Structure and Performance of Reclaimed Rubber Obtained by Different Methods

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ABSTRACT: Four different reclaiming methods involving important reclaiming factors such as temperature, shear force, and atmosphere were used to reclaim ground tire rubber. The structure and performance of the reclaimed rubber were investigated. The reclaimed samples were all found to be mixtures of three parts: the sol part, a loosely crosslinked gel part, and low molecular substances. For a reclaimed product to have both good processability and mechanical properties, the ideal structure should be that the sol fraction and its molecular weight (M_n) are as high as possible. However, the high sol fraction and high M_n cannot be reached at the same time because of the nonselective scission of the main chain and crosslink bonds. Thus, for a reclaimed rubber to have high quality, the presence of some amount of gel fraction is essential. Our preliminary results showed that the recommended reclaiming method would be a process under oxygen-free atmosphere, without severe shear force, and at relative low temperature. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 999–1007, 2013

INTRODUCTION

With the fast development of the auto industry, the production of waste rubbers is also growing rapidly. Because vulcanized rubbers having a three-dimensional crosslinked structure do not decompose easily, reusing waste rubbers in an efficient and environmentally friendly manner is not only good for resolving pollution problems but also conducive to saving raw materials. Thus, the recycling of waste tire rubber, which accounts for the majority of waste rubber, appears especially important.

Pulverizing the waste tire rubber using ambient[1] or cryogenic grinding[2] is one way to recycle waste tires. However, the direct addition of ground tire rubber (GTR) to virgin rubber results in poor properties due to the undestroyed crosslinked structure of the GTR and the weak interfacial adhesion between the GTR particles and matrix rubbers.[3] Reclaiming the waste tires is preferable to other recycling methods in solving these problems. During the reclaiming process, the three-dimensional network is broken down at the crosslink sites or in the main chain bonds.[4] The crosslink bond scission (called devulcanization) changes the

vulcanizates back to its original form, while the main chain scission will shorten molecular chains causing a deterioration of mechanical properties. An ideal reclaiming process should selectively break the crosslink bonds, leaving the main chain intact.

Basic understandings of the cleavage of crosslink and main-chain bonds are mainly focused on two theories: bond energy difference theory[5] and elastic constant difference theory.[6] Based on these two theories, a number of techniques have been developed to reclaim the crosslinked rubbers including the GTR. These techniques include mechanical,[7] thermo-mechanical,[8] microwave,[9] ultrasonic,[10] twin-screw extruder,[11,12] and some chemical reclaiming processes.[13–15]

However, the quality of the rubbers, especially the GTR, reclaimed from these methods is not good enough to be widely used in rubber products. The scrap tire is of low quality because of the various aging effects during long-time use. What is more important is that hardly could these methods selectively break the crosslinks without destroying the main chain during the reclaiming process. On the other hand, a GTR composed of
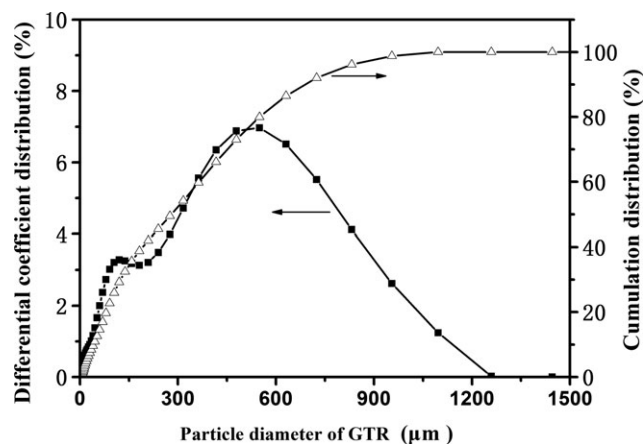
Figure 1. Particle size distribution of GTR.

mainly NR and SBR is more apt to main-chain scission than some saturated rubber such as EPDM.[16] Murakami et al.[17] proposed that degradation occurred at crosslinked sites on the secondary carbon atom adjacent to the crosslink moiety when *cis*-polyisoprene was heated beyond 200°C, especially when the crosslink was broken. Farris et al.[18] elaborated that the conjugated double bond formed by main-chain scission resulted in a deterioration of properties. If the crosslink bonds cannot be broken selectively, it is important to find out what structure of the reclaimed rubber will lead to good processing and mechanical properties and what reclaiming process will help us realize this goal.

In this study, four different reclaiming methods combining several important reclaiming factors, such as temperature, shear force and atmosphere, were used to reclaim the GTR. The effects of the reclaiming conditions on the structure and properties of the reclaimed rubbers were thoroughly discussed, based on which a feasible reclaiming process was proposed.

EXPERIMENTAL SECTION

Materials

The GTR used in this study was kindly supplied by Qiangwei Rubber and Plastics Technology (China). The exact composition of the GTR was unclear. The average particle size was 22 mesh, and the particle size distribution shown in Figure 1 was obtained by a laser particle size distribution analyzer (LS-Pop3, OMEC Technology, China). From Figure 1, we can see that most of the GTR particles are smaller than 900 μm, and with the majority between 300 and 800 μm. The NR was provided by Xishuang Banna Eastwind Farmland, China. Pine tar was

bought from Shanghai Jiaote Chemical Industry. The rubber regeneration activator 420 (RA 420) and diphenyl disulfide (DD) were purchased from Henan Jinfeng Chemical Industry and Acros Organics, USA, respectively. Carbon Black N330 was from Tianjin Dolphin Carbon Black Development. Other compounding ingredients, such as sulfur (S), zinc oxide (ZnO), and the accelerator TBBS, were bought locally. Solid carbon dioxide was obtained from Beijing Tiangang, China.

Reclaiming Methods

To observe the effects of different reclaiming conditions on the structure and properties of the reclaimed rubber, four different reclaiming methods were used, and their main differences are shown in Table I.

Low-Temperature Shear Reclamation (LTSR). A two-roll mill (diameter 160 mm) with a roller spacing of 0.5 mm was used to reclaim the GTR premixed with pine oil (15 wt %) and RA 420 (0.5 wt %). During the reclaiming process, cooling water was circulated to maintain a low reclaiming temperature (<40°C), and the effect of shearing time (5, 10, 20, 30, and 40 min) was observed.

High Temperature Shear Reclamation (HTSR). A two-roll mill heated up to 180°C was used to reclaim the GTR premixed with pine oil (15 wt %) and RA 420 (0.5 wt %). Effect of different shearing time (5, 10, 20, 30, and 40 min) on the reclaiming effects was observed.

Twin-Screw Extruder Reclamation (TSER). Reclamation was carried out by using an intermeshing corotating twin-screw extruder (Model HTG-36, Nanjing Rubber and Plastics Machinery Factory, China). The extruder has 12 heating/cooling zones and a screw diameter of 37 mm with an *L/D* ratio of 52. The temperature of the first to the fourth zone was fixed at 150°C, that of the tenth to the eleventh zones was fixed at 150°C, and that of the twelfth zone was fixed at 100°C. The temperature of the fifth to the ninth zones, the barrel temperature, was set at three levels: 200, 220, and 240°C. The screw speed and the feed rate were constant in this study. Furthermore, the combination of reversed thread components and kneaders was used to build up enough pressure for reclamation. The reclamation additives were pine oil (4.0 wt %) and RA420 (0.5 wt %).

Supercritical Carbon Dioxide ($_{sc}CO_2$) Reclamation (SCO$_2$R). The GTR (50 g) was reclaimed in supercritical CO_2 by using 4 g of diphenyl disulfide (DD) as a reclaiming reagent in a high-pressure reactor (inner volume 1800 mL) obtained from Weihai Hangyu Chemical Industry, China. After purging the air in the reactor with dry ice, we added the preweighed GTR, DD, and some more dry ice. The reactor was immediately sealed off, heated

Table I. Comparisons of Reclamation Conditions of Four Different Methods

Reclaiming methods	Shear force	Atmosphere	Temp (°C)	Reaction time (min)	Reclaiming agents	RA content (wt %)
LTSR	Strong	Air	<40	5–40	RA420	0.5
HTSR	Strong	Air	180	5–40	RA420	0.5
TSER	Very strong	Vacuum	200–240	≈5	RA420	0.5
SCO$_2$R	Mild	scCO$_2$	180	120–360	DD	6.0

Table II. Formulation of Reclaimed Rubber Compound (phr)

Ingredients	Reclaimed rubber	ZnO	SA	S	TBBS
Weight	100	2.50	0.34	1.20	0.80

up to a temperature (180°C) at a heating rate of 3°C min^{-1}, and maintained at this temperature for various soaking times (2, 3, 4, 5, and 6 h). Then, the reactor was cooled down to 80°C and decompressed. The reclaimed rubber was taken out of the reactor.

Characterization

Sol Fraction Measurements. Because the composition of the GTR was unclear, thermal gravimetric analysis (TGA) was used to determine the residual rubber content in the insoluble part and then a modified equation was proposed to calculate sol fraction. After the reclamation, Soxhlet extraction was used to separate the soluble fraction from the insoluble. First, acetone was used to remove the low molecular weight substances such as processing oils for 12 h. Second, after the sample was distilled and dried in vacuum at room temperature to constant weight (m_1), toluene was used as solvent to separate the soluble from the insoluble in the residue for 72 h. Distilled and dried in vacuum at room temperature to another constant weight (m_2), the insoluble part was then measured by TGA. The actual sol fraction was calculated by eq. (1):

Actual sol fraction (%) = weight of reclaimed rubber/
molecular weight of pure rubber incompound

$$= (m_1 - m_2)/((m_1 - m_2) + m_2 \times a\%) \times 100\%, \quad (1)$$

where $a\%$ is the percentage loss of the first thermogravimetric loss step of the insoluble part.

Percent of Devulcanization (Crosslink Density)

The crosslink density of the gel of a sample was measured by the swelling technique using toluene as solvent. Small pieces of the sample were immersed in toluene for 72 h at 30°C. The crosslink density was calculated by using the Flory–Rehner equation[19] and an interaction parameter X of 0.393 for toluene. A modified Kraus correction factor C of 1.11 was used because of the presence of carbon black.[20] The percent of devulcanization was calculated by eq. (2):

$$\text{Percent devulcanization} = (v_1 - v_2)/v_1, \quad (2)$$

where v_1 and v_2 are the crosslink densities of the sample before and after the reclamation, respectively.

Gel Permeation Chromatography Measurement

The molecular weight and its distribution of the sol component of all the obtained samples were determined with gel permeation chromatography (GPC515-2410 System, Waters, USA). The gel permeation chromatography (GPC) analyses were performed at a tetrahydrofuran (THF) flow rate of 1.0 mL min^{-1} at 35°C. Polystyrene was used as the standard.

Mooney Viscosity

The Mooney viscosity of the devulcanized samples was measured according to ASTM D 2084 and ASTM D 1646 (ML100°C (1+4) min) by a Mooney viscometer (M3810C, Beijing Huanfeng Chemical Industry, China).

Cure Characteristic Measurement

The cure characteristics of the reclaimed rubber and NR/reclaimed rubber blends were measured by a no-rotor rheometer (Beijing Huanfeng Chemical Industry, China) at 145°C.

Determination of Mechanical Properties

Prior to the revulcanization, the reclaimed samples with curatives were homogenized and compounded by a two-roll mill. The formulations of the revulcanized reclaimed rubber and its blend with raw NR are shown in Tables II and III, respectively. The compounds were vulcanized in a platen press at 15 MPa and 145°C, according to the ASTM D 2084-07. Dumbbell-shaped tensile specimens were punched out from compression molded sheets along the mill grain direction. Physical properties were measured by using a CTM4104 testing machine (Shenzhen SANS Testing Machine, China) according to the ASTM D 2240 (hardness) and the ASTM D 412 (tensile strength) at room temperature.

Thermogravimetric Analysis

For the determination of the rubber content in the gel part, thermogravimetric analysis was performed with a thermogravimetric analysis (TGA) analyzer (Mettler-Toledo, Switzerland) at a heating rate of 10°C min^{-1} under a nitrogen atmosphere.

Scanning Electron Microscopy

The fracture surfaces of the revulcanizates were observed by a Hitachi S-4700 scanning electron microscope (SEM), Japan. The fracture surfaces of the tensile specimens were vacuum-plated with gold for electrical conduction.

RESULTS AND DISCUSSION

Sol Fraction Measurement

The actual sol fractions of the reclaimed rubber from four different methods are shown in Table IV. The sol fraction resulting from both main chain scission and crosslink bond scission indicates the extent of rubber network breakage.

From the comparison between LTSR and HTSR, the effect of temperature on the devulcanization of GTR under shear force and oxygen atmosphere can be evaluated. At low temperatures (<40°C), the sol fraction increases with increasing shearing time. The reclaimed rubbers by LTSR are incapable of flowing because of their low sol fractions, as confirmed later by the Mooney viscosity and recurring behavior. The sol fractions obtained by LTSR may be due to the combination of oxygen and molecular free radicals from shear force. Compared with the low temperature, dramatic increase of sol fraction is observed at high temperature (180°C) at the same shearing time. But the sol fraction obtained by HTSR first increases and then decreases over time, probably because of a more extensive

Table III. Formulation of Reclaimed Rubber and Raw NR Blends (phr)

Ingredients	NR	Reclaimed rubber	Carbon black N330	ZnO	SA	S	TBBS
Weight	80	20	40	2.50	0.34	1.20	0.80

Table IV. Characterization of Reclaimed Rubber Obtained by Different Methods

Samples	Temperature (°C)	Reaction time (min)	Sol fraction (%)	Percent devulcanization (%)	Mooney (ML100°C (1+4) min)	M_n	PDI[a]
LTSR-1	12	5	7.8	42.8	229	19502	1.7
LTSR-2	12	10	12.5	60.6	205	18530	1.9
LTSR-3	12	20	16.4	63.5	164	17853	2.2
LTSR-4	12	30	19.0	70.9	132	18032	2.6
LTSR-5	12	40	22.8	75.5	111	16530	2.7
HTSR-1	180	5	30.3	63.7	37	11150	4.7
HTSR-2	180	10	64.0	84.4	17	10342	5.1
HTSR-3	180	20	41.1	77.0	29	8205	5.8
HTSR-4	180	30	33.8	71.1	35	7304	6.4
HTSR-5	180	40	26.8	55.9	50	3311	9.2
TSER-1	200	5	39.8	67.0	35	14076	2.6
TSER-2	220	5	44.4	69.3	28	13779	3.7
TSER-3	240	5	50.0	77.6	15	10043	5.3
SCO₂R-1	180	120	36.3	72.7	75	8926	3.2
SCO₂R-2	180	180	38.0	73.9	64	7986	3.8
SCO₂R-3	180	240	41.0	78.4	60	7161	3.7
SCO₂R-4	180	300	45.7	76.5	48	7980	4.2
SCO₂R-5	180	360	43.4	75.5	50	2593	10.2

[a]Poly dispersity index.

generation of reactive radicals and the complex chemical transformations taking place at long shearing times and high temperatures. These chemical transformations include the breakup of main chain and polysulfidic, disulfidic, and monosulfidic crosslinks, transformation of sulfidic crosslinks into cyclic sulfidic structures on the elastomer backbone, and transformation of polysulfidic crosslinks into disulfidic and monosulfidic crosslinks.[21] These transformations with increasing devulcanization time leads to the formation of new intermolecular and intramolecular bonds resulting in a decrease of the rubber sol fraction above a certain shearing time. Thus, we can conclude that the GTR can be effectively devulcanized by shear force in the presence of oxygen, especially at high temperatures. But the presence of oxygen at high temperatures has side effects resulting in the scission of the main chain, as will be further confirmed by the molecular weights of the sol fractions.

From TSER results, we can see that the sol fraction increases with the increase of barrel temperature. The sol fraction can reach 50.0% at 240°C, indicating that the network was seriously broken. The sol fraction of rubber reclaimed by TER is almost entirely caused by shear force, heat, and RA420 because of the exclusion of oxygen in the use of twin-screw extruder and vacuum pump. In other words, the HTSR and TSER results indicate that shear force at high temperature can create a high sol fraction in reclaimed rubber regardless of the presence of oxygen, but cause the unselective scission of both the main chain and crosslink bonds.

SCO₂R, reported as an effective[22] or even complete[23] chemical reclaiming method, can give a high sol fraction by thermal degradation and chemical reactions. As a result, the GTR can be effectively devulcanized without shear force and oxygen, consistent with the results shown in Table IV. The above analysis shows that the temperature, shear force, reaction time, oxygen, and reclaiming agent are all determining factors for the devulcanization of the crosslinked rubber, and combinations of these factors can effectively break the crosslinked network through different reclaiming mechanisms, resulting in different sol factions and reclaimed structures.

Crosslink Density of Gel Fraction

The crosslink density of rubber network decreases during the devulcanization process, and the percent of devulcanization is used for assessing the level of network destruction. The results of percent of devulcanization for different reclaiming methods are shown in Table IV. The percent of devulcanization for LTSR, like the sol fraction, increases with increasing shearing times. Such correlation between sol fraction and percent of devulcanizaiton is also found in HTSR, TSER, and SCO₂R.

To determine the ratio of main-chain to crosslink scission during devulcanization, Horikx's theory[24] is used. According to Horikx's theory, a theoretical relationship between the soluble fraction after degradation of a network and the relative decrease in crosslink density is established.[19] There are two limiting cases: (1) only main chain scission taking place and (2) only crosslink scission taking place. The relative decrease in crosslink density for the first case is given by eq. (3):

$$1 - \left(\frac{\nu_f}{\nu_i}\right) = 1 - \left[\frac{\left(1 - s_f^{1/2}\right)^2}{\left(1 - s_i^{1/2}\right)^2}\right], \qquad (3)$$

where s_i is the sol fraction of the untreated vulcanizate, s_f is the soluble fraction of the obtained reclaimed rubber, ν_i is the
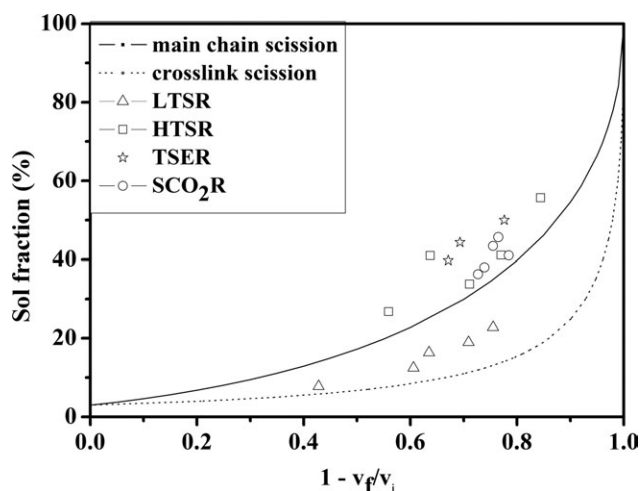
Figure 2. Sol fraction of reclaimed rubber against relative decrease in crosslink density under different reclaiming conditions.

crosslink density of the untreated vulcanizate, and v_f is the crosslink density of the obtained reclaimed rubber.

For the second case, the soluble fraction is related to the relative decrease in crosslink density by eq. (4):

$$1 - \left(\frac{v_f}{v_i}\right) = 1 - \left[\frac{\gamma_f \left(1 - s_f^{1/2}\right)^2}{\gamma_i \left(1 - s_i^{1/2}\right)^2}\right], \quad (4)$$

where the parameters γ_i and γ_f are the average number of crosslinks per chain in the remaining gel before and after reclamation, respectively.

Figure 2 shows the sol fraction of the reclaimed rubber as a function of the relative decrease in crosslink density for different reclaiming methods. The solid curve corresponds to the situation where only main chains are broken [eq. (3)], and the dashed curve corresponds to the case where only crosslinks are broken [eq. (4)]. For crosslink scission, almost no sol is produced until most of the crosslinks have been removed. In the case of main chain scission much more sol is produced for the same decrease in crosslink density. The LTSR results are all located between the two curves, an indication that the reclamation is caused by both main chain scission and crosslink scission. In addition, with increasing shearing time or sol fraction, the data move farther away from the crosslink scission curve, meaning that the reclamation is mainly due to main chain scission. Thus, pure shear force breaks both the main chain and crosslinks at low temperatures. The HTSR, SCO$_2$R, and TSER results, unlike the LTSR results, are all positioned above the main chain scission curve, meaning that the reclamation is all controlled by main chain scission resulting from the thermal degradation under high temperatures. Furthermore, because of the presence of oxygen and shear force, lots of main chain free radicals were produced to promote the main chain scission. With the protection of $_{sc}$CO$_2$ and the absence of shear force, SCO$_2$R theoretically can be well controlled to obtain different sol fractions. But the purpose of using SCO$_2$R is to obtain a high sol fraction by employing high amounts of reclaiming

agents, long reaction times, and at high temperatures, all of which result in main chain scission. From the analysis above, we can conclude that the reclaiming process is dominated by main chain scission under the conditions of strong shear force and high temperatures regardless of the presence of oxygen, but the reclaiming process is dominated by crosslink scission at low temperatures. A high sol fraction is gained at the expense of breaking the main chain, while a low sol fraction is mainly the result of crosslink scission in chemical reclaiming methods in the absence of oxygen.

Molecular Weight of Sol Component of Reclaimed Rubber

To further confirm the main-chain scission during reclamation, we determined the molecular weight of the sol fraction by GPC measurements, and the results are shown in Table IV. Generally speaking, NR—the main component of GTR—consists of two fractions with different molecular weights: a high molecular weight (M_n) of $\sim 2.5 \times 10^6$ g mol^{-1} and a low molecular weight (M_n) of $\sim 1 \times 10^5$ g mol^{-1}. During reclamation, the low molecular weight fraction, which contains fewer crosslinks, will preferentially be released from the network. After reclamation these low molecular weight components will preferentially end up in the sol fraction. Table IV shows that the M_n of the sol fraction is of the order of 10^4 or even lower regardless of the type of reclaiming method. These results support the idea that extensive main chain scission has occurred during the reclamation along with crosslink scission. Besides, a higher sol fraction usually leads to a lower M_n and a wider PDI, which means that severer main chain scission occurs during the process of gaining higher sol content. Thus, strong shear force and thermal degradation can lead to severe main chain scission and a dramatic decrease of molecular weight, especially at high sol fractions.

Through the analysis of the structure of the reclaimed rubber by characterizing sol fraction, percent devulcanization and the M_n of the sol, we can learn that the increase in sol fraction is inevitable based on the breakage of main chain, and the higher the sol fraction, the severer the main chain scission. Thus, to break the network effectively and reduce the main chain scission as much as possible, we need a high percent devulcanization and a low sol fraction.

ML100°C (1 + 4 min)

Usually the flowability and processability of elastomeric compounds are determined by the Mooney viscosity value, and the Mooney viscosity value of a reclaimed rubber is determined by the rubber's structure and composition. Generally, the more the low molecular weight substances such as processing oils, the higher the sol fraction, and the lower molecular weight of the sol fraction, the lower the Mooney viscosity value. Furthermore, we can speculate that the higher the percent of devulcanization, the lower the Mooney viscosity value. Table IV shows the Mooney viscosity values of all reclaimed rubber samples, and Figure 3 shows the correlation between the Mooney viscosity and the sol fraction or M_n. We can see from Figure 3 that the Mooney viscosity of the reclaimed rubber decreases with the increase of sol fraction or decrease of the M_n because of the plasticization effect of the low molecular weight sol fractions, especially those obtained from severe main chain degradation.
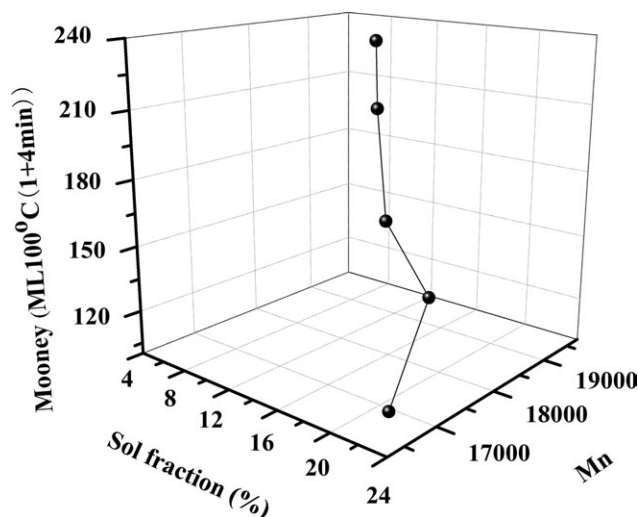
Figure 3. Correlation between Mooney values and sol fraction or M_n of samples reclaimed by LTSR.

Such correlation between the Mooney viscosity and the sol fraction or M_n is also the explanation for the large differences in Mooney value between the reclaimed samples obtained by LTSR and HTSR, as shown in Table IV.

Conversely, the role of low molecular weight substances in the processability of the reclaimed rubber can be clearly seen from the comparison between HTSR-3 and SCO2R-3, which have similar sol contents and molecular weights. Because of the forward addition of processing oils (15 wt %) by HTSR, the Mooney viscosity of the rubber reclaimed by HTSR is much lower than that of the rubber reclaimed by SCO2R at the same sol content and M_n. To further strengthen the role of processing oils in improving the processablity of the reclaimed rubber, the rubbers reclaimed by LTSR and HTSR were extracted by acetone for 24 h to remove the processing oils. After the extraction of about 14 wt % of the processing oils, the Mooney viscosity of the extracted reclaimed rubbers increases sharply, as shown by Figure 4. The role of addition of processing oils is not only in improving the processability of the reclaimed rubber, but also in facilitating the impregnation of reclaiming agent into the vulcanized network. Such impregnation under the protection of vapor or other oxygen-free medium is apt to the uniformly disperse the reclaiming agent in the network. As a result, the reclaiming process can take place evenly in the network, resulting in a continuous uniform structure for the reclaimed rubber.

Cure Behavior
The cure behavior of various reclaimed rubber samples are shown in Figure 5(a), and their cure recipes are shown in Table II. We can see that all the reclaimed samples are well revulcanized with the addition of curing agents, indicating the presence of active functional sites characteristic of reclaimed rubber.[7]

Figure 5(a) shows that different revulcanized rubbers have more or less the same scorch time and optimum cure time. But blends of various reclaimed rubbers with NR have longer scorch times than the corresponding reclaimed rubber cured individually, as shown in Figure 6, because of the crosslinked gel part in the reclaimed rubber.
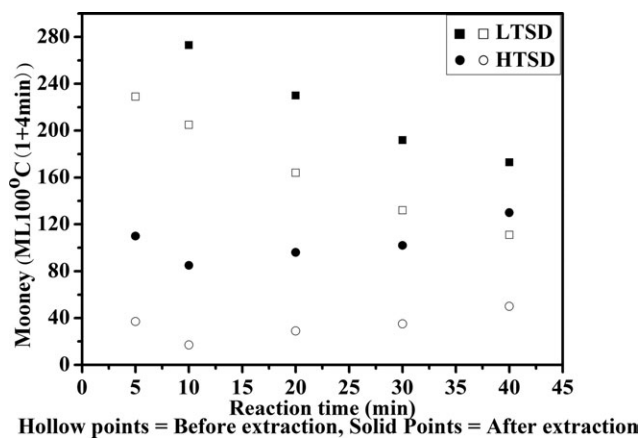

Figure 4. Mooney viscosity (before and after extraction by acetone) of reclaimed rubbers by LTSR and HTSR.

During the revulcanizing process, the diffusion of sulfur from the rubber matrix to the crosslinked gel part of the reclaimed rubber lowers the concentration of sulfur in the rubber matrix.

Generally, the minimum torque, which is a measure of the stock viscosity, mirrors the processability of the reclaimed samples.
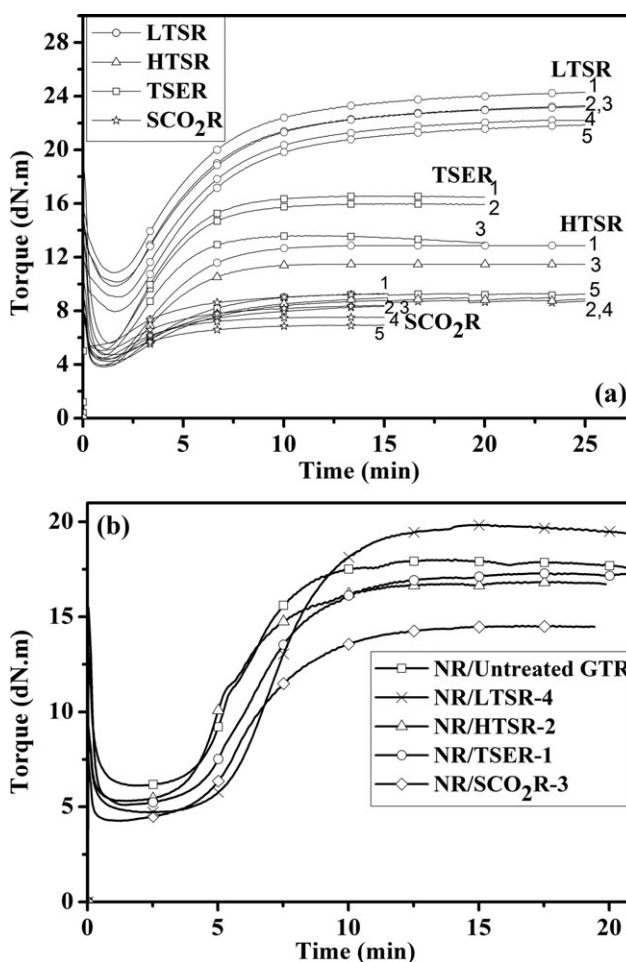

Figure 5. Cure behavior of reclaimed rubber samples and selected blends with raw NR: (a) samples reclaimed by LTSR, HTSR, TSER, and SCO2R; (b) blends with raw NR.

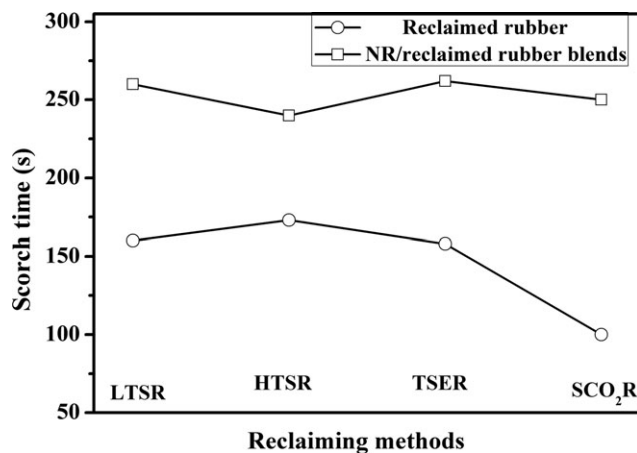**Figure 6.** Scorch time of the reclaimed rubber individual vs. their blends with NR.

We can see from Figure 7 that the minimum torque of rubbers reclaimed by LTSR is much higher than those of rubbers reclaimed by other methods. Visual inspections showed that the samples LTSR-1, LTSR-2, and LTSR-3 were hardly flow, in agreement with Mooney viscosity results.

Furthermore, the value of △torque of a revulcanizate, which is calculated by subtracting the minimum torque from the maximum torque, is related to the crosslink density of the revulcanizate. We can clearly see from Figure 7 that samples reclaimed by LTSR exhibit the highest △torque. On the other hand, samples reclaimed by SCO$_2$R show the lowest △torque because of the high percent of devulcanization and low sol fraction obtained by LTSR, both of which produce enough active sites promoting the curing process. However, samples reclaimed by SCO$_2$R experience serious main chain degradation producing many short rubber chains with low molecular weight. In addition, the residual DD—the reclaiming agent for SCO$_2$R—seriously impedes the curing process discussed in detail by our previous work.[23] Both phenomena reduce the crosslink density of samples reclaimed by SCO$_2$R. Another noteworthy phenomenon is that △torque decreases with increasing sol fraction irrespective of the reclaiming method. During the revulcanizing process, the curing agents
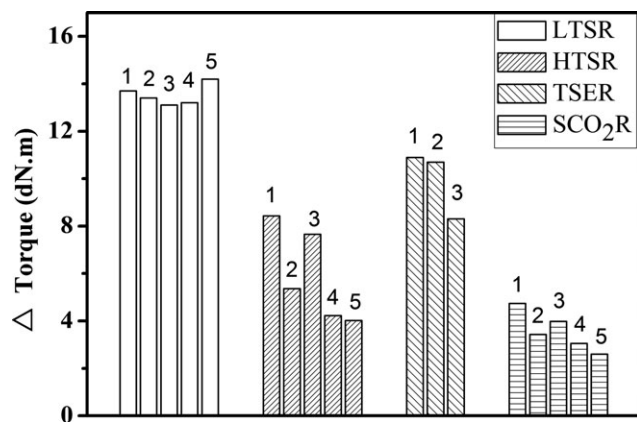

Figure 7. Comparisons of △Torque of rubbers reclaimed by different reclaiming methods.

Table V. Mechanical Properties of Revulcanized Reclaimed Samples

Samples	Tensile strength (MPa)	Elongation at break (%)	100% modulus (MPa)	Hardness (Shore A)
LTSR-1	11.4	324	2.82	74
LTSR-2	11.2	320	2.80	72
LTSR-3	11.3	325	2.58	70
LTSR-4	10.7	332	2.55	70
LTSR-5	10.9	341	2.52	69
HTSR-1	6.4	226	2.51	57
HTSR-2	3.4	185	1.81	47
HTSR-3	5.0	210	2.02	58
HTSR-4	3.2	148	2.20	59
HTSR-5	2.9	127	2.46	62
TSER-1	6.0	221	2.00	57
TSER-2	4.4	87	–	75
TSER-3	3.2	94	–	70
SCO$_2$R-1	2.7	273	0.74	40
SCO$_2$R-2	2.5	253	0.87	41
SCO$_2$R-3	3.2	238	1.19	44
SCO$_2$R-4	2.0	260	0.82	43
SCO$_2$R-5	1.8	223	0.80	37

are more inclined to disperse in the sol part than to pass into the crosslinked gel part. Thus, the higher the amount of sol parts with short rubber chains, the harder the revulcanization of the reclaimed rubber containing sol and gel parts.

Figure 5(b) shows the cure characteristics of blends of NR with selected rubbers reclaimed by different methods and untreated GTR at the ratio of 80 : 20. The selected reclaimed samples are LTSR-4, HTSR-2, TSER-1, and SCO$_2$R-3, and the cure recipes are shown in Table III. Similar to the corresponding reclaimed rubber samples, the blends of NR with the samples reclaimed by LTSR exhibit the highest △torque, while the blends of NR with the samples reclaimed by SCO$_2$R exhibit the lowest △torque. Blends of untreated GTR with NR show the highest minimum value among the blends studied, indicating that the processability of a blend is improved by a reclaiming process.

Mechanical Properties

Table V shows the tensile strength, elongation at break, modulus at 100% elongation, and hardness of the revulcanized reclaimed samples obtained at different reclaiming conditions and recured with the recipe shown in Table II. The mechanical properties are determined by the structure of the reclaimed rubber, and the reclaimed rubber is mainly composed of the following three parts: the sol part arising from main chain and crosslink scission, the gel part with a crosslink network insoluble in toluene, and the processing oils used in the reclaiming process. We can see that the revulcanizates of samples reclaimed by HTSR and TSER at high temperatures and strong shear forces show very low tensile strength and elongation at break. Two factors may be responsible for these low mechanical properties. First, a high sol fraction with low M_n and high PDI, an indication of severe
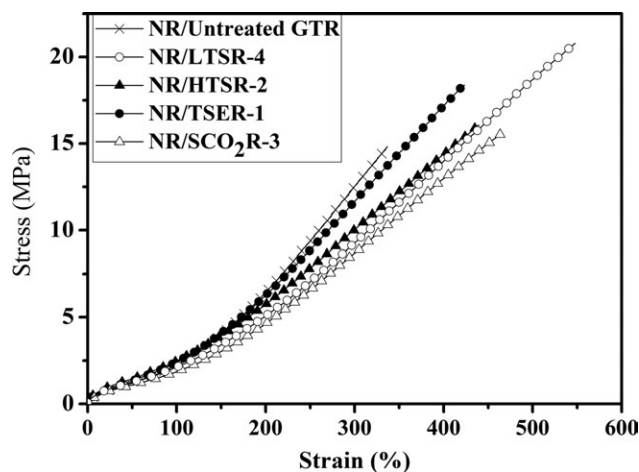
Figure 8. Stress–strain curves of NR/reclaimed rubber (80 : 20) blends.

chain degradation, is obtained in HTSR and TSER. During the process of stretching, the long molecular chains are essentially oriented in the direction of stretching, and crystallites are formed as a result, contributing to the high tensile strength and elongation at break. Thus, for the severely degraded samples, the main polymeric chain breaks before the formation of crystallites, and the values of elongation at break and tensile strength are low. The main chains of the gel parts of the samples reclaimed by TSER and HTSR are also severely broken by the strong shear force and high temperature, making the gel weak. The cure characteristics show that the gel structure of samples reclaimed by TSER and HTSR with a large amount of

short molecular chains cannot be effectively revulcanized, resulting in a sharp decrease of tensile strength and elongation at break. Samples reclaimed by SCO_2R show not only very low tensile strength and elongation at break but also lower 100% modulus and hardness than those reclaimed by HTSR and TSER. The lower properties are mainly caused by the large amount of sol parts with low molecular weight and difficulty in revulcanizing because of the residual reclaiming agent DD.

Samples reclaimed by LTSR, devulcanized by either crosslink scission or main chain scission, show relatively high tensile strength and elongation at break. A relatively low sol content, high M_n, and low PDI can effectively reduce the negative effects caused by main chain degradation. On the other hand, revulcanization can proceed efficiently because of the high percent of devulcanization. As a result, a high crosslink density can be reached, leading to increases of the tensile strength and elongation at break.

The strain–stress curves for vulcanizates of NR/reclaimed rubber blends are shown in Figure 8, and we can clearly see that the NR/untreated GTR blend shows the lowest tensile strength and elongation at break, while the blend of NR with rubber reclaimed by LTSR shows the highest tensile strength and elongation at break. The low tensile strength of the NR/untreated GTR blend is due to the undestroyed crosslink structure of the GTR and the weak interfacial adhesion between NR and the untreated GTR. Following the same trend in the unblended reclaimed rubbers, the best mechanical properties are found in the blend of NR with samples reclaimed by LTSR because of the loosely crosslinked network of the gel fraction of the LTSR reclaimed rubber and strong interfacial adhesion between the
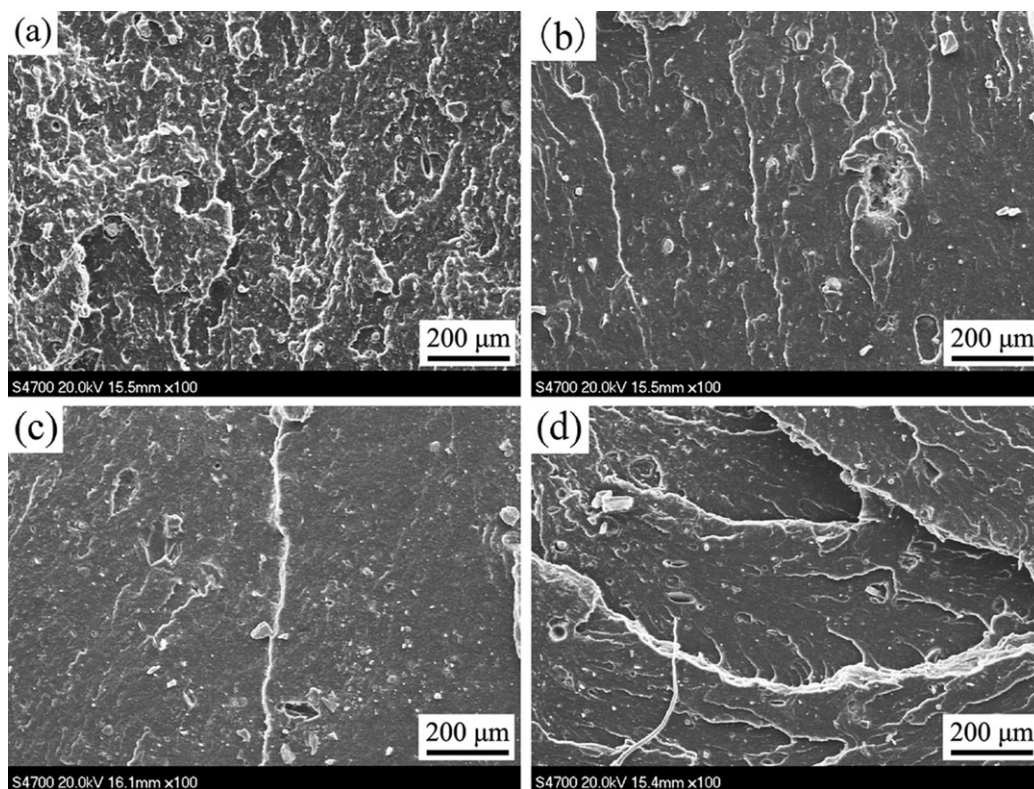

Figure 9. SEM photographs of (a) LTSR-4 revulcanizate, (b) HTSR-2 revulcanizate, (c) TSER-1 revulcanizate, and (d) SCO_2R-3 revulcanizate.

LTSR reclaimed rubber and NR, forming a continuous uniform network beneficial to good mechanical properties. Although the vulcanizates of the other blends show better properties than that of the blend of NR with untreated GTR, they are much worse than the blend of NR with LTSR reclaimed rubber. Any increase in tensile strength over that of untreated GTR is due to the improved interfacial adhesion resulting from network destruction, while decrease in tensile strength is due to the gel fraction of the reclaimed rubber acting as "weak sites" for stress transmission to its surroundings, resulting in a lower tensile strength.

In conclusion, under the actual dilemma that we can hardly selectively break the crosslink sites, to achieve both good processability and good mechanical properties of the reclaimed rubber, a loosely crosslinked gel part and the addition of processing oils are essential for such achievements. A possible reclaiming method for reaching such goals has the protection of an oxygen-free medium and operates without severe shear forces at relatively low temperatures.

SEM

Figure 9(a–d) show the SEM micrographs of the tensile fracture surfaces of revulcanizates of LTSR-4, HTSR-2, TSER-1, and SCO$_2$R-3, respectively, all at a magnification of 150×. The micrograph of the LTSR revulcanizate [Figure 9(a)] shows a rough surface with winding lines but no hole, suggesting the presence of crosslink bond, good homogeneity, and strong interaction between the sol part and loosely cosslinked gel part during the revulcanization, resulting in high tensile strength and elongation at break.

Although Figure 9(b–d) show smooth fractured surfaces, they all have irregular crack paths in different directions, making the vulcanizates vulnerable under mechanical stresses. There are many loose unrevulcanized gel particles and holes as a result of the detachment of unrevulcanized gel particles from the NR matrix, suggesting the low crosslink density of the revulcanizates in accordance with the results of the cure behavior. The low crosslink density results in very low tensile strength and elongation at break of the vulcanizates. Especially, the micrograph of SCO$_2$R revulcanizate [Figure 9(d)] shows the most loose particles and holes, an indication that this revulcanizate has the lowest crosslink density, as confirmed by the 100% modulus. A low elongation at break is probably responsible for the brittle failure evident in Figure 9(b–d).

CONCLUSIONS

A combination of several important reclaiming factors, such as temperature, shear force, reaction time, reclaiming atmosphere and reclaiming agent, can effectively devulcanize the ground tire rubber (GTR). However, the increase of sol fraction is inevitable based on the breakage of the main chain, and the higher the sol fraction, the severer the main chain scission. Strong shear force, oxygen and high temperature have negative effects because of their tendency to cause main chain scission. For good processability and mechanical properties of the reclaimed rubber, some amount of loosely crosslinked gel part and the addition of processing oils are essential. The recommended reclaiming method for reaching this goal would be a process with an oxygen-free medium, without high shear force, and at relatively low temperature. Based on such structure and reclaiming requirements, some novel effective and environmentally friendly reclaiming methods may be developed in the future.

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