Continuous Ultrasonic Devulcanization of Unfilled Butadiene Rubber

Jeong Seok Oh, A. I. Isayev

Institute of Polymer Engineering, University of Akron, Akron, Ohio 44325-0301

ABSTRACT: The devulcanization of sulfur-cured unfilled butadiene rubber (BR) with a grooved-barrel ultrasonic reactor under various processing conditions was carried out. The experiments indicated that BR had a narrow devulcanization window. Outside this window, significant degradation or no devulcanization occurred. Gel permeation chromatography (GPC) measurements were carried out with the sol part of virgin and devulcanized samples to study the breakdown of the polymeric chains. The GPC data showed a significant molecular weight reduction and a broadening of the molecular weight distribution upon devulcanization, indicating that the devulcanization and degradation of BR occurred simultaneously. The rheological properties showed that devulcanized BR was more elastic than the virgin gum. The vulcanizates of the blends of virgin and devulcanized BR showed a considerable enhancement of the mechanical properties. The thermal behaviors of the virgin and devulcanized BR were found to be different. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1166–1174, 2004

Key words: mechanical properties; recycling; rheology; rubber

INTRODUCTION

The recycling of waste rubbers is an important issue that the rubber industry is currently facing. To recycle waste rubbers, it is necessary to break down three-dimensional networks. Many methods have been developed to find more effective ways of recycling rubber, including microwaving,[1] catalysis,[2] bioreactors,[3] milling,[4] and solid-state shear pulverization.[5,6] Recently, extensive reviews on rubber recycling methods have been published.[7,8] The application of powerful ultrasound for the devulcanization of rubber is one of the most promising techniques. Ultrasonic devulcanization is a continuous process, allowing the recycling of rubbers without the use of any chemicals. The devulcanized rubber can be reprocessed, shaped, and revulcanized in the same way as the virgin rubber. Extensive studies of ultrasonic devulcanization have been carried out on various rubbers, including ground tire rubber,[9,10] natural rubber (NR),[11,12] silicone rubber,[13,14] styrene–butadiene rubber (SBR),[15] and ethylene–propylene–diene monomer (EPDM).[16]

Butadiene rubber (BR) has been widely used in tire and nontire applications because of its high resilience, abrasion resistance, good low-temperature flexibility, and good fatigue characteristics.[17] BR is composed of butadiene units joined linearly by *cis*-1,4- and *trans*-1,4-isomers and vinyl additions.

In this study, an extensive investigation of the continuous ultrasonic devulcanization of unfilled BR vulcanizates was carried out with the aim of establishing a devulcanization window for their recycling. The devulcanized BR samples and their revulcanizates and blends with virgin rubber were investigated to compare their properties with those of the virgin BR. The gel fraction and crosslink density, the mechanical and rheological properties, and the molecular weight of the sol part of the devulcanized BR samples were measured to elucidate the mechanism of the processes taking place during the ultrasonic devulcanization of BR.

EXPERIMENTAL

Materials

The BR used in our experiments was Budene 1207 obtained from Goodyear Chemical. The cis-1,4-content was 98%. The Mooney viscosity (ML_{1+4} at 100°C) was 55. The curing ingredients were sulfur, zinc oxide, stearic acid (Akrochem Corp., Akron, OH), and *N-tert*-butyl-2-benzothiazole sulfenamide (TBBS; Flexsys, Akron, OH).

Ultrasonic reactor

A grooved-barrel ultrasonic reactor was used in the devulcanization experiments. It consisted of a
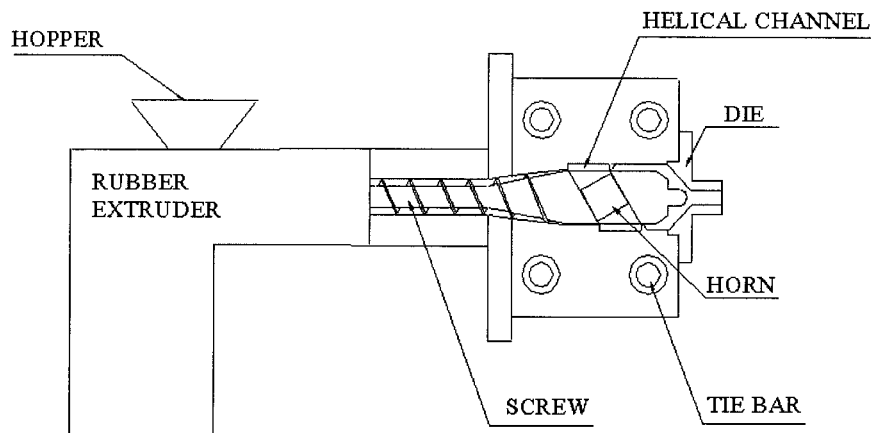
Figure 1 Schematic drawing of the grooved-barrel ultrasonic reactor.

38.1-mm rubber extruder with barrel and screw extension to accommodate ultrasonic transducers. A schematic drawing of the reactor is shown in Figure 1. A pair of 3.3-kW ultrasonic power supplies, a converter, and a 1:1 booster (Branson Ultrasonics Co.) provided the longitudinal vibrations of the horn with a frequency of 20 kHz and various amplitudes. Two ultrasonic water-cooled horns of square cross sections (38.1 $\times$ 38.1 mm^2) were inserted into the barrel through two ports. Two helical channels were made on the barrel surface (grooved barrel). In this reactor, rubber flowed in the helical channels through the gap created between the rotating shaft and the tips of the horns.

The clearances between the horns and the ports of the barrel were sealed by two Vespel gaskets. Vespel is a 40 wt % graphite filled polyimide that provides enhanced resistance to wear and friction as well as improved dimensional and oxidative stability. Vespel exhibits a sufficiently high stiffness and low friction coefficient to endure the effect of ultrasound waves on its sealing ability. This prevents the leakage of rubber during devulcanization and prevents metal-to-metal contact between the horn and the barrel.

In the devulcanization section, the screw diameter was 50.8 mm. This larger diameter provided a converging flow of rubber to the devulcanization zone. The latter may enhance the devulcanization process. A converging circular die was attached to the extruder at the exit from the devulcanization zone. The diameters at the die entrance and the exit were 58.4 and 39.9 mm, respectively. The length of the die was 50.8 mm.

Preparation of the vulcanizate, devulcanized, and revulcanized samples

The rubber was compounded with a two-roll mill (Dependable Rubber Machinery Co., Cleveland, OH) at room temperature. The nip of the rolls was kept at 2 mm. The cure recipe was 1. 5 phr sulfur, 3 phr zinc oxide, 2 phr stearic acid, and 0.9 phr TBBS. The total mixing time was 8 min.

The sample was then molded into slabs (260 mm $\times$ 260 mm $\times$ 12 mm) at a temperature of 160°C and a pressure of 13.8 MPa with a compression-molding press (model 12-12-2T, Wabash Metal Products Co., Wabash, IN). The cure time was 25 min, corresponding to T_{90} (time taken to reach 90% of cure), which was obtained with an Advanced Polymer Analyzer 2000 (APA 2000; Alpha Technologies, Akron, OH).[18] After the molding, the vulcanized samples were ground in a grinding machine with a 5-mm screen (model 01012M, Nelmor, N. Uxbridge, MA).

Vulcanized sheets (127 mm $\times$ 127 mm $\times$ 2 mm) were also obtained by compression molding and were used for mechanical testing. These sheets were cured for 25 min.

The ground rubber was then fed into the ultrasonic reactor. Devulcanization experiments were performed at barrel temperatures (T_B's) of 80 and 120°C. The screw speed was 50 rpm. The flow rates were 0.32, 0.63, and 1.26 g/s. The gap sizes in the devulcanization zone were 0.5, 0.75, 1.0, and 2.0 mm. The amplitudes of the ultrasonic waves were 5.0, 7.5, 10.0, and 12.5 μm. As discussed earlier,[8] the process of ultrasonic devulcanization was nonisothermal.

The devulcanized samples were collected after the process reached a steady-state condition, as determined through the pressure and power consumption measurements.

The devulcanized samples were heterogeneous. They consisted of a low-viscosity sol and a low-crosslink-density gel. Thus, the samples were homogenized with a two-roll mill and then revulcanized into sheets 2 mm thick at 160°C with the same recipe used for the virgin vulcanizates and T_{90} for each sample.

The devulcanized BR was blended with the virgin one. The blending was carried out with a two-roll mill.

The same amounts of the curing ingredients used in the virgin recipe were added to the blends. The revulcanization conditions for the blends were the same as those for the virgin vulcanizates.

Characterization

The gel fraction and crosslink density were determined with the Soxhlet extraction method with benzene as the solvent. The extraction time was 24 h. The crosslink density was calculated with the Flory–Rehner equation.[19] The interaction parameter $\chi = 0.4$ was used in the calculation.[20]

Gel permeation chromatography (GPC; Waters) was used to measure the molecular weights and their distributions in the sol part in virgin and devulcanized BR. Tetrahydrofuran (THF), used as a solvent, was run at room temperature, and conventional calibration was used against polystyrene standards. The samples used were those obtained after extraction with THF for 96 h in the Soxhlet apparatus.

An Instron model 5567 testing machine (Canton, MA) was used for the mechanical property measurements. All the tests were performed at room temperature at a crosshead speed of 500 mm/min (ASTM D 412).

The rheological behavior was investigated with the APA 2000 at 120°C within a frequency range of 1–200 rad/s and at a strain amplitude of 7.1%. A biconical rotor with an angle of 7° and a diameter of 63.5 mm was used.

Thermogravimetric analysis (TGA) was carried out with a Hi-Res TGA 2950 analyzer (TA Instruments, New Castle, DE) at a heating rate of 20°C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out with a TA Instruments DuPont 2100 (New Castle, DE) at a heating rate of 20°C/min under a nitrogen atmosphere. DSC was run from −120 to 40°C twice to remove the thermal history for crystallization experiments and from 150 to 550°C for the thermal degradation experiments.

RESULTS AND DISCUSSION

Ultrasonic devulcanization window

In the study of ultrasonic devulcanization, one of the most important tasks is to determine the optimum devulcanization. In this investigation, various processing conditions were used to establish the range of process parameters for successful devulcanization. Figure 2 presents the BR ultrasonic devulcanization windows in terms of different gaps and amplitudes at a constant flow rate of 0.63 g/s and in terms of different gaps and flow rates at a constant amplitude of 12.5 μm at $T_B = 120$°C. Unlike previous studies for ground tire rubber,[9,10] NR,[11,12] silicone rubber,[13] SBR,[15] and
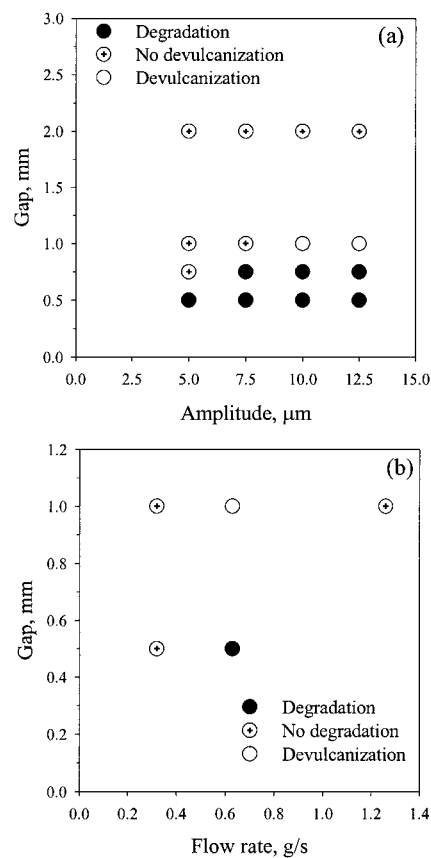

Figure 2 Ultrasonic devulcanization windows of BR in terms of (a) the gaps and amplitudes at a constant flow rate of 0.63 g/s and (b) the gaps and flow rates at a constant amplitude of 12.5 μm at $T_B = 120$°C.

EPDM,[16] which indicated a wide window for the parameters leading to devulcanization, BR exhibited a narrow devulcanization window. Strictly speaking, devulcanization in sulfur-cured rubber can be defined as the process of cleaving, totally or partially, polysulfide, disulfide, and monosulfide crosslinks that are formed during the initial vulcanization. However, in practice, devulcanization occurs along with some degradation of the main chains. In this case, devulcanization was successfully achieved only at amplitudes of 10 and 12.5 μm, at a gap of 1 mm, and at a flow rate of 0.63 g/s. The devulcanized samples were soft and sticky. Outside this window, significant degradation or no devulcanization occurred, as indicated by the corresponding symbols in Figure 2. In particular, vulcanizates were converted into liquids because of degradation or exited the extruder as powders when devulcanization did not happen. The crosslink density and gel fraction of these samples were not measured. For $T_B = 80$°C, which is not shown in Figure 2, among various amplitudes, only at an amplitude of 12.5 μm was it possible to achieve successful devulcanization at a gap of 1 mm and a flow rate of 0.63 g/s.

TABLE I
Ultrasonic Power Consumption and Pressure at the Entrance to the Devulcanization Zone During the Devulcanization of BR at a Flow Rate of 0.63 g/s and a Gap of 1 mm

Amplitude (μm)	T_B (°C)	Power consumption (W)	Pressure (MPa)
0	120, 80		3.10
10	120	700	2.76
12.5	120	750	2.41
12.5	80	775	2.2

TABLE II
Gel Fraction and Crosslink Density of the Virgin Vulcanizate and Devulcanized and Revulcanized BR

Sample	Amplitude (μm)	T_B (°C)	Gel fraction (%)	Crosslink density (mol/m^3)
Virgin vulcanizate			94.8	155
Devulcanized	10	120	77.8	61.7
	12.5	120	76.1	54.2
	12.5	80	74.8	48.3
Revulcanized	10	120	89.8	148
	12.5	120	88.6	137
	12.5	80	87.2	128

Power consumption and pressure

Table I shows the ultrasonic power consumption and pressure at the entrance to the devulcanization zone during the devulcanization of BR at a flow rate of 0.63 g/s and a gap of 1 mm. The power consumption at an amplitude of 12.5 μm was a little higher than that at 10 μm. The pressure decreased as the amplitude increased. This was previously explained as the combined effect of the softening of rubber due to devulcanization and the reduction in friction between particles and the die wall due to ultrasonic vibration.[10] Also, as shown in Table I, the power consumption and pressure obtained at $T_B = 80°C$ and $T_B = 120°C$ were not significantly different.

Curing, gel fraction, and crosslink density

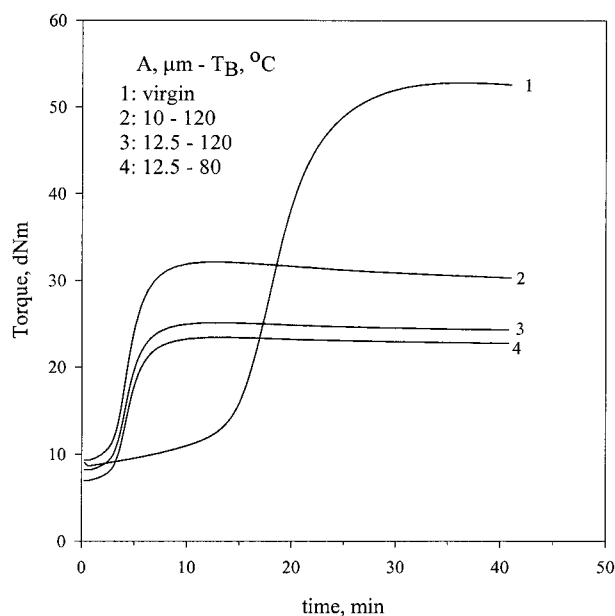The cure curves of virgin and devulcanized BR at 160°C are shown in Figure 3. The curing behavior of

Figure 3 Cure curves of virgin and devulcanized BR at 160°C.

devulcanized BR was quite different from that of virgin BR. The scorch time during the revulcanization of the devulcanized sample was much shorter than that of the virgin one. This indicates that the crosslinking reaction started more quickly. This can possibly be explained by the presence of residual curatives in the devulcanized sample, a characteristic of reclaimed rubber.[21] The maximum torques of the devulcanized samples were lower than that of the virgin sample. This may be explained by the breakup of main chains during the devulcanization.[11] Compared with NR,[11] silicone rubber,[14] SBR,[15] and EPDM[16] (even though a different ultrasonic reactor was used), BR showed the most severe drop of maximum torque after devulcanization.

The minimum torque of the devulcanized samples was similar to that of the virgin BR (Fig. 3). The devulcanized BR contained both sol and gel. The presence of gel could cause an increase in the viscosity, whereas the presence of sol, having a lower molecular weight than that of virgin BR, could lead to a decrease in the viscosity. Therefore, a competition between these two effects could lead to a situation in which the initial torque of the virgin and devulcanized BR would be similar, as shown in Figure 3.

Table II shows the gel fraction and crosslink density of virgin vulcanizate and devulcanized and revulcanized BR. Both the gel fraction and crosslink density decreased substantially after the ultrasonic devulcanization. The gel fraction and crosslink density of the devulcanized BR samples were similar to those of SBR.[15] The gel fractions and crosslink density of the revulcanized samples were lower than those of the virgin vulcanizate. This indicates that some amount of uncurable and less curable sol parts was generated during the ultrasonic devulcanization.

As reported earlier,[22] in the case of EPDM roofing membrane particles, their size was reduced after passing through the extruder in the absence of the action of ultrasound. However, this reduction of the particle size did not change the value of their gel fraction, and
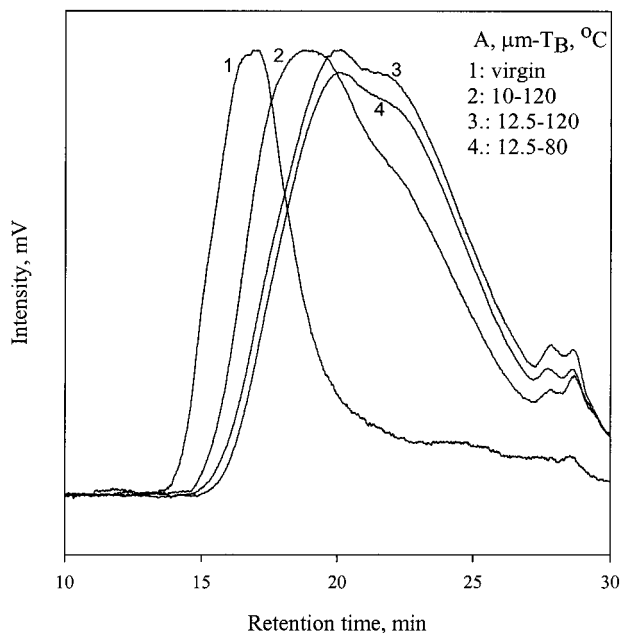
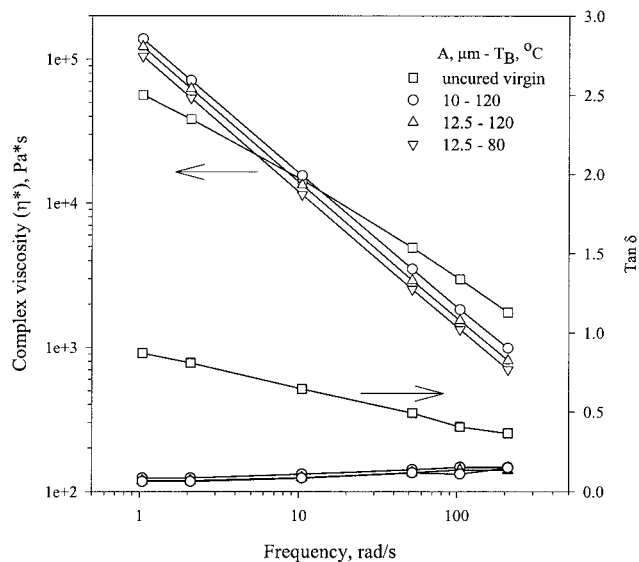**Figure 4** GPC traces related to the molecular weight distribution of the sol parts in virgin and devulcanized BR.

Figure 5 Complex dynamic viscosity and tan δ as functions of the frequency for uncured virgin and devulcanized BR at 120°C.

this indicated that simple mechanical shearing of the rubber in the extruder did not cause devulcanization.

Molecular weight of the sol

To investigate a breakdown of the polymeric chains during devulcanization, we measured the molecular weights and molecular weight distributions of the sol part in virgin and devulcanized BR by GPC. Figure 4 shows the intensity of the absorbance as a function of the retention time obtained from the GPC measurements. The molecular weight values calculated from these data are given in Table III. Because of degradation, there was a significant molecular weight reduction in the sol fraction of the devulcanized samples. A higher amplitude led to more degradation. Also, the molecular weight distributions were broadened. The ultrasonic treatment of BR vulcanizates caused both devulcanization and degradation. Other possible mac-

romolecular chain modifications could not be determined from the GPC measurements. For this purpose, NMR will be used in future studies. These GPC curves showed two peaks. One main peak at a shorter retention time corresponded to the polymer, and the other peak at a longer retention time corresponded to the presence of oligomers and low-molecular-weight ingredients.

Rheological properties

The variations of the complex dynamic viscosity and tan δ with the frequency for uncured virgin and devulcanized BR at 120°C are shown in Figure 5. At a low-frequency region, the complex viscosities of the devulcanized samples were higher than that of the virgin sample. This was due to the presence of a high amount of gel in the devulcanized samples. In particular, the viscosity of BR at the low-frequency region was indirectly related to the degree of devulcanization and the extent of degradation. However, at the high-frequency region, the complex viscosities of the devulcanized samples were lower than that of the virgin sample. This was due to significant degradation of the macromolecular chains, as discussed previously and shown in Table III, and their structural transformations during the ultrasonic treatment. The change in tan δ is also noted in the same figure. For the virgin sample, the value of tan δ decreased with the frequency, whereas those of the devulcanized samples were lower and increased only slightly with the frequency. A lower value of tan δ meant a more elastic sample. Yun and Isayev[16] reported that devulcanized EPDM was more elastic than virgin EPDM because of

TABLE III
Molecular Weights and Polydispersities of the Sol Part in Virgin and Devulcanized BR

Sample	Amplitude (μm)	T_B (°C)	M_n	M_w	M_w/M_n
Virgin			145,600	191,900	1.32
Devulcanized	10	120	14,100	33,956	2.40
	12.5	120	11,400	26,200	2.28
	12.5	80	11,294	25,100	2.23

M_n = number-average molecular weight; M_w = weight-average molecular weight.
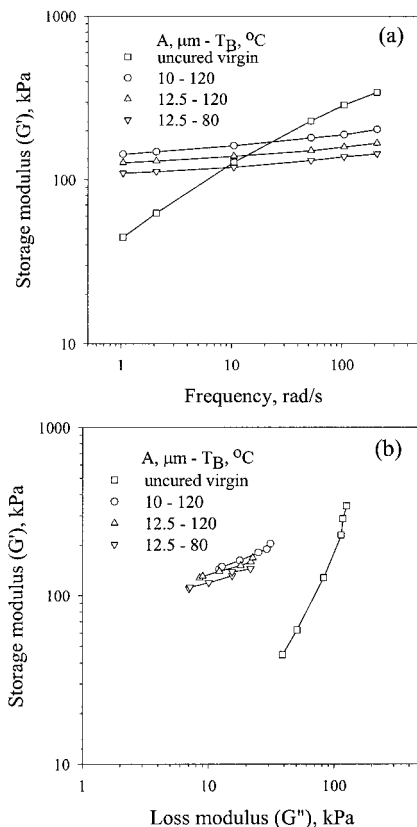
Figure 6 Storage modulus as a function of (a) the frequency and (b) the loss modulus for uncured virgin and devulcanized BR at 120°C.

the presence of gel. Similarly to EPDM, the presence of gel caused the devulcanized samples to be more elastic than the virgin sample.

Figure 6 shows the storage and loss moduli as functions of the frequency for uncured virgin and devulcanized BR at 120°C. Figure 6(a) shows that the storage modulus of the virgin sample significantly increased with the frequency, whereas that of the devulcanized samples increased slightly with the frequency. Similar to the complex dynamic viscosity, the values of the storage modulus for the devulcanized samples were higher at the low-frequency region. This was also due to the presence of a large amount of gel in the devulcanized samples. The lower values of the storage modulus in the high-frequency region were an indirect indication of degradation. Figure 6(b) shows that for the same value of the loss modulus, the storage modulus was always higher for devulcanized samples. This means that the devulcanized samples were more elastic than the virgin sample.

Figure 7 shows the storage and loss moduli as functions of the frequency for virgin vulcanizate and revulcanized BR at 120°C. Figure 7(a) shows that the storage moduli of both virgin vulcanizate and revulcanized samples were almost independent of the frequency. Also, the storage modulus of the revulcanized

sample was lower than that of the virgin vulcanizate. This means that, similarly to EPDM,[16] revulcanized BR samples were less elastic than the virgin vulcanizate. This statement is supported by Figure 7(b). At the same loss modulus, the virgin vulcanizate showed a higher storage modulus than the revulcanized samples.

Mechanical properties

Figure 8 shows the stress–strain curves of vulcanizates of virgin and devulcanized BR. The tensile strength of the revulcanized samples was reduced in comparison with that of the virgin vulcanizate. This was possibly due to the breakup of main chains during the ultrasonic treatment.[11,16] The samples devulcanized at a higher amplitude showed properties inferior to those of the samples devulcanized at a lower amplitude. The reason for this was that greater degradation happened at the higher amplitude.

To improve the performance characteristics of recycled BR obtained by ultrasonic devulcanization, we blended BR devulcanized at an amplitude of 10 μm, a gap of 1 mm, a flow rate of 0.63 g/s, and a T_B of 120°C with virgin rubber in various proportions. Figure 9
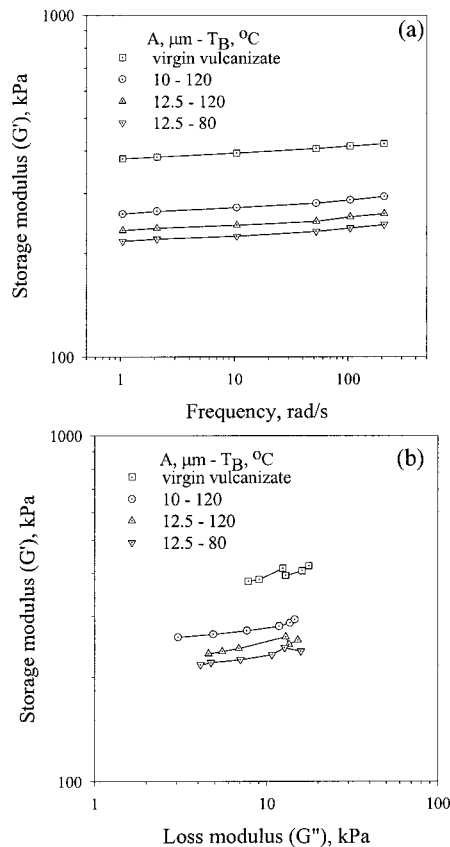

Figure 7 Storage modulus as a function of (a) the frequency and (b) the loss modulus for cured virgin and revulcanized BR at 120°C.
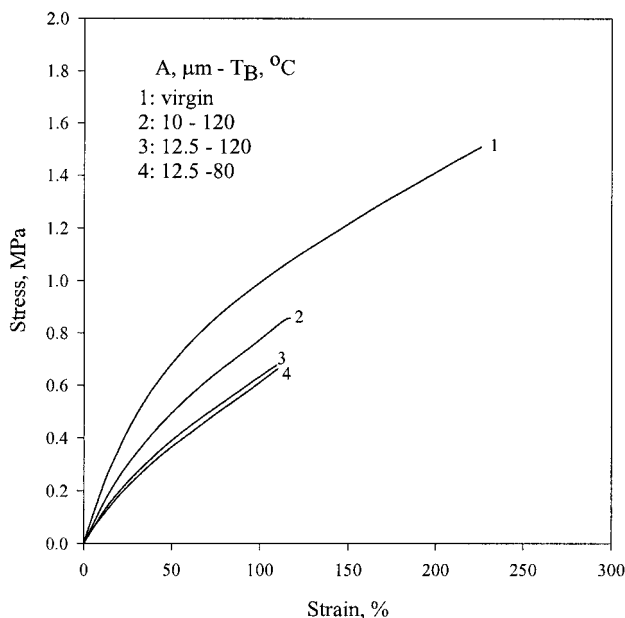
Figure 8 Stress–strain curves of vulcanizates of virgin and devulcanized BR.

shows the stress–strain curves of vulcanizates of blends and the tensile strength, elongation at break, and modulus at 100% as functions of the concentration of virgin BR in these blends. The values of the elongation at break of the blend vulcanizates containing up to 50% virgin rubber were higher than that of the virgin sample. The values of the tensile strength increased with the content of virgin rubber. These properties were well above the rule of mixture. It is thought that similar to blends of devulcanized and virgin NR,[23] ultrasonically devulcanized BR exhibits good bonding to virgin rubber. Moduli at 100% elongation of the blends were only slightly dependent on the composition. Surprisingly, even with such a significant molecular weight reduction in devulcanized BR, the mechanical properties of the blends remained at the level of the virgin vulcanizate.

Thermal properties

Figure 10 shows TGA curves of virgin gum, virgin vulcanizate, ultrasonically devulcanized, and revulcanized BR. The order of the thermal stability of the various samples was as follows: virgin gum > virgin vulcanizates > devulcanized samples > revulcanizates. The thermal degradation of the virgin vulcanizate began earlier than that of the virgin gum. The presence of curatives would likely accelerate the process of bond scission, as shown in an earlier study.[24] The thermal degradation of the devulcanized samples started earlier than that of the virgin gum and the virgin vulcanizate because degradation and devulcanization occurred during the imposition of ultra-

sound, possibly leading to the weakening of chemical bonds. The thermal degradation of the revulcanized samples began earlier than that of the devulcanized samples but was slower than that of the devulcanized samples. The lowest volatile fraction was found in virgin gum. Moreover, as shown in Figure 10, the nonvolatile fraction of the devulcanized samples was similar to that of the virgin vulcanizate. At the same time, the nonvolatile fraction of the revulcanized samples was higher than that of the devulcanized samples. This was possibly due to the fact that the vulcanizates contained curatives with some nonvolatile fraction.

Figure 11 shows the DSC curves of virgin gum, virgin vulcanizate, devulcanized, and revulcanized BR at a high temperature range. The presence of slightly overlapping exothermal and endothermal peaks is evident in this figure. The enthalpy values of these peaks separated by derivatives of these curves are given in Table IV. The exothermic peaks are probably due to cyclization and crosslinking reactions, and the endothermic peaks are associated with degradation.[25] The enthalpies of cyclization and crosslinking reactions (ΔH_{cx}) of the devulcanized samples were
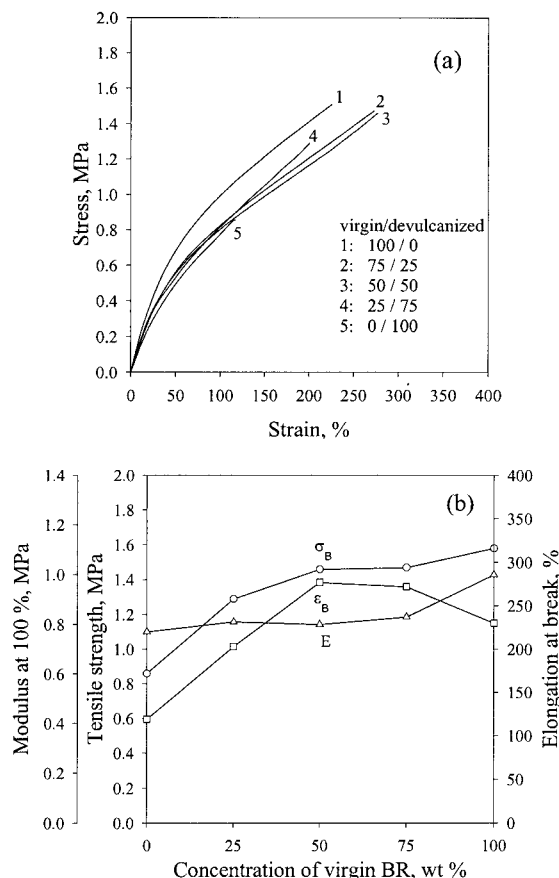

Figure 9 (a) Stress–strain curves and (b) mechanical properties of virgin and devulcanized BR blends. BR was devulcanized at an amplitude of 10 μm, a gap of 1 mm, a flow rate of 0.63 g/s, and a T_B of 120°C.
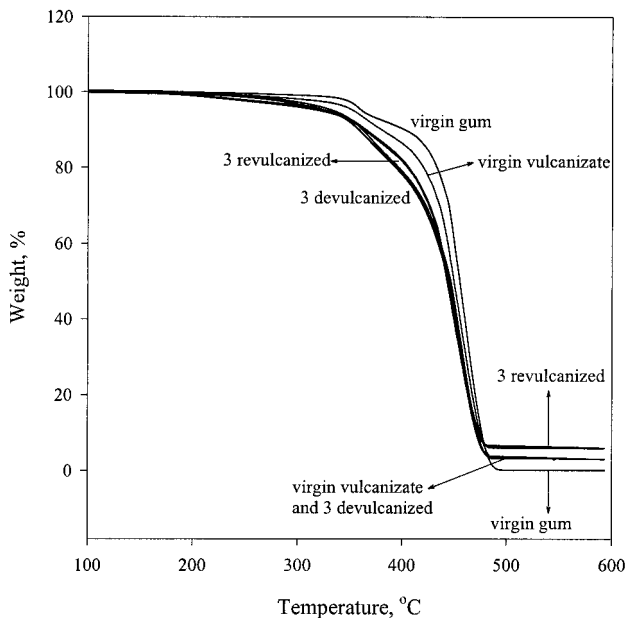
Figure 10 TGA curves of virgin gum, virgin vulcanizate, ultrasonically devulcanized, and revulcanized BR.

lower than that of the virgin gum because the number of double bonds of the devulcanized samples was smaller than that of virgin gum. Moreover, the value of ΔH_{cx} of the virgin vulcanizate was lower than that of the virgin gum. This was also due to the reduced number of double bonds. The enthalpies of degradation (ΔH_d) of the devulcanized samples were higher than that of the virgin gum.
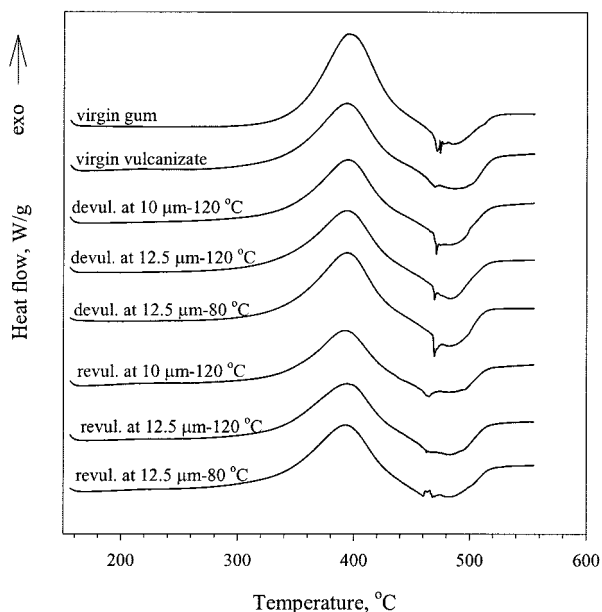
TABLE IV
ΔH_{cx} and ΔH_d of BR Samples

Sample	ΔH_{cx} (J/g)	ΔH_d (J/g)
Virgin gum	751	247
Virgin vulcanizate	621	243
Devulcanized		
10 μm, T_B = 120°C	481	287
12.5 μm, T_B = 120°C	505	276
12.5 μm, T_B = 80°C	550	280
Revulcanized		
10 μm, T_B = 120°C	477	181
12.5 μm, T_B = 120°C	492	232
12.5 μm, T_B = 80°C	525	241

Figure 12 shows DSC curves of virgin gum, virgin vulcanizate, devulcanized, and revulcanized BR at a low temperature range. The virgin gum exhibited crystallization and melting peaks. Vulcanization lowered the melting point and the heat of fusion of the virgin rubber, and this indicated a reduction in the crystallinity upon vulcanization. It is believed that vulcanization reduced the chemical regularities of the chains[26,27] and formed crosslinks that did not participate in melting. However, it is unclear why the crystallization peak was absent in the devulcanized samples, with the melting peaks of these samples being very small or absent. One possibility that we can suggest is that ultrasound caused the reduction of chemical regularities.

CONCLUSIONS

This study indicated that unfilled BR had a narrow devulcanization window. Outside this window, sig-

Figure 11 DSC curves of virgin gum, virgin vulcanizate, devulcanized, and revulcanized BR at a high temperature range.
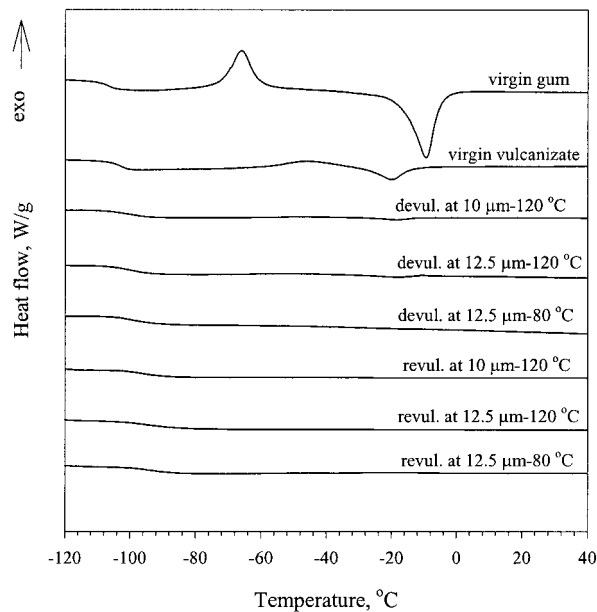

Figure 12 DSC curves of virgin gum, virgin vulcanizate, devulcanized, and revulcanized BR at a low temperature range.

nificant degradation or no devulcanization occurred. The gel fraction measurements of the revulcanized rubber showed that some additional amount of uncurable sol was generated during the ultrasonic devulcanization. GPC data obtained for devulcanized samples showed a significant molecular weight reduction and a broadening of the molecular weight distribution in comparison with the virgin gum. These data indicated that the devulcanization and degradation of BR occurred simultaneously during the imposition of ultrasound. The rheological properties showed that devulcanized BR was more elastic than uncured virgin BR. Vulcanizates of devulcanized BR showed mechanical properties inferior to those of virgin vulcanizates. However, the vulcanizates of the blends of virgin and devulcanized BR showed a considerable enhancement of the mechanical properties. The thermal degradation of the devulcanized BR began earlier than that of the virgin gum and virgin vulcanizate because of a possible weakening of chemical bonds upon ultrasonic treatment. ΔH_{cx} of devulcanized BR was lower than that of virgin gum because of the reduced number of double bonds in devulcanized BR. The crystallization and melting present in the virgin gum were found to be insignificant in devulcanized BR.

References

1. Fix, S. R. Elastomerics 1980, 112(6), 38.
2. Nicholas, P. P. Rubber Chem Technol 1982, 55, 1499.
3. Siuru, B. Scrap Tire News 1997, 11(12), 14.
4. Phadke, A. A.; Bhattacharya, A. K.; Chakraborty, S. K.; De, S. K. Rubber Chem Technol 1983, 56, 726.
5. Khait, K.; Torkelson, J. M. Polym Plast Technol Eng 1999, 38, 445.
6. Bilgili, E.; Arastoopour, H.; Bernstein, B. Rubber Chem Technol 2000, 73, 340.
7. Adhikari, B.; De, D.; Maiti, S. Prog Polym Sci 2000, 25, 909.
8. Isayev, A. I. In Rubber Technologist's Handbook; De, S. K.; White, J. R., Eds.; Rapra Technology: Shawbury, England, 2001; Chapter 15.
9. Yun, J.; Oh, J. S.; Isayev, A. I. Rubber Chem Technol 2001, 74, 317.
10. Isayev, A. I.; Chen, J.; Tukachinsky, A. Rubber Chem Technol 1995, 68, 267.
11. Tapale, M.; Isayev, A. I. J Appl Polym Sci 1998, 70, 2007.
12. Hong, C. K.; Isayev, A. I. J Appl Polym Sci 2001, 79, 2340.
13. Shim, S. E.; Isayev, A. I. Rubber Chem Technol 2001, 74, 303.
14. Diao, B.; Isayev, A. I.; Levin, V. Y. Rubber Chem Technol 1999, 72, 152.
15. Levin, V. Y.; Kim, S. H.; Isayev, A. I. Rubber Chem Technol 1997, 70, 120.
16. Yun, J.; Isayev, A. I. Gummi Fasern Kunstst 2002, 55, 628.
17. Brown, T. In The Vanderbilt Rubber Handbook; Ohm, R. F., Ed.; Vanderbilt: Norwalk, CT, 1990; Chapter 2, p 80.
18. Dick, J. S.; Harmon, C.; Vare, A. Polym Test 1999, 18, 327.
19. Flory, P. J.; Rehner, J., Jr. J Chem Phys 1943, 11, 512.
20. Barton, A. In CRC Handbook of Polymer–Solvent Interaction Parameters and Solubility Parameters; CRC: Boston, 1990; Chapter 7, p 56.
21. Makarov, V. M.; Drozdovski, V. F. Reprocessing of Tires and Rubber Wastes; Ellis Horwood: New York, 1991; Chapter 2.
22. Yun, J.; Isayev, A. I. Polym Eng Sci 2003, 43, 809.
23. Hong, C. K.; Isayev, A. I. J Mater Sci 2002, 37, 1.
24. Jiang, D. D.; Levchik, G. F.; Levchik, S. V.; Wilkie, C. A. Polym Degrad Stab 1999, 65, 387.
25. Luda, M. P.; Guaita, M.; Chiantore, O. Makromol Chem 1992, 193, 113.
26. Zeng, X.-R.; Ko, T.-M. J Appl Polym Sci 1998, 67, 2131.
27. Cataldo, F. Polym Int 1994, 34, 49.