

## The Effect of Devulcanization Level on Mechanical Properties of Reclaimed Rubber by Thermal-Mechanical Shearing Devulcanization

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**ABSTRACT:** Ground tire rubber (GTR) with crosslinked structure has hardly any plasticity and processability, which makes its property very poor. Thermal-mechanical shearing devulcanization method can effectively destroy the crosslinked structure and restore GTR a certain extent of plasticity and processability. This article investigated the characteristic and reprocessing performance of reclaimed rubber prepared through thermal-mechanical shearing devulcanization. The relationship between the devulcanization level (indicated by gel fraction and crosslink density) and the mechanical property was analyzed by sufficient experiments. Fourier transform infrared spectroscopy and elemental analyzer studies revealed the chemical structure of GTR changed and many complex reactions occurred after devulcanization. The gel permeation chromatography indicated the specific changes of molecular weight and molecular weight distribution in devulcanization process. The differential scanning calorimetry revealed various vulcanized abilities and vulcanized structures of reclaimed rubber. The scanning electron microscope further confirmed the recovery of plasticity after devulcanization and the distinct vulcanized structures between redevulcanizates. The determination of devulcanization level and mechanical properties verified that mechanical properties especially tensile strength reached to the optimum value only at an appropriate devulcanization level. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2598–2605, 2013

**KEYWORDS:** extrusion; rubber; recycling

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### INTRODUCTION

Ground tire rubber (GTR) has been highly valued all around the world for its disposal. The preparation of reclaimed rubber is one of the main ways for reuse or recycling. In China, reclaimed rubber has been rapidly developed as the third largest rubber resource. At present, many traditional devulcanization methods have been gradually eliminated because of some existing disadvantages such as serious pollution, low productive efficiency. Among the new devulcanization methods, for example, microwave regeneration,<sup>1</sup> microbial action,<sup>2,3</sup> Delink process,<sup>4</sup> ultrasonic regeneration, and so on,<sup>5,6</sup> thermal-mechanical shearing devulcanization method has an enormous industrialized potential.<sup>7,8</sup> Lots of researches on thermal-mechanical shearing devulcanization have been conducted. In the work of Maridass and Gupta,<sup>9</sup> the devulcanization of waste natural rubber powder using counter-rotating twin-screw extruder was investigated, in which they used response surface methodology to predict the optimality of process parameters. An investigation into the devulcanization of sulfur-cured ethylene propylene diene monomer (EPDM) rubber by twin-screw extruder was conducted by Mouri et al.<sup>10</sup> They found that the devulcanization could be

achieved under certain appropriate condition without adding any desulfurizer. Due to the advantages of speedy and continuous producing process, thermal-mechanical shearing devulcanization method is widely used in the devulcanization of GTR. Izumoto and Ohehima<sup>11</sup> invented a new method of producing reclaimed rubber by improving the screw configuration. This approach solved several problems such as high cost, low performance of product, and incapacity of production. The devulcanization process of the tread section of waste tires was conducted by Yazdani et al.<sup>12</sup> In their study, the percentages of devulcanization and sol fraction were found depending on the screw speed and barrel temperature, respectively. The mechanical properties of the compound containing desulfurized rubber were slightly inferior to those of the virgin compound. Recently, Balasubramanian used twin-screw extruder to study cure modeling and mechanical properties of GTR-NR blends.<sup>13</sup>

However, most researches on the thermal-mechanical shearing devulcanization of GTR were centered on technology optimization and macroscopic effect. The relationship between devulcanization level and mechanical property of redevulcanizate is still not revealed clearly. In this research, the desulfurized ground

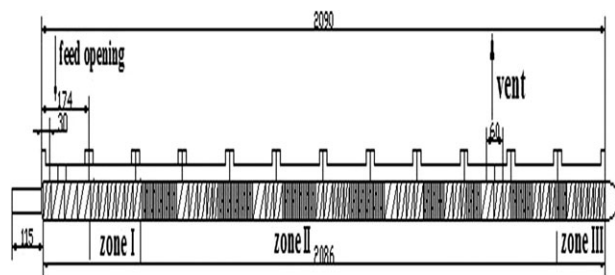


Figure 1. Screw configuration.

tire rubber (DGTR) obtained from thermal-mechanical shearing devulcanization has been characterized through Fourier transform infrared (FTIR), gel permeation chromatography (GPC), elemental analyzer (EA), differential scanning calorimetry (DSC), and scanning electron microscope (SEM) to investigate the changes in structures at different devulcanization conditions (changing devulcanization temperature and screw speed). Finally, through adequate determinations on gel fraction, crosslink density, and mechanical property, the relationship between devulcanization level and mechanical property of reclaimed rubber was clearly explained.

## EXPERIMENTAL

### Materials and Equipments

The GTR powder (30 mesh) was purchased from Nantong Huili rubber CO. (China). It contained 6% volatile component, 58% rubber, 30% carbon black, and 6% ash. Other compounding ingredients such as zinc oxide, stearic acid, sulfur, and accelerator NS (*N-tert*-butylbenzothiazole-2-sulphen-amide) were obtained commercially.

Figure 1 depicts the screw configuration used in this research. The screw configuration can be divided into three zones according to the main function: zone I (transportation), zone II (devulcanization), and zone III (transportation and dispersion).

### Experimental Procedure

**Preparation of Reclaimed Rubber.** GTR powders were extruded by co-rotating twin-screw extruder. The experimental settings of extruding parameters are showed in Table I, the optimum ratio of  $r_f/r_s$  ( $r_f$  is feeding speed,  $r_s$  is screw speed) was experimentally proved to be 1.4.

Table I. The Experimental Settings of Extruding Parameters

Exp. no	R (rpm)	T (°C)				
		160	180	200	220	240
A	80	a1	a2	a3	a4	a5
B	100	b1	b2	b3	b4	b5
C	120	c1	c2	c3	c4	c5
D	140	d1	d2	d3	d4	d5
E	160	e1	e2	e3	e4	e5

Notes: T—Devulcanization temperature (temperature in zone II); R—Screw speed ( $r_s$ ).

Table II. Revulcanization Formulation of Reclaimed Rubber

Ingredients	Weight (phr)
Reclaimed rubber	100
Accelerator NS	0.8
Zinc oxide	2.5
Stearic acid	0.4
Sulfur	1.2

**Revulcanization of Reclaimed Rubber.** The revulcanized formulation of reclaimed rubber is shown in Table II. The mixing was done in an open two-roll mill at a friction ratio of 1 : 1.2. During mixing, the roll temperature was kept at 50°C, and each sample was cured at 150°C under 10 MPa pressure for 15 min by curing press.

### Characterization of Reclaimed Rubber

**FTIR measurement.** FTIR measurement was done using an Avtar 370 spectrometer (USA) on the sol of GTR before and after devulcanization. The spectra were taken from 4000 to 400  $\text{cm}^{-1}$  in the transmission mode. To remove impurities in sol, the reclaimed rubber was first extracted using acetone as the solvent in Soxhlet extractor and then soaked in toluene for 24 h.

**Determination of sulfur content.** The sulfur content of the gel of GTR and reclaimed rubber was determined using EA (EA2400 II Perkin Elmer USA). The sulfur content was determined under pure oxygen condition during the sample was burning in appropriate reagent.

**GPC measurement.** The molecular weight and molecular weight distribution of sol of GTR powder before and after devulcanization were determined by a gel permeation chromatographer (GPC Waters 515, USA) at room temperature. The solvent was tetrahydrofuran, and the linear polystyrene was taken as the standard.

**Determination of gel fraction.** The gel fractions of GTR, reclaimed rubber (DGTR) were determined by Soxhlet extraction method. First, the samples were extracted with xylene in Soxhlet extractor for 24 h, and then dried to constant weight at 80°C in vacuum baking oven. The gel fraction was calculated as follows:

$$w = \frac{m}{m_0} \quad (1)$$

where  $w$  is the gel fraction,  $m_0$  is the weight of the sample before extraction, and  $m$  is the constant weight of the dry and insoluble part.

**Determination of crosslink density.** The crosslink density was determined by immersing a small amount of the sample in 100 mL toluene for 72 h at 30°C to attain equilibrium swelling. After the equilibrium swelling, the sample was taken out and the solvent was blotted from the surface of the sample and weighted immediately. The sample was then dried out at 80°C up to constant weight. The crosslink density was calculated by Flory-

Rehner equation.<sup>14</sup> Because of the presence of filler, the equation has been modified using the Kraus correction.<sup>15</sup>

**DSC Analysis.** A Perkin-Elmer DSC thermal analyzer was used to study the revulcanization of DGTR. The measurements were carried out in a nitrogen atmosphere at a heating rate of  $10^{\circ}\text{C min}^{-1}$ . Before being scanned, all samples were well mixed by an open two-roll mill according to the revulcanization formulation and then prepared as sheets.

**Determination of Mechanical Properties.** The mechanical properties of revulcanizate, mainly tensile strength and elongation at break, were measured according to GB/T 528 (China) specification by a WDT-50 Computer-controlled Electronic Universal Testing Machine at a crosshead speed of 500 mm/min. The specification specifies a dumb-bell testing specimen with a thickness of  $2.0 \pm 0.2$  mm and a width of  $4.0 \pm 0.2$  mm.

**Morphology Observation.** Morphological analyses of the GTR and DGTR before and after revulcanization were examined by SEM (JEOL JSM-6063LA, Japan). The samples were cryogenically broken in liquid nitrogen, and the fractured ends of the specimens were sputter-coated with a thin layer of gold to avoid electrostatic charging during examination.

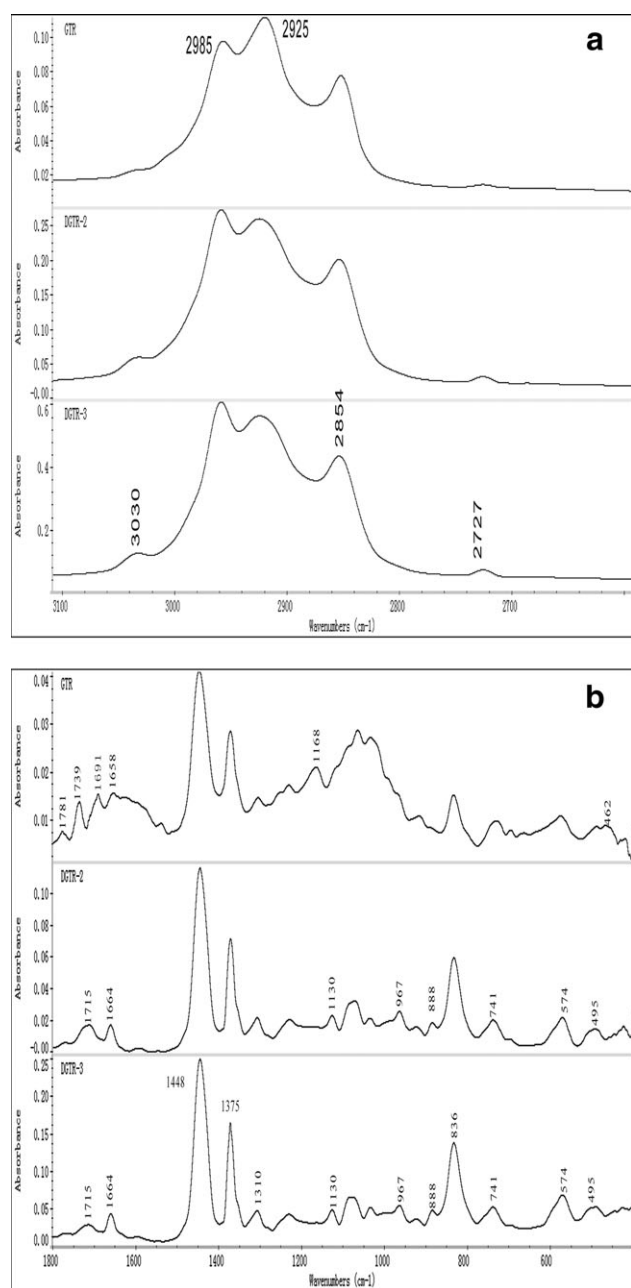
## RESULTS AND DISCUSSTION

### Characterization of Devulcanization

**FTIR Analysis.** FTIR spectra studies were conducted to obtain information on microstructure. Figure 2(a,b) presents the FTIR spectra of GTR before and after devulcanization. According to Lambert–Beer law,<sup>16,17</sup> the peak area is directly proportional to the thickness or concentration of a sample. Therefore, the peak area method can be used to evaluate the structural change of the samples.<sup>18,19</sup> In this way, the absorption band at  $1448\text{ cm}^{-1}$  assigned to  $-\text{CH}_2$  deformation was selected as the internal standard to analyze the infrared absorbance of the other bands.<sup>20</sup> The peak shape obviously remained the same after devulcanization.

The peak areas have been measured with the FTIR software, and the absorption peak area ratios of some bands to the internal standard are listed in Table III. It is clear that some peaks at  $3030\text{ cm}^{-1}$ ,  $2727\text{ cm}^{-1}$ ,  $1375\text{ cm}^{-1}$ ,  $1310\text{ cm}^{-1}$ ,  $741\text{ cm}^{-1}$ , and  $574\text{ cm}^{-1}$  remain almost the same, which meant the chemical structures did not change. In Figure 2(a), the biggest change was the ratio of  $A_{2925}/A_{1448}$ , which indicated molecular chains contained methyl and methylene groups changed after devulcanization.

In Figure 2(b), several absorption bands at  $1781\text{ cm}^{-1}$ ,  $1735\text{ cm}^{-1}$ , and  $1691\text{ cm}^{-1}$  disappear and then form a single band at  $1716\text{ cm}^{-1}$ , all of these peaks should be assign to the groups contained with  $\text{C}=\text{O}$ . Those results confirmed that the oxidative degradation partly occurred in main-chain during devulcanization process. The peak at  $1664\text{ cm}^{-1}$  characterizes  $\text{C}=\text{C}$  also emerged obviously after devulcanization. Surprisingly, this peak seems too weak, which may be effected by the atmospheric intrusion of  $\text{CO}_2$  that usually appears in transmission spectroscopy at about  $2300\text{ cm}^{-1}$ . In other FTIR studies,  $\text{C}=\text{C}$  band at  $1640\text{--}1660\text{ cm}^{-1}$  is referred as a strong band.<sup>21</sup> Nevertheless,



**Figure 2.** (a) FTIR spectra of GTR and DGTR in the range of  $3100\text{--}2600\text{ cm}^{-1}$ . (b) FTIR spectra of GTR and DGTR in the range of  $1800\text{--}400\text{ cm}^{-1}$ . Notes: 1—GTR; 2—DGTR-2 ( $180^{\circ}\text{C}$ , 120 rpm/min); 3—DGTR-3 ( $220^{\circ}\text{C}$ , 160 rpm/min).

these changes illustrated molecular chains contained with carbon–carbon double bonds were extracted from the broken crosslinked structure. In the range of  $1300\text{ cm}^{-1}$  to  $450\text{ cm}^{-1}$ , several new absorption peaks characterize sulfur-containing groups emerged, such as sulphone ( $-\text{R}-\text{SO}_2-\text{R}-$ ), sulphoxide ( $-\text{R}-\text{S}=\text{O}$ ), and sulfinic ester ( $-\text{R}-\text{SO}-\text{OR}$ ), etc.<sup>22</sup> Besides, the absorption bands characterizes  $\text{S}-\text{S}$  linkage moves from  $462\text{ cm}^{-1}$  to  $495\text{ cm}^{-1}$ , which might be related to some radicals nearby. Those bands between DGTR-2 and DGTR-3 have no big difference. These results indicated that some mono-, di-,

**Table III.** Absorption Peak Area Ratios of Some Bands to the Internal Standard

Sample	GTR (%)	DGTR-2 (%)	DGTR-3 (%)
A3030/A1448	4.51	4.42	5.75
A2925/A1448	72.43	34.18	35.52
A2727/A1448	3.35	3.52	3.72
A1375/A1448	31.20	31.07	31.61
A1310/A1448	6.76	7.35	7.55
A1130/A1448	None	4.11	4.29
A1087/A1448	None	14.57	13.74
A1038/A1448	None	1.64	2.42
A967/A1448	None	3.40	2.93
A836/A1448	25.43	39.76	42.13
A741/A1448	11.60	10.00	10.30
A574/A1448	17.51	17.85	17.68
A495/A1448	1.72 (A462)	7.88	6.64

and poly-sulfide linkages cleaved from crosslinked structure to form various sulfur-containing radicals.<sup>23</sup> These radicals reacted with oxygen in air and formed sulfur-containing groups hanging on the molecular chains.

Table IV lists the sulfur contents of gel of reclaimed rubber obtained from different devulcanization temperature. The decrease of total sulfur content in gel further confirmed that chemical changes occurred in mono-, di-, or poly-sulfide linkages. Some sulfur-contained radicals formed various groups hanging on the molecular chains through complex reactions or reacted with oxygen or hydrogen in air to produce gaseous matters such as SO<sub>2</sub>, H<sub>2</sub>S. While most of sulfur still presented in gel as crosslinking sites.

**GPC Analysis.** To obtain information on molecular weight and the molecular weight distribution, the GPC measurement was conducted. Table V lists the number averaged molecular weight ( $\bar{M}_n$ ), the weight average molecular weight ( $\bar{M}_w$ ), and the molecular weight distribution ( $\bar{M}_w/\bar{M}_n$ ) of sol of GTR before and after devulcanization. The corresponding molecular weight distribution curves were showed in Figure 3. It is evident that both  $\bar{M}_n$  and  $\bar{M}_w$  increased first and then decreased, and the molecular weight distribution broadened with increasing temperature. These changes further reflected the devulcanization process. The crosslinked structure of rubber part in GTR was destroyed to a certain extent at low devulcanization levels. Some macromolecu-

**Table IV.** The Sulfur Content with Change of Extruding Parameters

Samples in exp. no. B	S (wt %)
b0	2.520
b1	2.224
b2	2.108
b3	1.991

Notes: b0—before devulcanization.

**Table V.** Molecular Weight and Molecular Weight Distribution of Sol Obtained in Different Extruding Parameters

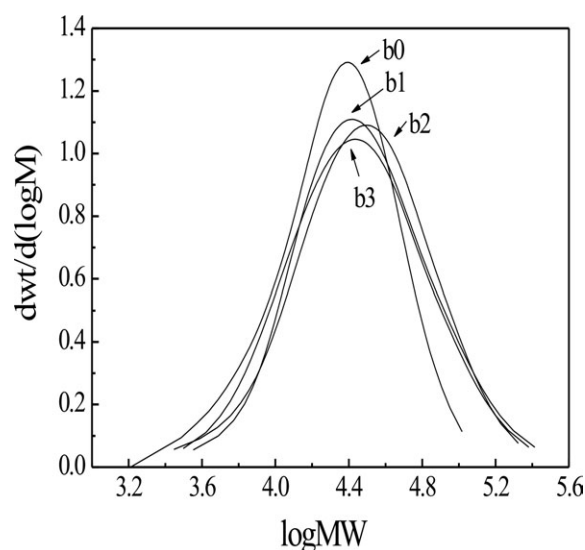
Samples in exp. no. B	Results		
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
b0	15,718	27,954	1.78
b1	19,163	42,890	2.24
b2	21,514	44,441	2.07
b3	18,186	42,176	2.32

Notes: b0—before devulcanization.

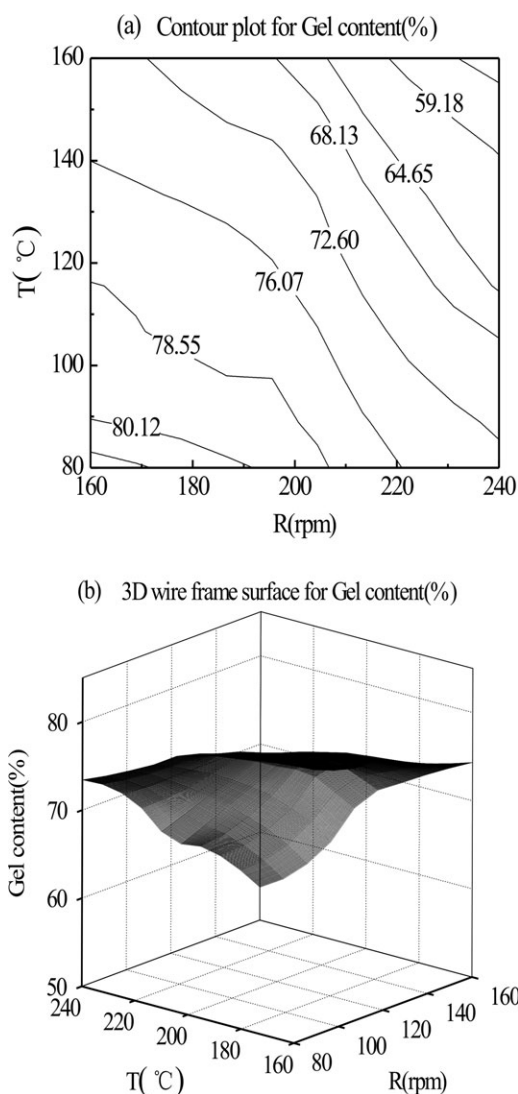
lar chains started to break or spin off, but still contained large molecular weight, which lead to a relative increase of molecular weight. When the temperature increased excessively, the cross-linked structure was broken so seriously that large amount of fractured chains formed from various macromolecular chains, ultimately lead to a decline in molecular weight again.

### Devulcanization Level

The devulcanization level can be indicated by gel fraction or crosslink density. Figures 4 and 5 show contour plot and 3D wire frame surface for gel fraction and crosslink density with respect to devulcanization temperature and screw speed, respectively. It is evident that both gel fraction and crosslink density decreased with the increasing temperature and the screw speed. Specifically, the gel fraction ranged from about 81% to 53%, whereas the crosslink density was changed between  $6.5 \times 10^{-5}$  mol·cm<sup>-3</sup> to  $2.5 \times 10^{-5}$  mol·cm<sup>-3</sup> (the gel fraction and the crosslink density of GTR powder were 87%,  $14.76 \times 10^{-5}$  mol·cm<sup>-3</sup>, respectively). These results indicated the plasticity and reprocessing performance of GTR were restored to a certain extent after the broken crosslinked structure due to the thermal-mechanical shearing devulcanization.



**Figure 3.** Molecular weight distribution curves of sol in different devulcanization temperature.



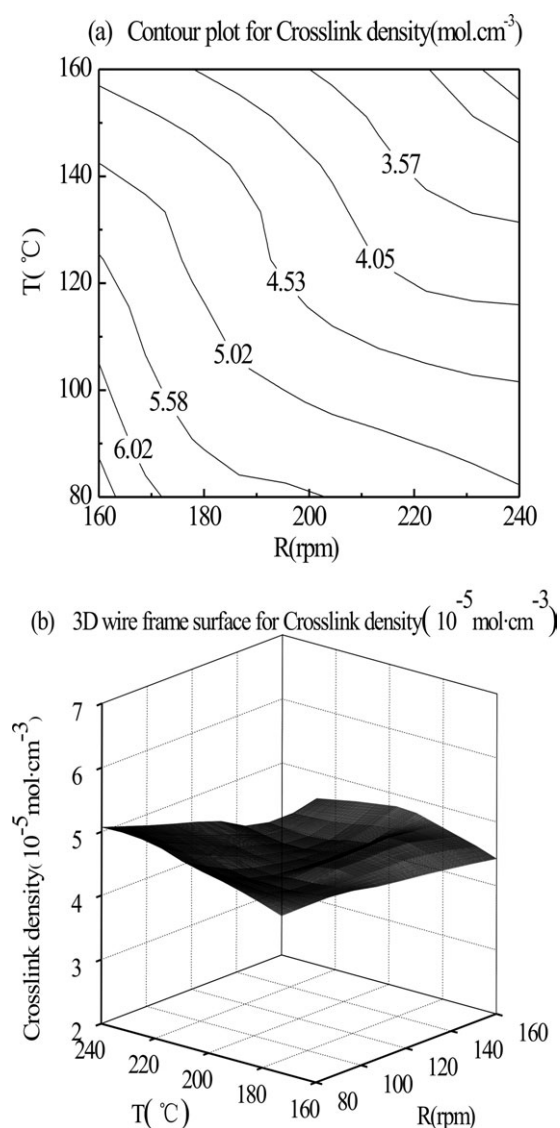
**Figure 4.** (a) Contour plot of gel content. (b) 3D wire frame surface of gel content.

### Mechanical Properties

The contour plot and 3D wire frame surface for tensile strength and elongation at break of revulcanizates are shown in Figures 6 and 7. Obviously, both the tensile strength and elongation at break reached the highest value (12.9 MPa tensile strength, 360% elongation at break) only at the appropriate extruding parameters ( $T = 180^{\circ}\text{C}$  and  $R = 100$  rpm). The variation can be well explained from the changes in microscopic structure and molecular weight. Table VI shows the mechanical properties of vulcanized GTR and DGTR. It is evident that the both the tensile strength and elongation at break of DGTR are much better than those of vulcanized GTR. Important thing is that these properties achieve or even exceed the national standard, which means the better application of reclaimed rubber obtained. These results indicated that the significance of desulfurization of GTR for improving performance.

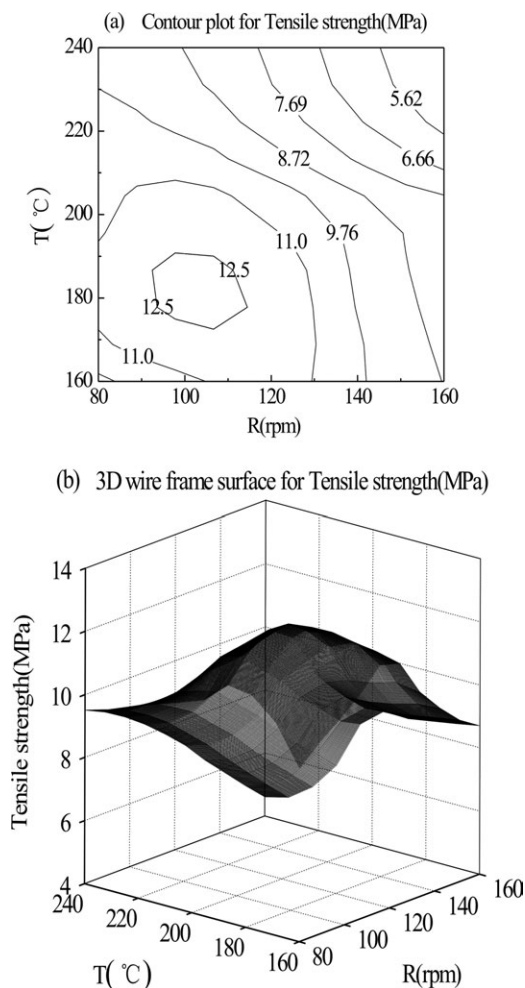
### DSC Analysis

To obtain information on vulcanized ability of DGTR, the DSC measurements were conducted. Figure 8 shows the DSC results



**Figure 5.** (a) Contour plot of crosslink density. (b) 3D wire frame surface of crosslink density.

for revulcanization of DGTR. It is clear that the thermal effects of DGTR obtained from different devulcanization processes were different. Curve 1 just showed a gentle exothermic peak, which means crosslinking reaction hardly occurred. This is because DGTR obtained from low devulcanization process still retained relatively compete crosslinked structure. During revulcanization, only a few radical molecular chains reacted with sulfur, which ultimately lead to the weak thermal effect. With the increasing intensity of devulcanization, a variety of molecular chains fractured from crosslinked structure and lots of complex reactions occurred in different degrees, which would make the reactivities of molecular chains change. As is shown in this figure, the exothermic peaks appeared from  $140^{\circ}\text{C}$  to  $220^{\circ}\text{C}$  in curve 2 and 3 obviously. However, the thermal effect in curve 3 was stronger than those in curve 2. The exothermic peak in curve 3 appeared at  $210^{\circ}\text{C}$ , whereas those in curve 2 appeared at  $200^{\circ}\text{C}$ . All these results indicated that changes in chemical structure should influence the reclaimed



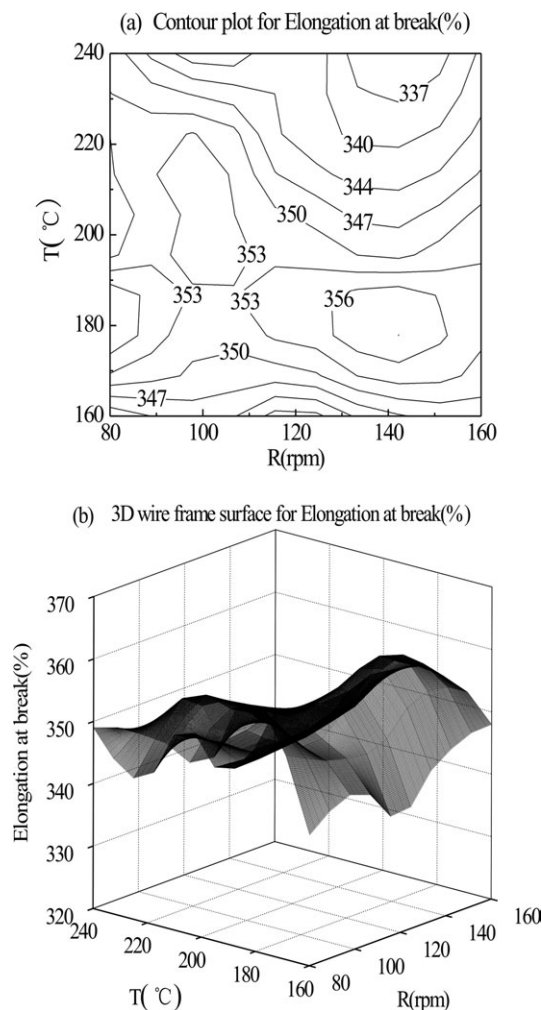
**Figure 6.** (a) Contour plot of tensile strength. (b) 3D wire frame surface of tensile strength.

rubber vulcanized ability, and thus alter the vulcanized structure which affects the mechanical properties directly.

### The Relationship between the Devulcanization Level and the Mechanical Properties of Reclaimed Rubber

Due to the significant difference in structure, the reclaimed rubber obtained from different extruding processes should be strictly divided into different types of rubber, which means it is not scientific to compare the mechanical properties based on the different degrees of cure in final products. As shown in Table VII, the degree of cure (also indicated by gel fraction and crosslink density) of revulcanizate showed no relevance with the significantly different mechanical properties especially tensile strength.

Actually, the devulcanization level is the central cause of various mechanical properties. It reflected the characteristic of vulcanized structure indirectly. Figure 9 shows the validation results of the relationship between the devulcanization levels and mechanical properties of revulcanizates. It is obvious that the tensile strength and the devulcanization level were not a simple linear relationship. When the gel content decreased to about 77%, and the crosslink density was about  $5 \times 10^{-5} \text{ mol}\cdot\text{cm}^{-3}$ , the tensile strength reached its highest value. This result is ascribed to the

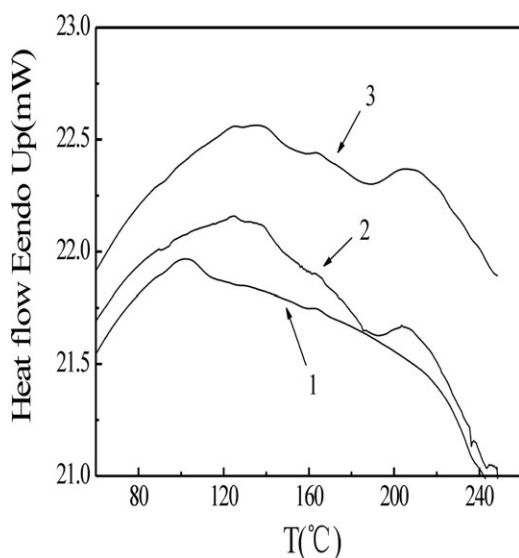


**Figure 7.** (a) Contour plot of elongation at break. (b) 3D wire frame surface of elongation at break.

changes in structure and molecular weight. At a relative low devulcanization level, the crosslink density was still so high that the blocked orientation arrangement of the molecular chains and uneven distribution of crosslinking occurred during revulcanization. These changes caused a more uneven stress distribution, and ultimately lead to the low tensile strength obtained.<sup>24</sup> On the contrary, at excessive devulcanization level, most molecular chains were seriously fractured. Crosslinking sites were difficult to form and the degree of vulcanization was extremely low during revulcanization, which also caused the tensile strength decrease largely. Only at an appropriate devulcanization level, when the crosslinked structure of GTR destroyed to

**Table VI.** Mechanical Properties of GTR and DGTR before and after Revulcanization

Item	National standard (GB/T 13460- 2008 (China))	GTR	DGTR
	Tensile strength (MPa)		
Elongation at break (%)	360	145	360



**Figure 8.** DSC results for the devulcanization of DGTR. Notes: 1—DGTR-1 (160°C,  $r = 100$  rpm/min); 2—DGTR-2 (200°C,  $r = 120$  rpm/min); 3—DGTR-3 (220°C,  $r = 140$  rpm/min).

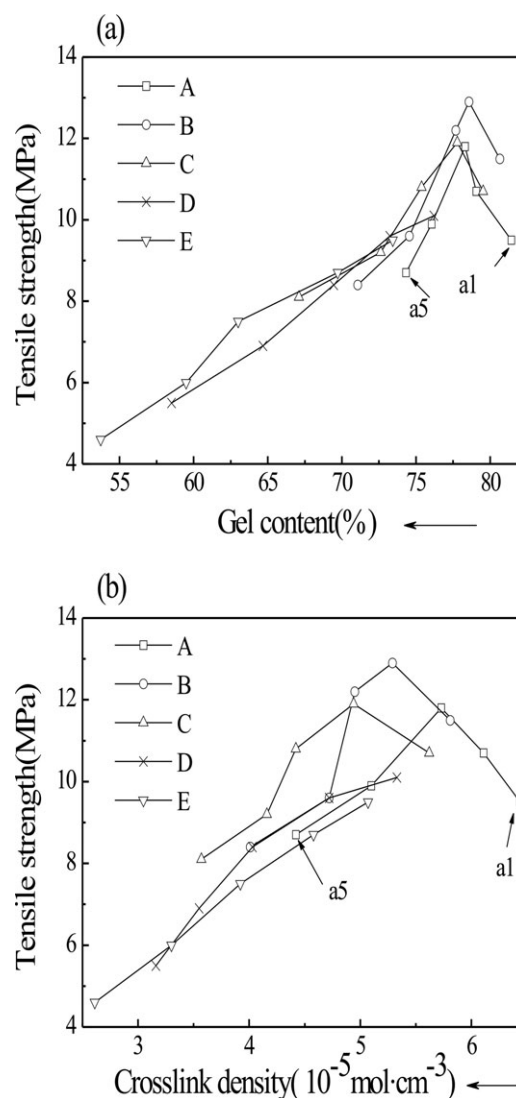
certain extent but still maintained sufficient macromolecular chains for certain degree of plasticity and deformability, the properties of reclaimed rubber would reach the optimum value.

#### Morphological Studies

Figure 10(a–c) shows the appearances of GTR before and after devulcanization. As displayed in SEM micrographs, the appearances of DGTR obtained from higher extruding process parameters (namely, high devulcanization level) became fuzzier, smoother, and ultimately presented melt shape. This result indicated the better recovery of mobility and plasticity of reclaimed rubber due to the increasing intensity of the structural breakage. The corresponding SEM micrographs of the cryogenically fractured surfaces after devulcanization are shown in Figure 10(d–f), respectively. From Figure 10(d), raw GTR after devulcanization had rough surface, winding lines, and some holes. Both the fractured surfaces in Figure 10(e,f) showed smooth surface, but more winding lines and scrappy layering emerged in Figure 10(f). These results indicated that the obtained samples was not similar in structure after devulcanization, the different devulcanization levels had a significant influence on the vulcanized structures despite the same devulcanization process, which affected mechanical property directly.

**Table VII.** Mechanical Properties and the Degree of Cure of Revulcanizate

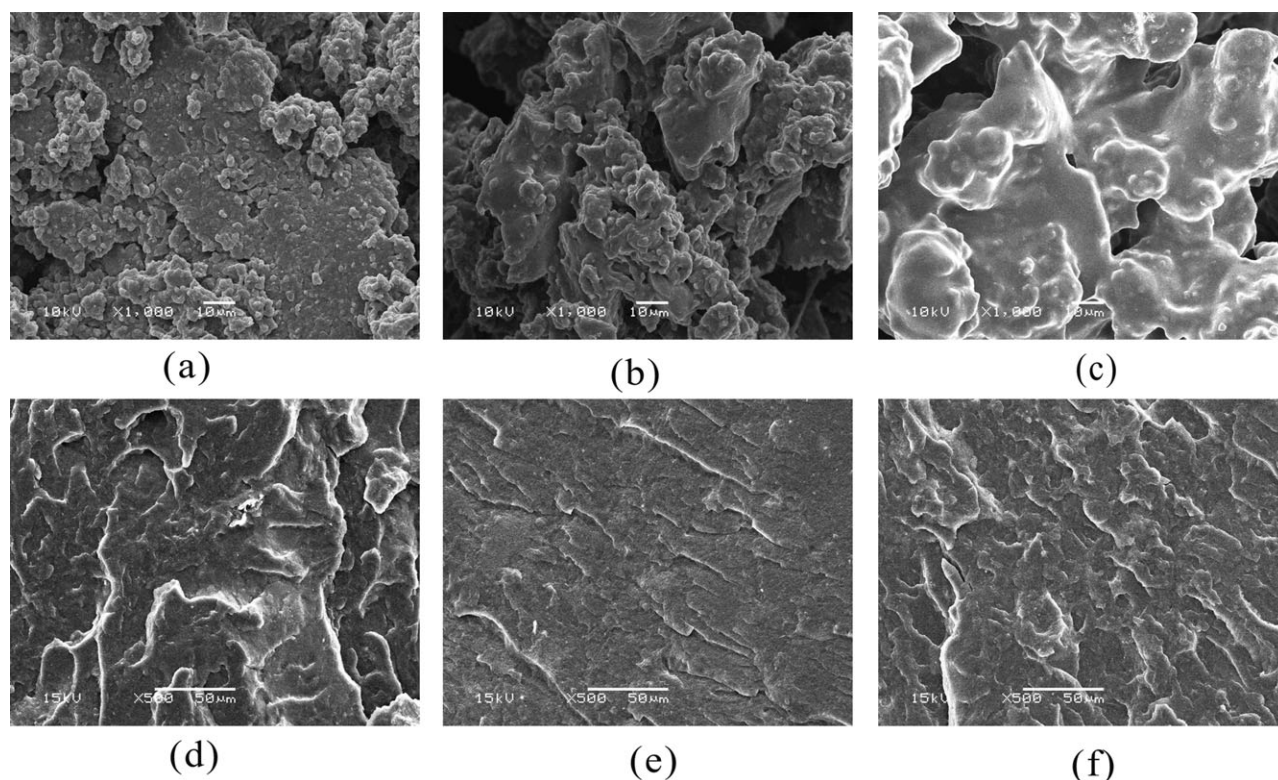
Samples in exp. no.	Tensile strength (MPa)	Elongation at break (%)	Gel fraction (%)	Crosslink density ( $10^{-4}$ mol·cm $^{-3}$ )
b1	10.7	345	89.18	5.79
b2	12.9	351	88.57	5.10
b3	11.9	354	89.24	6.31
b4	9.6	354	89.61	6.74
b5	8.7	338	88.73	5.32



**Figure 9.** Effect of gel content (a) and crosslink density (b) on tensile strength. Notes: A, B, C, D, E—Exp. no in Table I.

#### CONCLUSIONS

The devulcanization of GTR powder could be effectively carried out by extruder, and it was highly affected by devulcanization temperature and screw speed at a given screw configuration and raw materials. The FTIR and EA analyses revealed that the chemical structures changed greatly after different methodology for devulcanization (changing extruding parameters, etc.), and many complex reactions occurred on the molecular chains. The GPC measurement revealed the changes of molecular weight and molecular weight distribution in devulcanization process. The DSC revealed various vulcanized abilities and vulcanized structures of the reclaimed rubber despite the same devulcanization procedure the samples were processed. The appearances displayed in SEM micrographs not only further confirmed the different structures in reclaimed rubber obtained from different extruding processes but also showed the distinct surfaces of corresponding devulcanized products. All these analyses, combined with sufficient experiments on verification of the relationship



**Figure 10.** SEM photographs of GTR and DGTR before and after revulcanization. Notes: (a)—GTR; (b)—DGTR-1 (180°C,  $r = 100$  rpm/min); (c)—DGTR-2 (220°C,  $r = 140$  rpm/min). (d–f)—Revulcanized rubber of GTR, DGTR-1, DGTR-2, respectively.

between the devulcanization level and mechanical property, indicated that an appropriate devulcanization level obtained from appropriate extruding parameters would contribute greatly to the optimum physical property in product. When the gel content decreased to about 77% and the crosslink density was about  $5 \times 10^{-5}$  mol·cm<sup>-3</sup>, the tensile strength and elongation at break reached 12.9 MPa, 360%, respectively.

#### ACKNOWLEDGMENTS

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