

Continuous Ultrasonic Devulcanization of Unfilled Butyl Rubber

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ABSTRACT: The devulcanization of resin-cured unfilled butyl rubber with a grooved-barrel ultrasonic reactor under various processing conditions was carried out. The experiments indicated that, because of the lower unsaturation and good thermal stability of butyl rubber, its devulcanization could be successfully accomplished only under severe ultrasonic-treatment conditions. Gel permeation chromatography measurements were carried out for the virgin gum and sol part of devulcanized samples to study the changes in the rubber network during the devulcanization process. The obtained data showed a significant molecular weight reduction and a broadening of the molecular weight distribution upon devulcanization, which indicated that the devulcanization and degradation of butyl rubber occurred simultaneously. The rheological properties showed that devulcanized butyl rubber was more elastic than the virgin gum.

The vulcanizates of the devulcanized butyl rubber showed mechanical properties comparable to those of the virgin vulcanizate. The thermal behaviors of the virgin and devulcanized butyl rubber were different and were correlated to the double-bond content. The structural characteristics of the devulcanized butyl rubber were simulated with the Dobson–Gordon theory of rubber network statistics. A fairly good agreement between the experimental data and theoretical prediction was achieved. The simulation of devulcanized butyl rubber indicated that the rate of crosslink rupture was much higher than that of the main chain. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1316–1325, 2004

Key words: crosslinking; ultrasound; gels; mechanical properties; rheology; rubber

INTRODUCTION

Butyl rubber is a copolymer of isobutylene and isoprene. Generally, it contains less than 3% isoprene. Because of its low gas permeability, good thermal and oxidative stability, and excellent moisture and chemical resistance, butyl rubber is very useful in a wide variety of tire and nontire applications,¹ including inner tubes, tire inner liners, and rubber tire-curing bladders.

When Charles Goodyear made the discovery of curing rubbers by sulfur,² he could not have foreseen that it also brought with it a serious problem. Because of the three-dimensional crosslinked structure and the presence of stabilizers and other additives, rubbers do not decompose easily, and almost all rubbers after service are discarded. Therefore, the disposal of waste rubbers is becoming a more and more serious environmental issue facing the rubber industry in recent years.

To resolve this problem, many methods have been exploited. Because rubbers mostly come from irreproducible fossil resources, instead of simply landfilling waste rubbers or using them as fuel, the best way of using them is to recycle them into useful products and take advantage of their unique properties (e.g., high resilience). Many methods have been developed to find more effective ways of reclaiming rubber, including microwaving,² catalysis,⁴ bioreactors,⁵ milling,⁶ solid-state shear pulverization,^{7,8} and high-pressure and high-temperature sintering.⁹ Recently, extensive reviews on rubber recycling methods have been published.^{10,11} Among these methods, 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 (GTR),^{12,13} natural rubber (NR),^{14,15} silicone rubber,^{16,17} styrene–butadiene rubber (SBR),¹⁸ ethylene–propylene–diene rubber (EPDM),¹⁹ polyurethane rubber,²⁰ and butadiene rubber (BR).²¹

In this study, an extensive investigation of the continuous ultrasonic devulcanization of unfilled butyl

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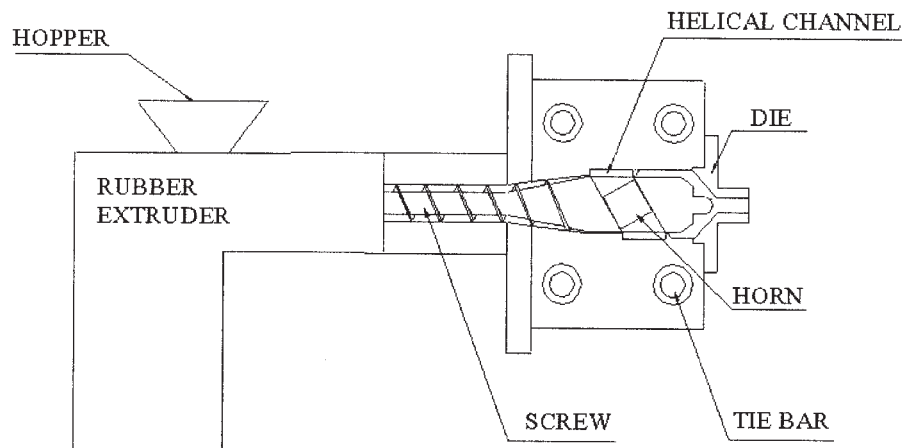


Figure 1 Schematic drawing of the grooved-barrel ultrasonic reactor.

rubber vulcanizate was carried out with the aim of establishing a devulcanization window for its recycling. The devulcanized butyl rubber samples and their revulcanizates were investigated to compare their properties with those of the virgin vulcanizate. The gel fractions, crosslink densities, mechanical properties, rheological properties, and molecular weights of the sol parts of the devulcanized butyl rubber samples were measured to elucidate the mechanism of the processes taking place during the ultrasonic devulcanization of butyl rubber.

EXPERIMENTAL

Materials

The butyl rubber used in this study was Exxon Butyl 268, which was kindly supplied by Exxon Chemical Co. (Baytown, TX). Unsaturation was 1.5–1.8 mol %.²² The Mooney viscosity (ML1 + 8) at 125°C was 51. The curing ingredients used were zinc oxide, stearic acid (Akrochem Corp., Akron, OH), and brominated octylphenol/formaldehyde resin SP-1055 (Schenectady International, Schenectady, NY).

Grooved-barrel ultrasonic reactor

A grooved-barrel ultrasonic reactor was used in the devulcanization experiments. It consisted of a 38.1-mm rubber extruder with barrel and screw extension to accommodate the 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., Danbury, CT) 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 × 38.1 mm²) were inserted into the barrel through two ports. Two helical chan-

nels 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 sufficiently high stiffness and a low friction coefficient to endure the effect of ultrasonic waves on its sealing ability. This prevented the leakage of rubber during devulcanization and avoided metal-to-metal contact between the horn and the barrel.

In the devulcanization section, the screw diameter was 50.8 mm. The larger diameter provided a converging flow of rubber to the devulcanization zone. A converging circular die was attached to the extruder at the exit from the devulcanization zone. The diameter of the die entrance was 58.4, and the diameter of the die exit could be varied as 39.9 (large die), 29.2 (medium die), or 17.5 mm (small die). The length of the die was 50.8 mm.

Preparation of the vulcanizates and devulcanized and revulcanized samples

The rubber was compounded with Moriyama internal mixer (model 03-7.5, Osaka, Japan) at room temperature. The cure recipe was 100 phr butyl rubber, 12 phr SP-1055, 5 phr zinc oxide, and 1 phr stearic acid. The total mixing time was 8 min.

The sample was then molded into slabs (260 × 260 × 12 mm³) at a temperature of 180°C and a pressure of 17.2 MPa with a compression-molding press (model 12-12-2T, Wabash Metal Products Co., Wabash, IN). The cure time was 40 min, which corresponded to T_{90} (torque to attain 90% cure state), which was obtained

with an advanced polymer analyzer (APA 2000, Alpha Technologies, Akron, OH).²³ After the molding, the vulcanized samples were ground in a Nelmor (N. Uxbridge, MA) 01012M grinding machine with a 5-mm screen. Vulcanized sheets with dimensions of $127 \times 127 \times 2 \text{ mm}^3$ were also obtained by compression molding and were used for mechanical testing.

The ground rubber was then manually fed into the ultrasonic reactor. The devulcanization experiments were performed at a barrel temperature of 120°C. The screw speed was 50 rpm. The flow rate was about 1 g/s. The gap size in the devulcanization zone was adjustable. The amplitudes of the ultrasonic waves were 5.0, 7.5, and 10.0 μm .

The devulcanized samples were then homogenized with a two-roll mill and then revulcanized into sheets 2 mm thick at 180°C with the same recipe used for the virgin vulcanizates to T_{90} .

Characterization

The gel fractions and crosslink densities were determined by the Soxhlet extraction method with cyclohexane as the solvent. The extraction time was 24 h. The crosslink density was calculated with the Flory–Rehner equation.²⁴ An interaction parameter ($\chi = 0.43$) was used in the calculation.²⁵

The molecular weights and molecular weight distributions of the virgin gum and sol part in the devulcanized butyl rubbers were determined with a gel permeation chromatography (GPC) instrument equipped with a series of three Styragel HR columns (Waters Co., Milford, MA) and a Viscotek (Houston, TX) viscosity detector, a refractive-index detector (Waters 410 differential refractometer), and a laser light scattering detector at 90° angle (Wyatt Technology, Santa Barbara, CA). GPC analyses were performed at a flow rate of 1.0 mL/min in tetrahydrofuran (THF; Fisher, Fair Lawn, NJ) at 35°C. The samples used were those obtained after extraction with THF for 48 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 curing behavior was investigated with the APA 2000 at a temperature of 180°C with a frequency of 10.47 rad/s and an angular amplitude of 3°.

The rheological behavior was investigated with the APA 2000 at a temperature of 120°C within a frequency range of 0.1–200 rad/s and an angular amplitude of 0.3° (strain amplitude = 4%). 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 TGA 2050 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 DuPont 2100 (TA Instruments) at a heating rate of 20°C/min under a nitrogen atmosphere in the range of –180 to 100°C.

RESULTS AND DISCUSSION

Ultrasonic devulcanization window

In the study of ultrasonic devulcanization, one of the most important tasks is to determine the optimum conditions for devulcanization. In this investigation, various processing conditions were used to establish the range of processing parameters for successful devulcanization. Figure 2 presents the butyl rubber ultrasonic devulcanization windows in terms of different gap sizes versus amplitudes at a die exit diameter of 29.2 mm and in terms of different gap sizes versus die exit diameters at an amplitude of 10 μm at a flow rate of 1 g/s and a barrel temperature of 120°C. This window was determined by a visual observation of the rubber exiting the extruder. Devulcanized samples exited the extruder as continuous extrudates, whereas samples that were not devulcanized exited the extruder as powders. Unlike previous studies for GTR,^{12,13} NR,^{14,15} silicone rubber,^{16,17} SBR,¹⁸ and EPDM,¹⁹ butyl rubber exhibited a narrow devulcanization window. Devulcanization was successfully achieved only under very severe treatment conditions corresponding to a 0.5-mm gap size, small and medium die exit openings, and high amplitudes. Devulcanization did not occur when the gap size was greater than 0.5 mm at any die exit openings or when a 0.5-mm gap size was used in combination with a 39.9-mm die exit opening. This was evidently due to the fact that there was no significant pressure buildup and there was low ultrasonic power consumption, as indicated in Figure 3. Because butyl rubber has good thermal stability due to the low unsaturation of its main chain, it is reasonable to assume that it will require more severe conditions for devulcanization than other highly unsaturated rubbers.

A very narrow devulcanization window was also observed for BR.²¹ However, for BR, because of high unsaturation, this was caused by preferential degradation under the conditions of devulcanization.

Power consumption and die pressure

Figure 3 shows the ultrasonic power consumption and pressure at the entrance to the devulcanization zone during the devulcanization of butyl rubber at a flow rate of 1 g/s, a gap of 0.5 mm, and a die exit opening of 29.2 mm. As observed for other rubbers,^{14,26} the power consumption increased with the increase in the ultrasonic amplitude, and the die pressure decreased

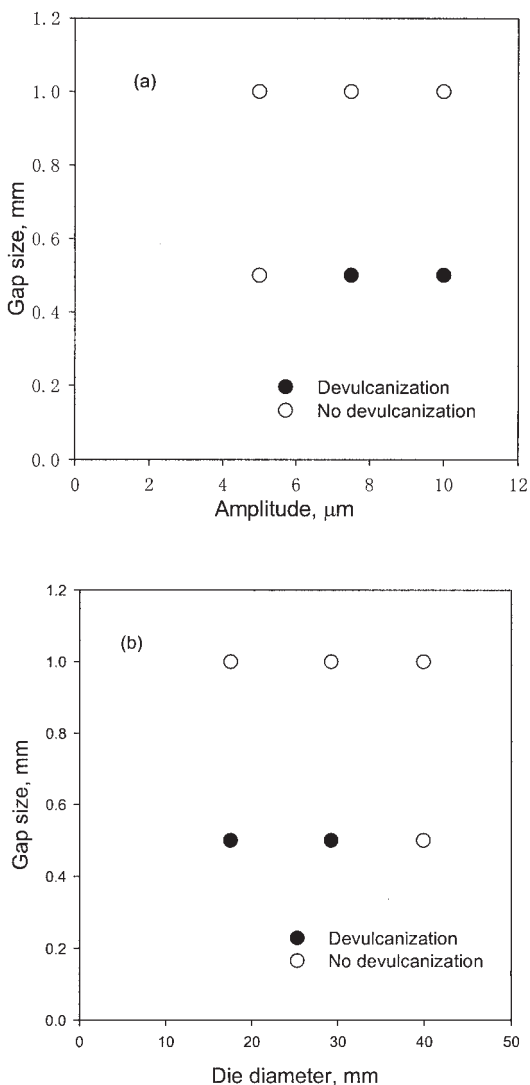


Figure 2 Ultrasonic devulcanization windows for butyl rubber obtained (a) with a medium die at various gaps and amplitudes and (b) with various gaps and dies at amplitude of 10 μm at a flow rate of 1 g/s.

with the increase in the ultrasonic amplitude. This was explained as the combined effect of the softening of rubber due to devulcanization, the reduction in friction between rubber particles and the horn surface, and an increasing material temperature at the treatment zone due to ultrasonic vibration.¹³

Curing, gel fraction, and crosslink density

The curing curves of virgin and devulcanized butyl rubber at 180°C are shown in Figure 4. Unlike the sulfur-curing recipe, the final torque for the resin-curing recipe did not reach a maximum torque value; even after 40 min of curing, the torque was still marching, and this indicated that the crosslinking reaction was not complete. This was also a reason that the

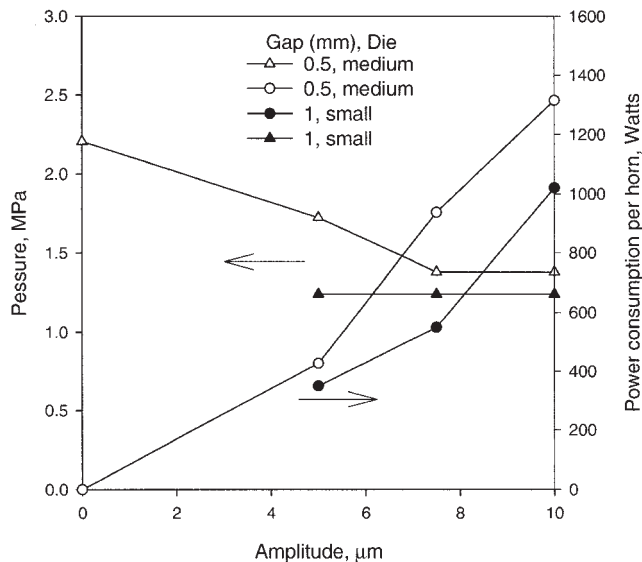


Figure 3 (▲,△) Die pressure and (●,○) power consumption versus the ultrasound amplitude at a flow rate of 1 g/s.

ground butyl vulcanizate could undergo further vulcanization. The curing behavior of the devulcanized butyl rubber was quite different from that of the virgin butyl rubber. The scorch time during the revulcanization of a devulcanized sample was shorter than that of a virgin one. This indicated 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.²⁷ Depending on the ultrasonic amplitude, the minimum torque in devulcanized rubbers was lower or higher than that of virgin rubber. Evidently, this was affected by the amount of gel and sol present in

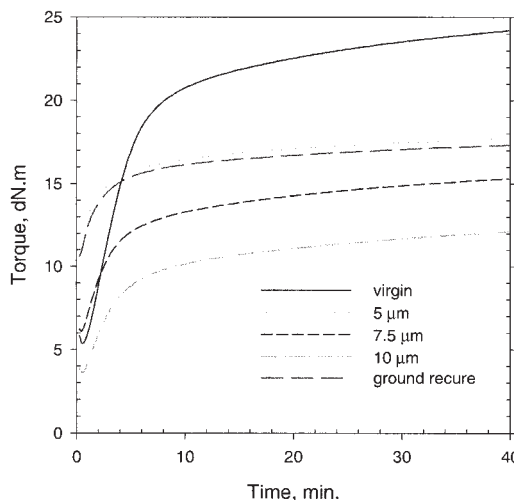


Figure 4 Cure curves of virgin and devulcanized butyl rubber obtained with a medium die at various amplitudes, a gap of 0.5 mm, and a flow rate of 1 g/s.

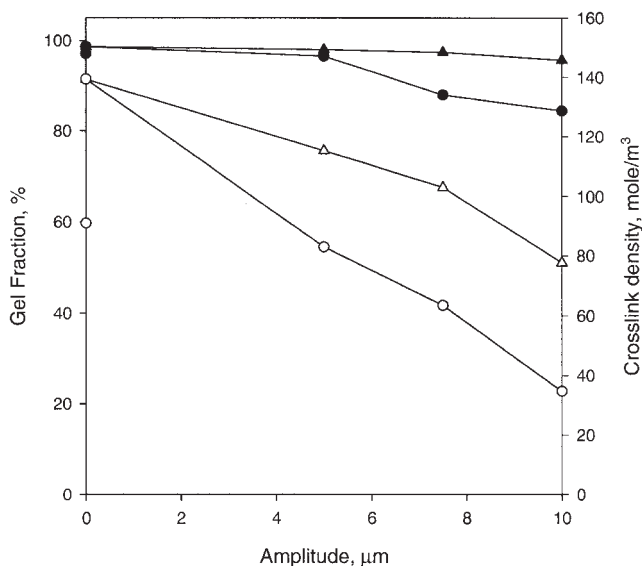


Figure 5 (●,▲) Gel fractions and (○,△) crosslink densities of (●,○) devulcanized and (▲,△) revulcanized unfilled butyl rubber obtained at a gap of 0.5 mm and a flow rate of 1 g/s with a medium die.

the devulcanized rubbers and the level of degradation of the rubber. The final torque values of the devulcanized samples were lower than that of the virgin sample. This may be explained by the breakup of main chains leading to the formation of some amount of incurable sol during the devulcanization¹⁴ and the reduction of the crosslink density in the revulcanized rubbers. In comparison with NR,¹⁴ silicone rubber,¹⁷ SBR,¹⁸ and EPDM¹⁹ (even though a different ultrasonic reactor was used), the devulcanized butyl rubber showed a drop in the final torque value during curing, which was due to a lower crosslink density of the revulcanized rubber in comparison with that of the virgin vulcanizate, as indicated in Figure 5. This observation differed from that for SBR,¹⁸ which showed a higher crosslink density for the revulcanized rubber than for the virgin vulcanizate. For the revulcanization of butyl rubber, fewer double bonds were available for crosslinking than for the revulcanization of SBR.

Figure 5 shows the gel fraction and crosslink density of the virgin vulcanizate and devulcanized and revulcanized butyl rubber as a function of the ultrasonic amplitude. Both the gel fraction and crosslink density decreased substantially after ultrasonic devulcanization. This decrease was more significant as the amplitude increased. The results were similar to those observed for SBR¹⁸ and EPDM.¹⁹ Also, the gel fractions of the revulcanized samples were slightly lower than that of the virgin vulcanizate. This indicated that some amount of incurable sol was generated during the ultrasonic devulcanization.

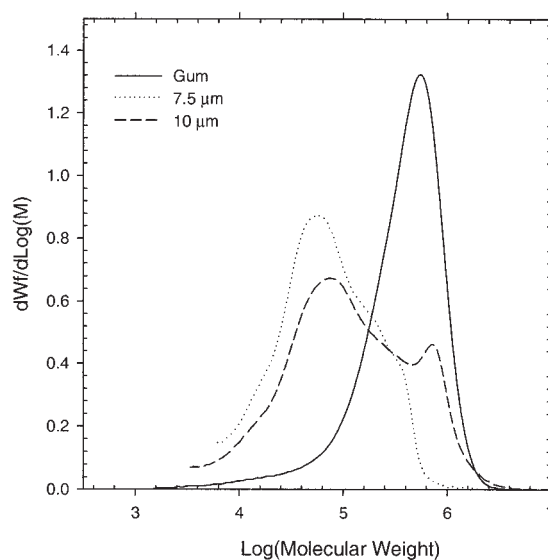


Figure 6 Molecular weight and molecular weight distribution of the butyl gum and sol parts in devulcanized butyl rubber obtained at a gap of 0.5 mm and a flow rate of 1 g/s with a medium die.

Molecular weight of the sol

To investigate the breakdown of the polymeric chains during devulcanization, we measured the molecular weight and molecular weight distribution of the virgin gum and the sol part of devulcanized butyl rubbers by GPC (Fig. 6). These data were obtained for a sample devulcanized at a gap size of 0.5 mm, a die opening of 29.2 mm, and a flow rate of 1 g/s. The molecular weight values calculated from the data are given in Table 1. Because of degradation, there was a significant reduction in the molecular weight in the sol fraction of the devulcanized samples. A higher amplitude led to greater degradation, as shown by the higher sol content in the devulcanized rubber (Fig. 5). The ultrasonic treatment of the butyl rubber vulcanizates caused both devulcanization and degradation. These GPC curves showed a bimodal distribution with low- and high-molecular-weight peaks, as vividly shown at a higher ultrasonic amplitude (10 μm). The high-molecular-weight peak corresponded to longer polymer

TABLE I
Molecular Weights and Polydispersities of Virgin Butyl Rubber and the Sol Part of Devulcanized Butyl Rubber

Sample	Amplitude (μm)	M_n	M_w	Polydispersity
Virgin		171,500	514,100	3.0
Devulcanized	7.5	46,670	155,300	3.33
	10	50,620	425,700	8.41

M_n = number-average molecular weight; M_w = weight-average molecular weight.

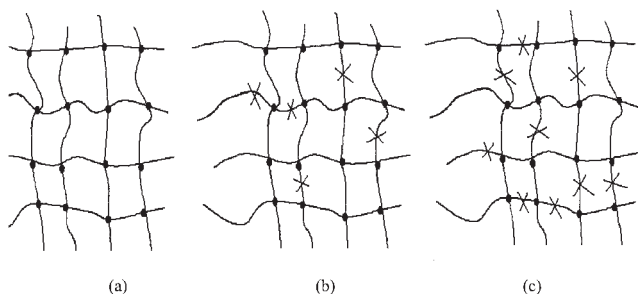


Figure 7 Schematic representation of the rubber network of (a) original vulcanizates and (b,c) ultrasonically devulcanized rubber obtained at low and high amplitudes, respectively. The crosses indicate locations of breakage of the rubber network.

chains, and the low-molecular-weight peak corresponded to the presence of oligomers or shorter polymer chains. At a higher amplitude, sol of higher molecular weight was generated. Also, the molecular weight distributions were broadened. This can be explained, to a certain extent, by the higher power consumption at the higher amplitude, which led to more breakage of both crosslink and main-chain bonds. Therefore, the chance of obtaining longer chain and higher molecular weight sol was more likely, as shown in Figure 7.

Rheological properties

The variations of the complex dynamic viscosity (η^*) and loss tangent ($\tan \delta$) with the frequency for virgin gum and devulcanized butyl rubber at 120°C are shown in Figure 8. In the low-frequency region, the η^* values of the devulcanized samples were higher than that of the virgin sample [Fig. 8(a)]. This was due to the presence of a large amount of gel in the devulcanized samples. In particular, the viscosity of the butyl rubber in the low-frequency region was indirectly related to the degree of devulcanization and the extent of degradation. However, in the high-frequency region, the η^* values of the devulcanized samples were lower than that of the virgin sample. This was due to significant degradation of macromolecular chains and their structural transformation during the ultrasonic treatment, as indicated by the gel fraction, crosslink density (Fig. 5), and molecular weight (Fig. 6). The change in $\tan \delta$ is also noted in Figure 8(b). For the virgin sample, $\tan \delta$ decreased with the frequency, whereas that of the devulcanized samples was lower and only slightly increased with the frequency. A lower value of $\tan \delta$ meant a more elastic sample. As reported earlier,¹⁹ devulcanized EPDM was more elastic than the virgin gum because of the presence of gel. Similarly to EPDM, the presence of gel caused the

devulcanized butyl rubber to be more elastic than the virgin sample.

Figure 9 shows the storage modulus as a function of the frequency and loss modulus (Cole–Cole plot) for virgin gum and devulcanized butyl rubber at 120°C. Figure 9(a) shows that the storage modulus of virgin gum significantly increased with the frequency, whereas that of devulcanized samples increased only slightly with the frequency. Similarly to η^* , the values of the storage modulus for the devulcanized samples were higher in the low-frequency region and lower in the high-frequency region. This higher value of the storage modulus 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 indication of degradation. Figure 9(b) shows that for the same value of the loss modulus, the storage modulus was always higher for devulcanized samples. This meant that the devulcanized samples were more elastic than the virgin sample. However, as the amplitude increased, the slope of the Cole–Cole plot also increased, and this indicated

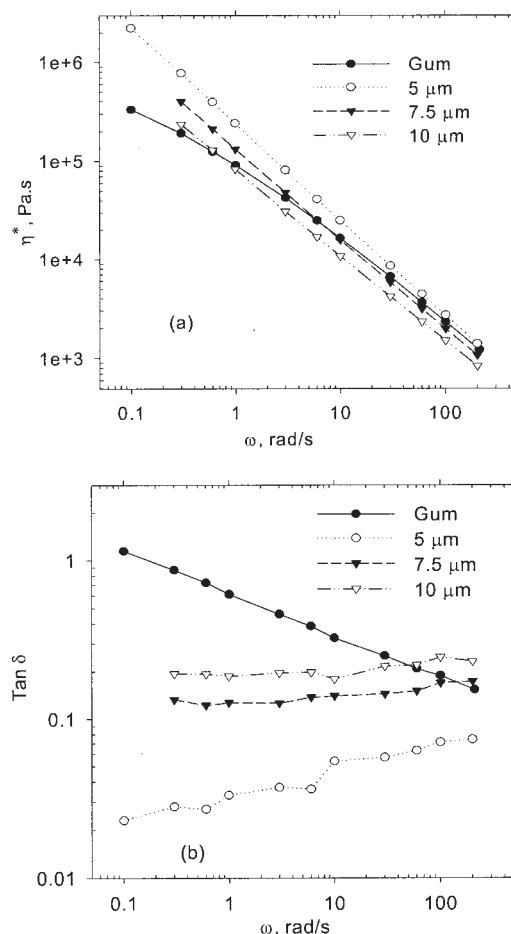


Figure 8 (a) η^* and (b) $\tan \delta$ as functions of the frequency for virgin gum and devulcanized butyl rubber obtained at a gap of 0.5 mm and a flow rate of 1 g/s with a medium die.

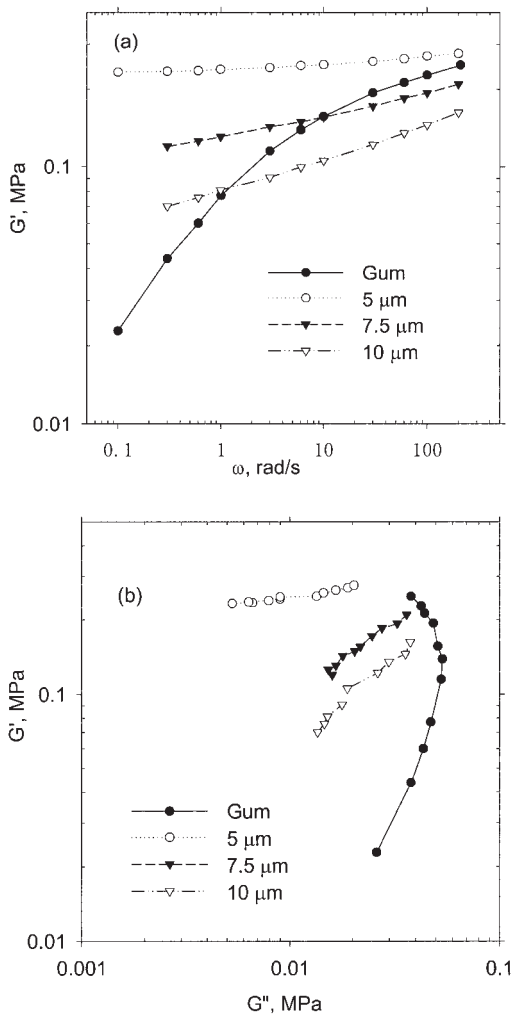


Figure 9 Storage modulus (G') as a function of (a) the frequency (ω) and (b) the loss modulus (G'') for virgin gum and devulcanized butyl rubber obtained at a gap of 0.5 mm and a flow rate of 1 g/s with a medium die.

that the devulcanized rubber behaved more like gum rubber because more gel was broken into sol.

Figure 10 shows the storage modulus as a function of the frequency and loss modulus for the virgin vulcanizate and revulcanized butyl rubber at 120°C. Figure 10(a) shows that the storage modulus of both the virgin vulcanizate and revulcanized samples was slightly dependent on the frequency. Also, the storage modulus of the revulcanized sample was lower than that of the virgin vulcanizate. This means that, like the devulcanization of EPDM,¹⁹ revulcanized butyl rubber samples were less elastic than the virgin vulcanizate. This statement is also supported by Figure 10(b). At the same loss modulus, the virgin vulcanizate had a higher storage modulus than the revulcanized samples.

Mechanical properties

Figure 11 shows the stress–strain curves of vulcanizates of virgin and devulcanized butyl rubber. It was

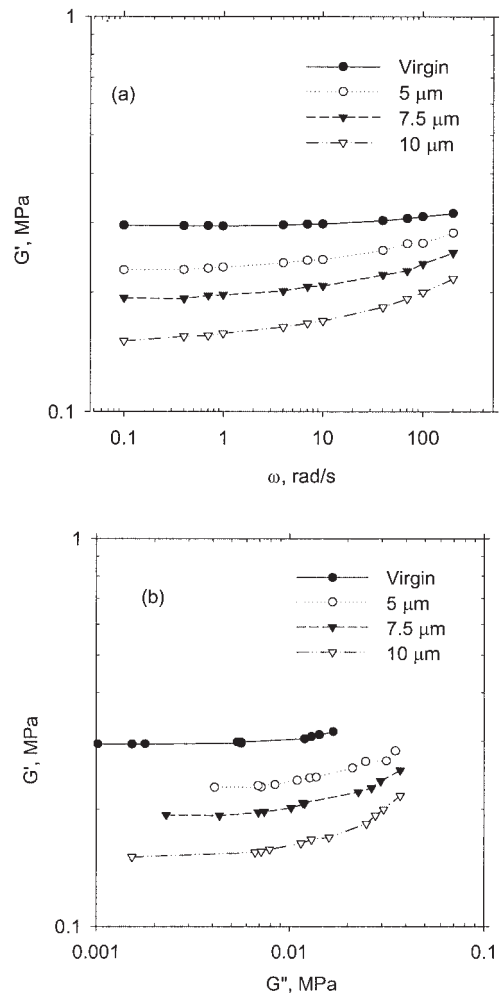


Figure 10 Storage modulus (G') as a function of (a) the frequency (ω) and (b) the loss modulus (G'') for virgin vulcanizate and revulcanized butyl rubber obtained at a gap of 0.5 mm and a flow rate of 1 g/s with a medium die.

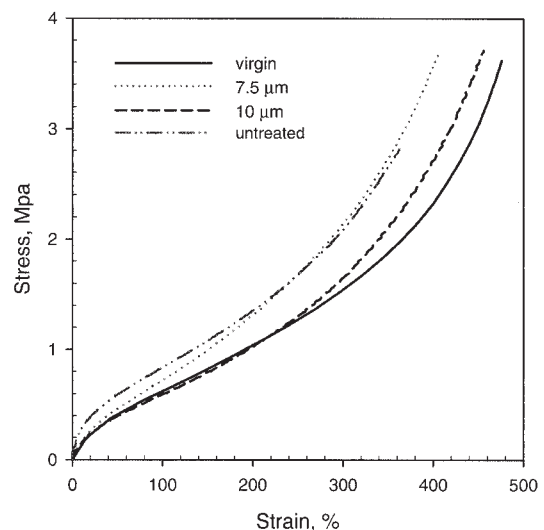


Figure 11 Stress–strain curves of vulcanizates of virgin and devulcanized butyl rubber obtained at a gap of 0.5 mm and a flow rate of 1 g/s with a medium die.

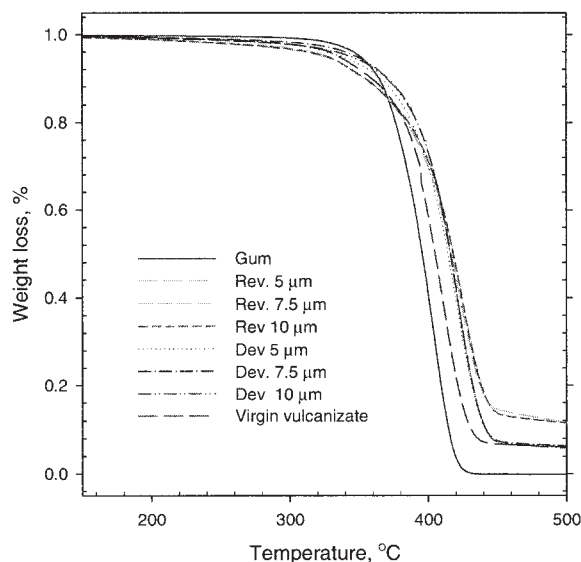


Figure 12 TGA curves of virgin gum, virgin vulcanizate, and ultrasonically devulcanized and revulcanized rubber. The devulcanization conditions were a gap of 0.5 mm, a flow rate of 1 g/s, and a medium die.

still possible to revulcanize the untreated butyl rubber. However, because of the higher gel content (97%) in the sample (Fig. 5), it was hard to mix it with the curing agents, and many voids were observed in the compression moldings of this sample. This was the reason that this sample showed a lower strength and elongation. The tensile strength of the revulcanized samples was similar to that of the virgin vulcanizate, whereas the elongation was reduced. This reduction was possibly due to the breakup of main chains during the ultrasonic treatment.^{14,19} The samples of devulcanized rubber at higher amplitudes showed better properties than the samples devulcanized at lower amplitudes. The reason for this was that greater degradation occurred at higher amplitudes, and this gave the devulcanized rubbers better processability.

Figure 11 shows that the modulus of the revulcanized rubbers was greater than that of the virgin vulcanizate. However, according to the final torque values shown in Figure 4, the modulus of the virgin vulcanizate should have been higher. The reason for this discrepancy is not clear.

Thermal properties

Figure 12 shows TGA curves of virgin gum, virgin vulcanizate, and ultrasonically devulcanized and revulcanized butyl rubber. During the initial stage, the weight loss was mainly due to the loss of the volatile curing agent in the samples; the weight loss of the revulcanized samples was faster than that of devulcanized and virgin gum because there were more curing agent in the revulcanized samples. However, at a later

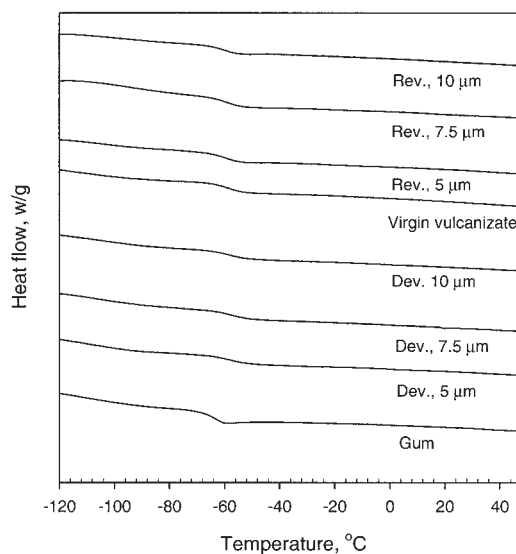


Figure 13 DSC curves of virgin gum, virgin vulcanizate, and devulcanized and revulcanized butyl rubber. The devulcanization conditions were a gap of 0.5 mm, a flow rate of 1 g/s, and a medium die.

stage, the order of the thermal stability of various samples was as follows: virgin gum < virgin vulcanizate < devulcanized samples < revulcanizates. This sequence was clearly related to the amount of unsaturation present in the samples. In particular, the virgin gum had more double bonds than the other samples. The presence of unsaturation was likely to accelerate the process of bond scission by thermal degradation, as shown in an earlier study.²⁸ Moreover, as Figure 12 shows, the lowest nonvolatile fraction was found in the virgin gum, whereas 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 due to the fact that the vulcanized rubbers contained additional amounts of curatives (5 phr) in comparison with the devulcanized samples.

Figure 13 shows DSC curves of the virgin gum, virgin vulcanizate, and devulcanized, and revulcanized butyl rubber, indicating the presence of one glass-temperature temperature (T_g) from -120 to 50°C . The T_g values are listed in Table II. The T_g values

TABLE II
 T_g of Gum, Devulcanized Butyl Rubber, and Their Vulcanizates

	Uncured	Cured
Gum	-63.4	-58.2
5 μm	-58.7	-56.9
7.5 μm	-58.7	-57.6
10 μm	-60.0	-58.2

TABLE III
Physical and Chemical Properties of the Butyl Rubber Used in the Simulation

Density (kg/m ³)	0.92
M_n (g/mol)	171,500
M_w (g/mol)	514,100
Monomeric unit weight (g/mol)	56.2
Gel fraction	0.987
Crosslink density (kmol/m ³)	0.139

M_n = number-average molecular weight; M_w = weight-average molecular weight.

of the devulcanized and revulcanized samples were higher than those of the virgin gum and its vulcanizate. Also, the values of T_g of the devulcanized and revulcanized samples decreased with an increase in the amplitude. The virgin vulcanizate and revulcanized samples had higher T_g 's than the corresponding virgin gum and devulcanized samples. Clearly, the glass-transition temperatures of butyl rubber increased upon crosslinking because of the reduced mobility of the chains, as typically observed for other rubbers.²⁶

Simulation of the structural characteristics

As described before, the normalized crosslink density and normalized gel fraction for ultrasonically devulcanized rubber can be correlated by a universal master curve that is independent of processing conditions (e.g., ultrasonic amplitude, pressure, and gap size).²⁹ To simulate the structural characteristics of devulcanized butyl rubber, we used the Dobson–Gordon theory of rubber network statistics;^{30,31} the simulation procedure was similar to that described in an earlier article.²⁹ The material parameters of the butyl rubber used in this simulation are shown in Table III. Figure 14 shows the experimental and simulation results for devulcanized butyl rubber. The ratio of the scission rate of the main chain (k_p) to that of the crosslink (k_α) was the adjustable parameter of the model. There were two limiting cases: k_p/k_α approaching ∞ , when only rubber main chains were subjected to breakage but crosslinks were intact, and k_p/k_α approaching 0, when only crosslinks broke but main chains remained intact. In Figure 14, these two cases are represented by solid and dashed lines, respectively. Degradation through the rupture of crosslinks led to more loose gel because the crosslink density was lower at a given gel fraction.

Figure 14 shows that the experimental data lie between these two limiting cases, indicating that both the breakage of main chains and the rupture of crosslinks occurred during the devulcanization of butyl rubber. The dotted line represents the results of calculations with an adjusted value of k_p/k_α of 5.14

$\times 10^{-3}$ for resin-cured butyl rubber. For comparison, k_p/k_α is 3×10^{-2} in sulfur-cured SBR,¹⁸ 8.74×10^{-4} in peroxide-cured silicone rubber,¹⁷ 1.84×10^{-3} in sulfur-cured EPDM,¹⁹ and 2.67×10^{-2} in sulfur-cured BR. We concluded that a higher rate of crosslink scission than that of main-chain bond rupture occurred during the devulcanization of butyl rubber. The data for five different rubbers showed that k_p/k_α followed the following order: silicone rubber < EPDM rubber, butyl < BR, SBR. This was quite reasonable because the main chain of silicone rubber has a stronger Si—C bond than the C—C bond in the main chain of other rubbers.^{32–34} Butyl rubber, like EPDM, has fewer double bonds and better thermal stability than BR and SBR. Moreover, resin-cured butyl rubber has C—C crosslinks instead of C—S or S—S crosslinks in sulfur-cured EPDM, and this gives EPDM a higher k_α value. On the other hand, EPDM does not have a double bond in its main chain, and this gives EPDM a lower k_p value; in all, EPDM has a lower k_p/k_α value than butyl rubber.

CONCLUSIONS

This study indicated that the devulcanization of unfilled butyl rubber, which had less unsaturation, required more severe ultrasonic treatment conditions than other rubbers with a higher degree of unsaturation. The gel fraction measurements of the revulcanized rubber showed that some additional amount of the incurable sol part was generated during the ultrasonic devulcanization. GPC data obtained for the devulcanized samples showed significant molecular

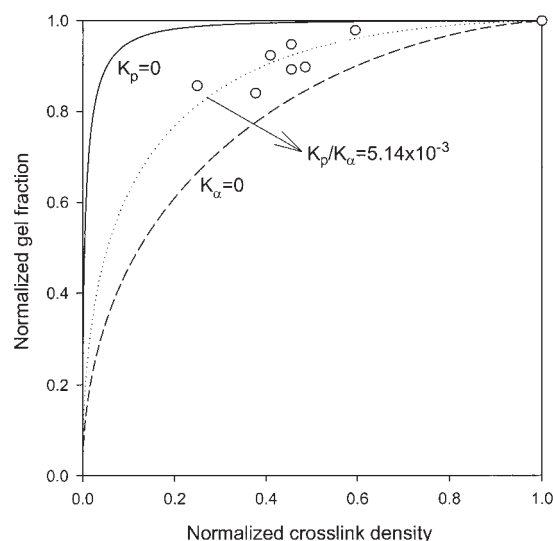


Figure 14 Normalized crosslink density versus the normalized gel fraction for ultrasonically devulcanized butyl rubber obtained under various devulcanization conditions. The symbols represent experimental data, and the lines represent simulated results.

weight reduction and broadening of the molecular weight distribution in comparison with the virgin gum. These data were a direct indication that devulcanization and degradation of butyl rubber occurred simultaneously during the imposition of ultrasound. The rheological properties showed that devulcanized butyl rubber was more elastic than uncured virgin rubber. Vulcanizates of devulcanized butyl rubber showed mechanical properties comparable to those of virgin vulcanizates. The thermal degradation of the revulcanized butyl rubber occurred at a higher temperature than that of the virgin gum and virgin vulcanizate because fewer double bonds were left after devulcanization and revulcanization. The structural characteristics of the devulcanized butyl rubber were simulated with the Dobson–Gordon theory of rubber network statistics. A fairly good agreement between the experimental data and theoretical prediction was achieved. The simulation of devulcanized butyl rubber indicated that the rate of crosslink rupture was much higher than that of main chains. The differences in the bond energies of the various rubbers were used to qualitatively explain this observation.

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References

- Kresge, E.; Wang, H.-C. In *Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I., Ed.; Wiley: New York, 1993; Vol. 8, p 934.
- Hofmann, W. *Rubber Technology Handbook*; Hanser: New York, 1989; Chapter 3, p 52.
- Fix, S. R. *Elastomerics* 1980, 112(6), 38.
- Nicholas, P. P. *Rubber Chem Technol* 1982, 55, 1499.
- Siuru, B. *Scrap Tire News* 1997, 12, 14.
- Phadke, A. A.; Bhattacharya, A. K.; Chakraborty, S. K.; De, S. K. *Rubber Chem Technol* 1983, 56, 726.
- Khait, K.; Torkelson, J. M. *Polym Plast Technol Eng* 1999, 38, 445.
- Bilgili, E.; Arastoopour, H.; Bernstein, B. *Rubber Chem Technol* 2000, 73, 340.
- Morin, J. E.; Williams, D. E.; Farris, R. J. *Rubber Chem Technol* 2002, 75, 955.
- Adhikari, B.; De, D.; Maiti, S. *Prog Polym Sci* 2000, 25, 909.
- Isayev, A. I. In *Rubber Technologist's Handbook*; De, S. K.; White, J. R., Eds.; Rapra Technology: Shawbury, England, 2001; Chapter 15, p 511.
- Yun, J.; Oh, J. S.; Isayev, A. I. *Rubber Chem Technol* 2001, 74, 317.
- Isayev, A. I.; Chen, J.; Tuchachinsky, A. *Rubber Chem Technol* 1995, 68, 267.
- Tapale, M.; Isayev, A. I. *J Appl Polym Sci* 1998, 70, 2007.
- Hong, C. K.; Isayev, A. I. *J Appl Polym Sci* 2001, 79, 2340.
- Shim, S. E.; Isayev, A. I. *Rubber Chem Technol* 2001, 74, 303.
- Diao, B.; Isayev, A. I.; Levin, V. Y. *Rubber Chem Technol* 1999, 72, 152.
- Levin, Y. V.; Kim, S. H.; Isayev, A. I. *Rubber Chem Technol* 1997, 70, 120.
- Yun, J.; Isayev, A. I. *Gummi Fasern Kunstst* 2002, 55, 628.
- Ghose, S.; Isayev, A. I. *J Appl Polym Sci* 2003, 88, 980.
- Oh, J. S.; Isayev, A. I. *J Appl Polym Sci* 2004, 93, 1166.
- Okay, O.; Durmaz, S.; Erman, B. *Macromolecules* 2000, 33, 4822.
- Dick, J. S.; Harmon, C.; Vare, A. *Polym Test* 1999, 18, 327.
- Flory, P. J.; Rehner, J., Jr. *J Chem Phys* 1943, 11, 512.
- Barton, A. *CRC Handbook of Polymer–Solvent Interaction Parameters and Solubility Parameters*; CRC: Boston, 1990; Chapter 9, p 72.
- Yun, J.; Isayev, A. I.; Kim, S. H.; Tapale, M. *J Appl Polym Sci* 2003, 88, 434.
- Makarov, V. M.; Drozdovski, V. F. *Reprocessing of Tires and Rubber Wastes*; Ellis Horwood: New York, 1991; Chapter 2.
- Jiang, D. D.; Levchik, G. F.; Levchik, S. V.; Wilkie, C. A. *Polym Degrad Stab* 1999, 65, 387.
- Yashin, V. V.; Isayev, A. I. *Rubber Chem Technol* 2000, 73, 325.
- Gordon, M. *Proc R Soc London Ser A* 1962, 268, 240.
- Dobson, G. R.; Gordon, M. *J Chem Phys* 1965, 43, 705.
- Patai, S.; Rappoport, Z. *The Chemistry of Organic–Silicone Compounds*; Wiley: New York, 1989.
- Kircher, K. *Chemical Reactions in Plastic Processing*; Hanser: New York, 1987; Chapter 11.
- Feldstein, M. C. In *Polymer Encyclopedia*; Kargin, V. A., Ed.; Soviet Encyclopedia: Moscow, 1977; Vol. 1, p 541.