, leading to an increase in the concentration of DD molecule radicals in the rubber matrix. The rate of reaction (A) or (B) increased, generating more polymer chain radicals. Consequently, more sol component was generated according to reaction (D) and (E) in Scheme 2. During the termination reaction, the concentration of DD molecule radicals decreased markedly, and those fragmented uncapped polymer radicals like (1), (2), and (4) in Scheme 2 may couple themselves, leading to an increase in the molecular mass of the sol component. Besides, it is said that the TMTD left in the rubber matrix may also make these polymer radicals couple themselves.[29]

Characterization of Reclaimed Butyl Rubber
Molecular Mass of Sol Component in Reclaimed Rubber and Mooney Viscosity of Reclaimed Rubber. The results of GPC and Mooney viscosity measurements are shown in Table IV and Figure 6.

Table IV shows that the molecular mass of the uncured compound are lower by about 30% than the corresponding values of virgin butyl rubber. After devulcanization, the number average molar mass of the sol component decreased to 5.7×10^4 g/mol—about 40% of that of virgin butyl rubber. The PDI of the uncured compound and sol component are higher than that of virgin butyl rubber. Moreover, some low-molecular-weight segments of uncured compound and sol component were generated from Figure 6. During devulcanization, thermal degradation could lead to main chain scission and result in a decrease of the molecular mass and an increase of the PDI of the sol component. What is more, the combination of DD molecule radicals and butyl rubber polymer radicals may bring about

Table IV. Molecular Mass and Mooney Viscosity of Virgin Butyl Rubber, Uncured Compound, and Sol Component of Reclaimed Butyl Rubber

	M_n[a] (g mol^{-1})	M_w[b] (g mol^{-1})	PDI	ML 100°C (1+4)
Virgin butyl rubber	141,000	457,000	3.24	–
Uncured compound	98,700	409,000	4.14	64.6
Sol component	57,000	336,000	5.86	29.2[c]

[a]Number average molar mass, [b]Weight average molar mass, [c]The Mooney viscosity of reclaimed butyl rubber value was 29.2.

further decrease of the molecular mass of the sol component. During devulcanization, those main chains with many crosslinking sites might break down into many low-molecular-weight segments, leading to the increase of PDI. As a result, the Mooney viscosity of the reclaimed butyl rubber decreased markedly, an indication that the reclaimed rubber could be processed easily.

Chemical Structure of Sol Component in Reclaimed Butyl Rubber. The structure of virgin rubber and the sol component of the reclaimed butyl rubber were analyzed. The ^{1}H-NMR spectra are shown in Figure 7.

As can be seen from Figure 7, the high frequency resonances at 1.108 ppm and 1.412 ppm were attributed to the methyl proton and methylene proton of the polyisobutylene units of butyl rubber.[24,30] Because of the low unsaturation, the weak frequency resonances in the region of 1.50–2.20 ppm were assigned to the isoprenyl units. Especially, the weak frequency resonance at 5.072 ppm was assigned to the olefinic proton in Figure 7.[31] However, there is hardly any frequency resonance of olefinic proton at 5.072 ppm for the sol component. Instead, some weak frequency resonances in the region of 5.0–6.0 ppm could be seen for the sol component. As discussed above, the thermal degradation and devulcanization caused by DD did not break down the double bonds. Besides, some sulfurated functional groups were grafted onto the main chain during vulcanization. These polar sulfurated groups might affect the chemical shift of the olefinic proton.[32] Based on the above results, we conclude

that the weak frequency resonance in the region of 5.0–6.0 ppm is mainly attributed to the olefinic protons.

Thermal Properties of Reclaimed Rubber. The thermal properties of the virgin butyl rubber, vulcanized butyl rubber, and reclaimed butyl rubber were analyzed by DSC and TGA, and the results are shown in Figures 8 and 9.

Figure 8 shows that the vulcanized butyl rubber and sol component have a slightly higher T_g than that of virgin butyl rubber. Some phenyl groups that were derived from the devulcanizing reagent attached onto the main chain during the devulcanization may result in a decrease of molecular mobility and increase of T_g.

Figure 9 shows the TGA curves of virgin, vulcanized, and reclaimed butyl rubber. It can be seen that there is a sharp degradation at 390°C for the three samples. This is mainly due to the main chain degradation and implies that the thermal stability of the reclaimed butyl rubber was not disturbed, though main chain scission took place during the devulcanization. In addition, a small degradation can be seen for the vulcanized and the reclaimed butyl rubber around 300°C. For the former sample, the slight weight loss was mainly due to the loss of the volatile curing agents such as SA in the sample.[33] However, more or less 6% weight loss of the later sample was mainly due to the loss of DD molecules left after devulcanization and that of low-molecular-weight segments of sol component generated during devulcanization. Furthermore, the lowest nonvolatile fraction found in the vulcanized butyl rubber was the same as that in the reclaimed butyl rubber because the vulcanized and
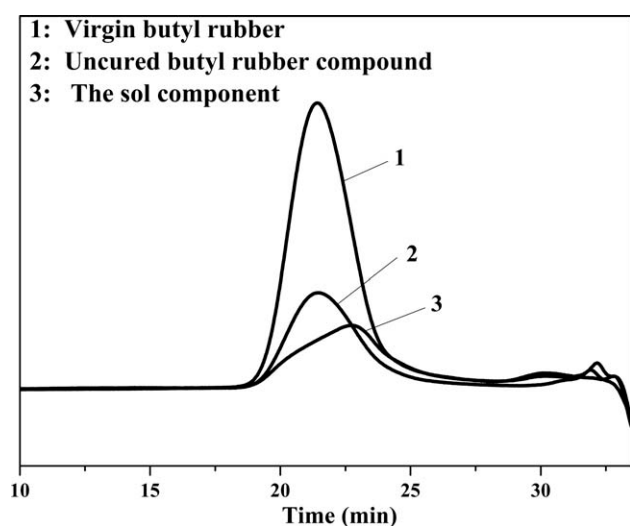

Figure 6. GPC data showing molecular mass distribution of virgin butyl rubber, uncured compound, and sol component of reclaimed butyl rubber.
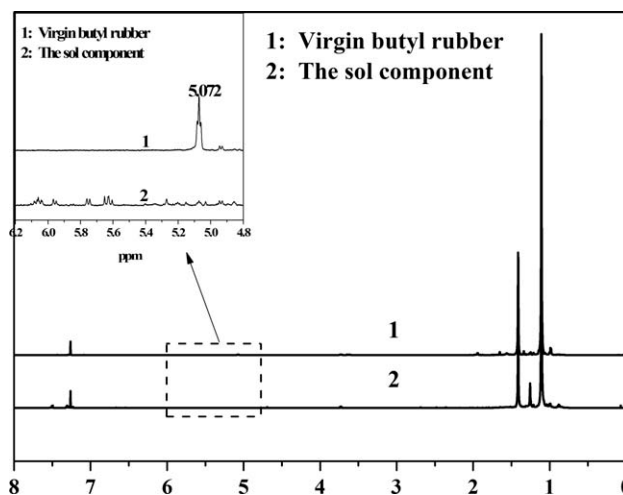

Figure 7. ^{1}H-NMR spectrum of virgin butyl rubber and sol component of reclaimed butyl rubber.
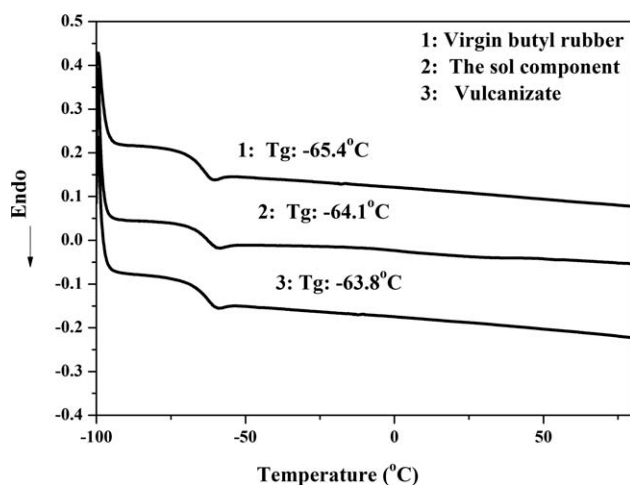
Figure 8. DSC curves of virgin butyl rubber, vulcanized butyl rubber, and sol component.

Figure 10. Cure behavior of virgin and reclaimed butyl rubber by using sulfur as curing agent at 160°C.

the reclaimed butyl rubber contained the same amount of curatives such as zinc oxide.

Revulcanization of Reclaimed Butyl Rubber

Both virgin butyl rubber and reclaimed butyl rubber were revulcanized by using sulfur as the curing agent. The recipes are shown in Table I (Sample A and Sample F) and the curing curves are shown in Figure 10.

As seen from Figure 10, there is no increase in rheometric torque of the reclaimed butyl rubber compound by using sulfur as curing agent. That is, sulfur could not vulcanize the reclaimed butyl rubber. The question naturally arises as to why such reclaimed butyl rubber could not be cured by sulfur. As illustrated in the ^{1}H-NMR spectrum, the signal of the olefinic proton shifted because of the substitution of the allylic hydrogen by sulfurated functional groups. This change might result in the numerous decreases in active crosslinking sites in the main chain and further lead to the difficulty of revulcanization of reclaimed butyl rubber by using sulfur as the curing agent. On
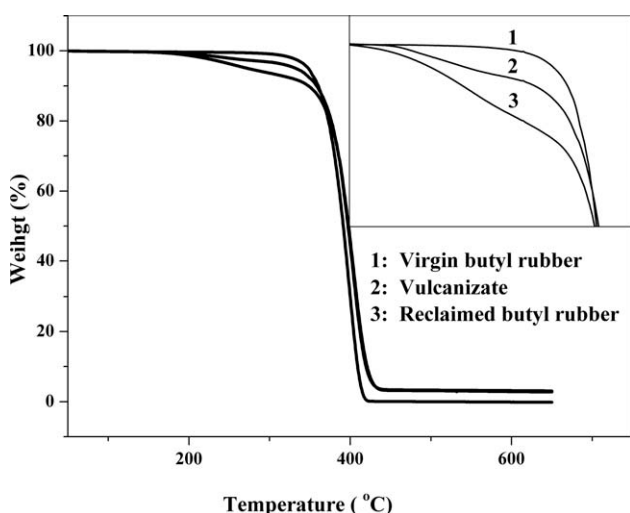
the other hand, because of the finite impregnation efficiency of supercritical CO_2, some DD that had dissolved in supercritical CO_2 remained after devulcanization.[19] DD left in the reclaimed rubber may affect the revulcanization.

Behavior of DD During Vulcanization. As illustrated above, as a devulcanizing reagent, DD in an appropriate amount could make the devulcanization effective, and some phenyl groups derived from DD were attached onto the main chain. It is interesting to know whether DD affects the vulcanization. To verify the effect of DD on vulcanization, the following study was carried out, the vulcanizing recipes are shown in Table I (Samples A, B, C, D, and E) and the results are shown in Figure 11.

It can be concluded from Figure 11 that the compounds using DD as curing and accelerating agent could not be cured. In other words, DD was not able to play the role of curing and accelerating agent, though it has been reported that DD could make model compound crosslink at high temperatures.[34] However, Figure 11 shows that with increasing content of DD in the compound, the
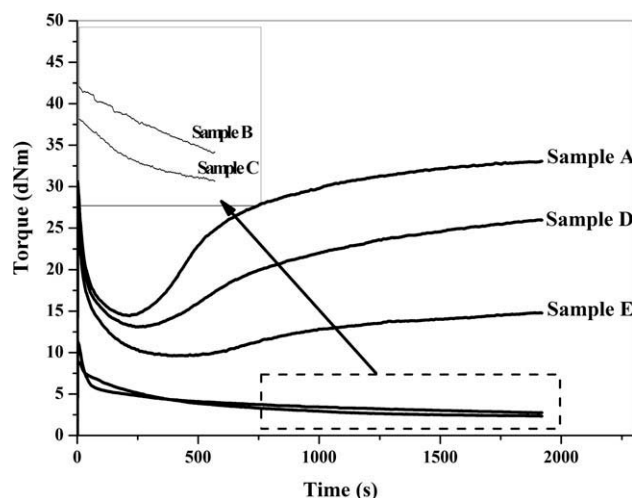

Figure 9. TGA curves of virgin, vulcanized, and reclaimed butyl rubber.

Figure 11. Cure behavior of virgin butyl rubber with different amounts of DD.
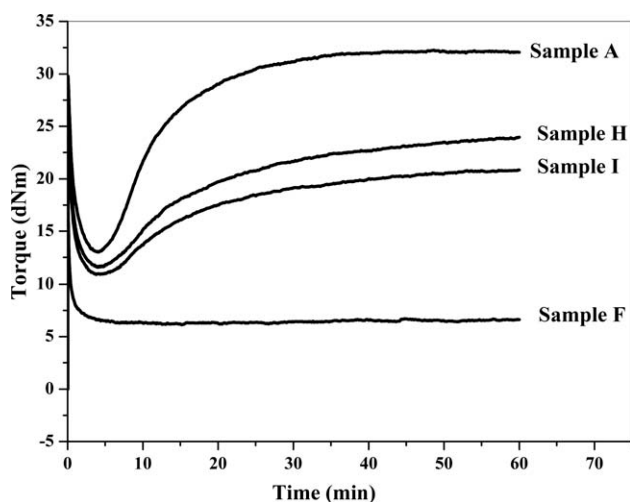
Figure 12. Cure behavior of blends of virgin butyl rubber with different contents of reclaimed butyl rubber at 160°C.

minimum and maximum torque decrease, and corresponding, the scorch time and the optimum cure time increased. It was noteworthy that DD could decompose rapidly into radicals at 160°C. These radicals could delay and even prevent vulcanization.

As discussed above, an excess amount of DD could delay and even prevent the curing of the compound. Thus, we had reasons to believe that the DD that remained in reclaimed butyl rubber made the reclaimed butyl rubber uncurable when sulfur was used as the curing agent.

To further investigate the use of DD in the revulcanization of reclaimed butyl rubber, we extracted the reclaimed butyl rubber for 96 h by using acetone as the solvent to remove the devulcanizing reagents DD that had not reacted with the polymer chains. The reclaimed butyl rubber was dried *in vacuo* at room temperature to constant weight before being subjected to revulcanization by using sulfur as the curing agent. The revulcanizing recipes are shown in Table I (Sample G) and the results are shown in Figure 10.

As seen from Figure 10, the reclaimed butyl rubber could be cured after extraction, though the torque increment ($T_{max} - T_{min}$) was low. The small torque increment might be due to the low molecular weight of the reclaimed rubber and the number decrease in the active crosslinking sites in the main chain. Curve G confirms that the DD left in the reclaimed butyl rubber prevented crosslinking.

It is interesting to note that reclaimed NR devulcanized in the same method could be revulcanized by using sulfur as the curing agent.[35] We believe that the low unsaturation of butyl rubber makes the main chain susceptible to reduction in active crosslinking sites. The effect of any DD left in the reclaimed butyl rubber on revulcanization was thereby amplified. However, this effect is negligible for reclaimed NR because of the high unsaturation of NR.

Nevertheless, the reclaimed butyl rubber could be sulfur-revulcanized by blending with virgin butyl rubber, and the revulcanizing recipes are shown in Table I.

Cure Behavior. The blends with different contents of reclaimed rubber and virgin butyl rubber were cured according to the recipes shown in Table I (Samples A, F, H, and I). Figure 12 shows the cure behavior of the blends of virgin butyl rubber with different contents of reclaimed butyl rubber. With increasing content of reclaimed butyl rubber in the blend, the minimum torque and maximum torque as well as the torque increment ($T_{max} - T_{min}$) decrease, while the scorch time and T_{90} increase. As illustrated above, the reclaimed butyl rubber could not be cured by sulfur. Thus, the majority of reclaimed butyl rubber in the blends plays the role of plasticizer, resulting in the decrease in the crosslink density of the revulcanizates. The decrease in crosslink density is the main reason for the decrease in torque.

Mechanical Properties. Prior to revulcanization, the blends with different contents of reclaimed rubber were homogenized and compounded with curatives on a two-roll mill. Then the different blends were cured. The mechanical properties of the revulcanizates are shown in Table V and Figure 13.

Figure 13 shows that with increasing content of reclaimed butyl rubber in the blend, the modulus at 100% elongation and the modulus at 300% elongation decrease, while the elongation at break and tensile strength increase pronouncedly. Besides, some degree of strain-induced crystallization could be found in the compound with 30% of reclaimed butyl rubber. The results are shown in Table V. Apart from the decrease in the modulus at 100% and modulus at 300%, hardness and tear strength also decrease with the addition of reclaimed butyl rubber. Some low-molecular-weight molecules and the majority of uncured reclaimed butyl rubber made the hardness and modulus decrease. Besides, it is noteworthy that the crosslink density of the revulcanizates decreased with increasing content of reclaimed butyl rubber. This was the main reason for the decrease in the modulus and tear strength. As we all know, a moderate crosslink density is conducive to high tensile strength. Additionally, strain-induced crystallization is closely related to the elongation at break. Thus, the tensile strength of the revulcanizates increased and some degree of strain-induced crystallization could be found.

CONCLUSIONS

Sulfur-cured butyl rubber can be completely devulcanized in supercritical CO_2. The optimum condition for devulcanization was obtained and a maximum of 98.5% of sol component of reclaimed butyl rubber could be obtained. As the devulcanizing reagent, DD could make the devulcanization effective and did

Table V. Mechanical Properties of Revulcanized Rubber

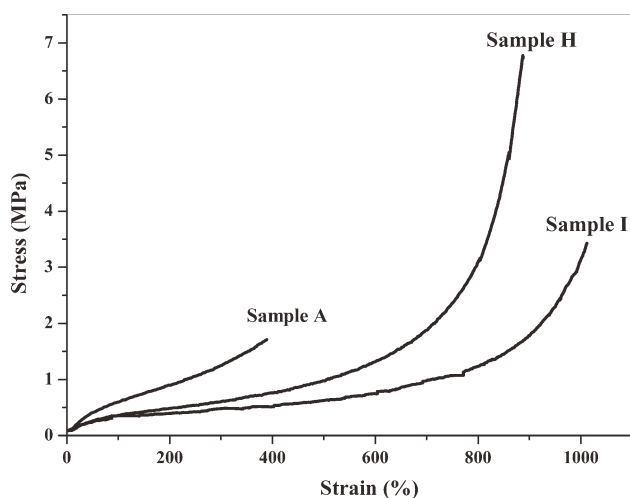| Content of reclaimed butyl rubber (%)	0	30	50
Tensile strength (MPa)	1.7	6.8	5.5
Tear strength (kN/m)	14.8	10.8	8.9
Elongation at break (%)	400	890	1010
Modulus at 100% (MPa)	0.6	0.4	0.4
Modulus at 300% (MPa)	1.3	0.6	0.5
Hardness (Shore A)	34.0	29.0	23.2

Figure 13. Stress–strain behavior of virgin butyl rubber/reclaimed butyl rubber blend systems.

not take part in the crosslinking reaction. However, an excess amount of DD may affect the revulcanization. According to the optimum condition for devulcanization, a possible mechanism for butyl rubber devulcanization was proposed.

The molecular mass of the sol component was lower and the PDI was higher than the corresponding values for virgin butyl rubber. At the same time, some low-molecular-weight segments were generated. The Mooney viscosity of the reclaimed butyl rubber was significantly lower than that of virgin butyl rubber. The signal of the olefinic proton shifts. The T_g of the sol component is similar to that of virgin butyl rubber, and the thermal stability of the reclaimed butyl rubber is not affected.

As a result of the numerous decreases in the active crosslinking sites and the remaining DD, reclaimed rubber could not be cured by sulfur. The blends of virgin butyl rubber and different contents of reclaimed rubber were revulcanized and their mechanical properties investigated.

REFERENCES

1. Adhikari, B.; De, D; Maiti, S. *Prog. Polym. Sci.* **2000,** *25*, 909.

2. Gnoella, L. B.; Zattera, A. J.; Zeni, M.; Oloveira, R. V. B.; Canto, L. B. *J. Elastom. Plast.* **2009,** *41*, 302.

3. Phadke, A. A.; Bhattacharya, A. K.; Chakraborty, S. K.; De, S. K. *Rubber. Chem. Techno.* **1983,** *56*, 726.

4. Watando, H.; Saya, S.; Fukaya, T.; Fujieda, S.; Yamamoto, M. *Polym. Degrad. Stab.* **2006,** *91*, 3354.

5. Yashin, V. V.; Hong, C. K.; Isayev, A. I. *Rubber. Chem. Technol.* **2004,** *77*, 50.

6. Cialone, A. M. WO Pat. 137,585 (**2009).**

7. Scuracchio, C. H.; Waki, D. A.; da Sivla, M. L. C. P. *J. Therm. Anal. Calorim.* **2007,** *87*, 893.

8. Jeong, S. O.; Sayata, G.; Isayev, A. I. *J. Polym. Sci. Part B: Polym. Phys.* **2003,** *41*, 2959.

9. Feng, W.-L.; Isayev, A. I. *J. Appl. Polym. Sci.* **2004,** *94*, 1316.

10. Rajan, V. V.; Dierkes, W. K.; Joseph, R. J.; Noordermeer, W. M. *J. Appl. Polym. Sci.* **2006,** *102*, 4194.

11. Anderson, E. J. U.S. Pat. 454,467,5 (**1985)**

12. Myers, R. D.; Nicholson, P.; Macleod, J. B.; Moir, M. E. U.S. Pat. 560,218,6 (**1997).**

13. Warner, W. C. *Rubber. Chem. Technol.* **1994,** *67*, 559.

14. Onwudili, J. A.; Williams, P. T. *J. Supercrit. fluids* **2009,** *49*, 356.

15. Goto, M. *J. Supercrit fluids.* **2009,** *47*, 500.

16. Nalawade, S. P.; Picchioni, F.; Janssen, L. P. B. M. *Prog. Polym. Sci.* **2006,** *31*, 19.

17. Kojima, M.; Tosaka, M.; Funami, E.; Nitta, K.; Ohshima, M.; Kohjya, S. *J. Supercrit. Fluids* **2005,** *35*, 175.

18. Kojima, M.; Kohjiya, S.; Ikeda, Y. *Polymer* **2005,** *46*, 2016.

19. Kojima, M.; Tosaka, M.; Ikeda, Y. *Green Chem.* **2004,** *6*, 84.

20. Kojima, M.; Ogawa, K.; Mizoshima, H. *Rubber Chem Technol* **2003,** *76*, 957.

21. Tzoganakis, C. U.S. Pat. 7,189,762 B2 (**2007).**

22. Kroschwitz, J. I. Concise Encyclopedia of Polymer Science Engineering; Wiley-Inter-Science: New York, **1990.**

23. Zhang, Y.; Gangwani, K. K.; Lemert, R. M. *J. Supercrit. Fluids* **1997,** *11*, 115.

24. Rajan, V. V.; Dierkes, W. K.; Joseph, R.; Noordermeer, J. W. M. *J. Appl. Polym. Sci.* **2007,** *104*, 3562.

25. González, L.; Rodríguez, L.; Delcampo, A.; Marcos-Fernández, A. *Rubber Chem. Technol.* **2000,** *73*, 89.

26. Jipa, S.; Giurginca, M.; Setnescu, T.; Setnescu, R.; Ivan, G.; Mihalcea, I. *Polym. Degrad. Stab.* **1996,** *54*, 1.

27. Mathew, A. P.; Packirisamy, S.; Thomas, S. *Polym. Degrad. Stab.* **2001,** *72*, 423.

28. Debapriya, D.; Amit, D.; Debasish, D.; Brojendranath, D.; Subhus, C. D.; Bidhan, C. R. *Eur. Polym. J* **2006,** *42*, 917.

29. Motero, B. V. L.; Lincoln, S.; Agullo, N.; Borros, S. *J. Appl. Polym. Sci.* **2008,** *108*, 1969.

30. Mclnenly, P. J.; Drewitt, M. J.; Baird, M. C. *Macromol. Chem. Phys.* **2004,** *205*, 1707.

31. Feng, W.-L.; Isayev, A. I. *J. Polym. Sci. Part B: Polym. Phys.* **2005,** *43*, 334.

32. Chu, C. Y.; Vukov, R. *Macromolecules* **1985,** *18*, 1423.

33. Pretsch, E.; Bühlmann, P.; Affolter, C. Spectral Data for Structure Determination of Organic Compounds, 2nd ed.; Springer-Verlag: Berlin, **1991.**

34. Debapriya, D.; Debasish, D.; Singharoy, G. M. *Polym. Eng. Sci* **2007,** *47*, 1091.

35. Kojima, M.; Tosaka, M.; Ikeda, Y.; Kohjiya, S. *J. Appl. Polym. Sci* **2005,** *95*, 137.