

# Recycling of Unfilled Polyurethane Rubber Using High-Power Ultrasound

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Received 9 April 2002; accepted 11 June 2002

**ABSTRACT:** This investigation deals with the recycling of polyurethane rubber by the application of high-power ultrasound in a continuous ultrasonic coaxial reactor. The cured rubber has been devulcanized at various feed rates and various gap sizes and then revulcanized again with certain adjustments in the curing recipe. The die pressure and the total power consumption have been recorded as a function of the processing conditions. The rheological and mechanical properties, hardness, gel fraction, and crosslink density of the original, devulcanized, and revulcanized samples have been measured and compared in an attempt to determine the optimum condition for devulcanization. Gel permeation chromatography (GPC) has been carried out with the sol part of the devulcanized samples to study the devulcanization and degradation. The results show that at low flow rates and narrow gaps, the material is degraded very

quickly and, therefore, exhibits very poor mechanical properties. However, increasing the feed rate results in an improvement of the mechanical properties. Measured values of the crosslink densities and gel fractions indicate the processing conditions under which greater devulcanization and degradation of the samples take place. The lower molecular weights of the sol, extracted from the devulcanized samples, obtained in the GPC experiments in comparison with polyurethane gum indicate a breakdown of the polymeric chains as a result of devulcanization. The devulcanized samples show a higher activation energy of viscous flow, possibly because of the formation of branched structures. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 980–989, 2003

**Key words:** polyurethanes; rubber; mechanical properties; crosslink density; gels

## INTRODUCTION

Polyurethane (PU) rubber was invented by Otto Bayer way back in 1937.<sup>1</sup> Millable urethanes are a form of urethane that can be processed on conventional rubber machinery. The urethane rubbers are produced with a lower ratio of isocyanates to polyols, and in this case, the material needs further crosslinking or vulcanization.

PU rubber is a specialty rubber that finds use in many common rubber articles such as skate wheels, conveyor belts, rubber-covered rolls, and other applications for which urethane is used because of its properties. Urethane rubber possesses excellent abrasion resistance, solvent and oil resistance, high tensile and tear properties, good resistance to ozone and oxygen, and good low-temperature properties.<sup>2</sup>

As for any crosslinked material, recycling becomes a major issue in this environmentally conscious world. Attempts have been made to recycle flexible PU foam into solid PU elastomers by compression molding<sup>3</sup> or by pressure shear pulverization followed by compres-

sion molding,<sup>4</sup> to recycle mechanically ground reaction injection molding (RIM) PUs by hot compression molding,<sup>5</sup> to recycle foam waste by solid-state shear extrusion,<sup>6</sup> and to recycle with chemical methods such as hydrogenation, hydrolysis, glycolysis, aminolysis, and pyrolysis.<sup>7–9</sup> Spent-PU-based propellant has been recovered by the method of swelling in chloroform with subsequent prolonged (up to 50 min) applications of ultrasound to swollen and pulverized samples in a beaker.<sup>10</sup>

So far, most of the recycling work on PUs has focused on PU foams and RIM PUs. Very little work has been done on PU elastomers.<sup>11</sup> The effects of ultrasound on polymer solutions have been studied extensively. An elaborate compilation of these studies was presented by Price.<sup>12</sup> Ultrasonic chain scission of polymers in solution<sup>13,14</sup> is characterized as being nonrandom, and this means that the breakage of polymeric chains will occur near the middle of the chain. This chain scission occurs because of cavitation collapse.<sup>12</sup> The process is not as random as thermal degradation.<sup>15,16</sup> The mechanism of the ultrasonic degradation of crosslinked elastomers is, however, still not clearly understood. It has been assumed that the process occurs because of cavitation, the rapid growth and decay of microbubbles, as the ultrasonic wave is propagated through the rubber medium.<sup>17–20</sup> The application of ultrasound for the devulcanization of rub-

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Contract grant sponsor: National Science Foundation; contract grant number: DMI-0084740.

ber is a comparatively recent approach, but the approach has been successful in the recycling of various rubbers such as ground rubber tire (GRT), natural rubber (NR), styrene butadiene rubber (SBR), ethylene-propylene-diene monomer (EPDM), and silicone rubber.<sup>21–34</sup>

This article deals with recent experiments on the recycling of PU rubber with an ultrasonic reactor developed in our laboratory. From the investigations carried out so far, the optimum processing conditions for the devulcanization of a polyester-based PU rubber have been determined. The devulcanized samples have successfully been revulcanized with suitable recipes, and comparisons of the various properties have been made with those of the original. They include measurements of the mechanical and rheological properties, hardness, gel fraction, and crosslink density as well as the determination of the molecular weights of the sol part of the devulcanized samples.

## EXPERIMENTAL

### Materials and methods of investigations

The PU rubber used for the experiments was a polyester-based millable PU rubber (Vibrathane 5008, Uniroyal Chemicals, Middlebury, CT) with a weight-average molecular weight ( $M_w$ ) of about 70,000. The rubber was compounded with the following ingredients: 0.5 phr zinc stearate (ZnSt; Synpro, Ferro, Cleveland, OH), 2 phr 2-mercaptobenzothiazole (Akrochem Rubbermakers, Akron, OH), 4 phr 2,2'-dibenzothiazyl disulfide (Akrochem Rubbermakers), 1 phr 2,2'-benzothiazyl disulfide zinc chloride complex (Caytur 4, Uniroyal Chemicals), and 2 phr sulfur (Akrochem Rubbermakers).

The rubber was compounded in a two-roll mill (Deublin Rubber Machinery Co., Northbrook, IL) at room temperature. ZnSt acted not only as an accelerator for sulfur vulcanization but also as a releasing agent to prevent the gum rubber from sticking to the rolls. The total mixing time was 8 min.

The sample was then compression-molded (Wabash) into slabs ( $260 \times 260 \times 12 \text{ mm}^3$ ) at a temperature of  $150^\circ\text{C}$  and at a pressure of 41.4 MPa (6000 psi) for 20 min. The time for curing was calculated from the maximum torque value of the cure curve, which was obtained with a Monsanto (Akron, OH) curometer according to ASTM D 2084 and with an Advanced Polymer Analyzer (APA) 2000 (Alpha Technologies, Akron, OH).<sup>35,36</sup>

After the molding, the vulcanized samples were ground in a Nelmor grinding machine (N. Uxbridge, MA) with a 5-mm screen. The ground rubber was then fed into a rubber extruder with a coaxial ultrasound die attachment that was developed in our laboratory as described in refs. 22 and 23. The temperature of the

barrel was set at  $120^\circ\text{C}$ . The screw speed was 20 rpm, and the cooling water flow rate for both the die and horn was  $0.09 \text{ m}^3/\text{h}$ . Experiments were carried out at two gap sizes ( $\delta$ , the gap between the die plate and horn) of 2.5 and 3 mm. The flow rates were 0.63, 1.26, and 2.52 g/s. A 3300-W ultrasonic power supply, a converter, and a booster were used to provide longitudinal vibrations to the horn at a frequency of 20 kHz. The amplitudes of the ultrasonic waves were 5, 7.5, and 10  $\mu\text{m}$ . The total power consumption and the die entrance pressures were recorded for the various conditions of devulcanization, and the devulcanized samples were collected.

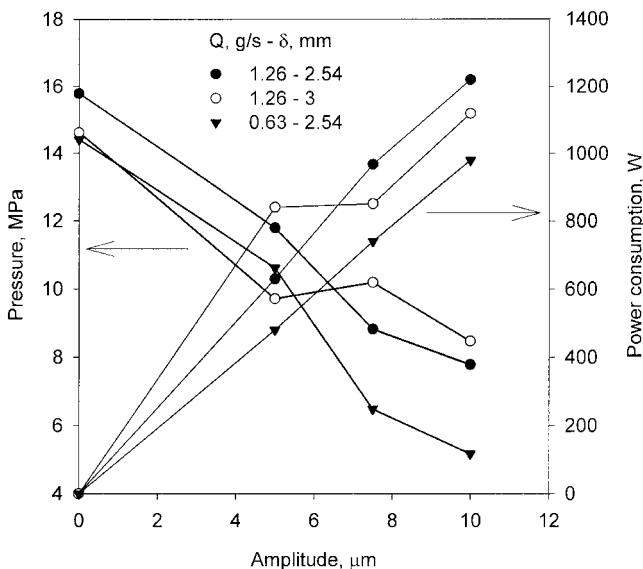
The devulcanized material was then homogenized in the two-roll mill and revulcanized. For samples devulcanized at a flow rate of 1.26 g/s, a change in the compounding recipe had to be made as band formation on the two-roll mill took place only with the elimination of ZnSt from the recipe. The cure curves of these samples at  $150^\circ\text{C}$  were obtained with the APA 2000 (Alpha Technologies), whereas the cure curves of the samples devulcanized at 0.63 g/s were obtained with the Monsanto curometer.

For mechanical testing, samples of the original vulcanized and revulcanized rubber samples were prepared by compression molding in a mold ( $127 \times 127 \times 2 \text{ mm}^3$ ). The tests were performed at room temperature according to ASTM D412 with an Instron (Canton, MA) model 5567 tensile tester with a load cell of 500 N and a crosshead speed of 500 mm/min.

Dynamic tests of the original and devulcanized samples were carried out with the APA 2000 (Alpha Technologies) at temperatures of 90, 100, and  $120^\circ\text{C}$  within a frequency range of 0.2–200 rad/s and at a strain amplitude of  $\gamma_0 = 0.042$  ( $0.3^\circ$ ). The gel fraction and crosslink density were determined by the Soxhlet extraction method with tetrahydrofuran (THF) as the solvent. The extraction time was 24 h. After 24 h, the weight of the swollen sample was measured after the removal of the surface solvent. The samples were dried in an oven at  $65^\circ\text{C}$  for 24 h and then allowed to stand at room temperature before the weight was taken again. The crosslink density was calculated with the Flory–Rehner equation.<sup>37</sup>

The hardness of the original and revulcanized samples was measured with a shore A durometer according to ASTM D 2240.

Molecular weight measurements were carried out with a Waters 410 differential refractometer, a Waters 486 tunable absorbance detector, and a Waters 510 HPLC pump. THF as a solvent was run at room temperature, and conventional calibration was used against polystyrene standards. The range of the light intensity for the absorbance detector was between 196 and 600 nm, with the primary use in the UV range (190–380 nm). The sensitivity range was 0.001–2.0 absorbance units (full scale). The pump flow rate was set



**Figure 1** Die entrance pressure and power consumption versus the amplitude for unfilled PU rubber at feed rates of 0.63 and 1.26 g/s and gaps of 2.5 and 3 mm.

at 1 mL/min. The specifications of the optical component were a path length of 10 mm (standard, analytical) and a cell volume of 8  $\mu\text{L}$  (standard, analytical). Experiments were carried out on the gum (which was directly soluble in THF) and on the sol part of the devulcanized samples obtained after extraction with THF for 96 h in the Soxhlet apparatus.

## RESULTS AND DISCUSSION

### Pressure and power consumption

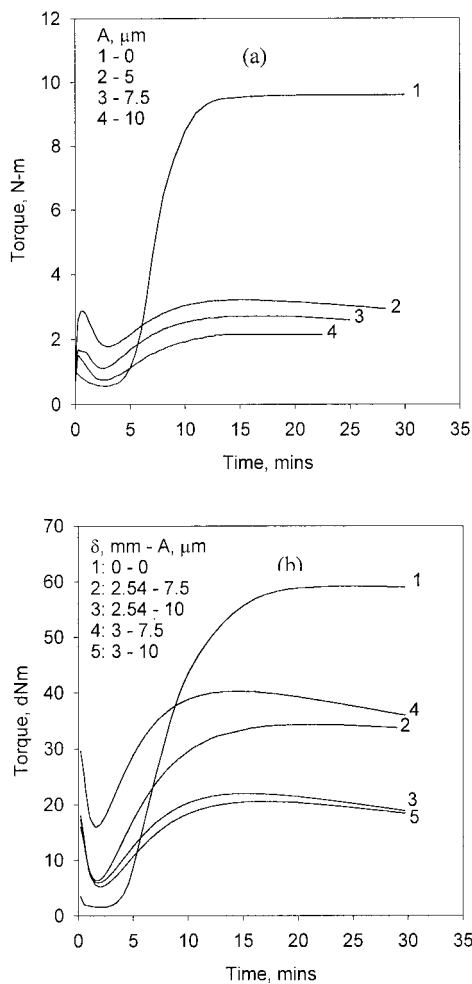
Although the experiments have been carried out at a high feed rate of 2.52 g/s, there is no devulcanization of samples at this flow rate. Instead, a significant reduction in the size of the particles takes place. However, at lower flow rates of 0.63 and 1.26 g/s, substantial devulcanization of the samples takes place. Figure 1 shows the die entrance pressure and power consumption during devulcanization. For the 2.54-mm gap and feed rates of 0.63 and 1.26 g/s, the pressure decreases with an increase in the amplitude. Ultrasound facilitates the flow of the rubber through the gap, first because of a reduction of friction and second because of the effect of devulcanization, which increases the fluidity of samples, allowing it to pass through them more easily. Also, for the same die gap, the pressure increases with the flow rate. This is because the die pressure is a function of the average residence time of the rubber in the treatment zone and the residence time is inversely proportional to the rubber flow rate.<sup>24</sup> However, an unusual trend is observed for the 3-mm gap. From 5 to 7.5  $\mu\text{m}$ , there is an increase in pressure followed by the traditional decrease of pressure with an increase in amplitude from

7.5 to 10  $\mu\text{m}$ . This happens because at an amplitude of 5  $\mu\text{m}$ , there is no devulcanization taking place and the sample just passes through the extruder with a decreased size of the exiting particles. However, at 7.5  $\mu\text{m}$ , devulcanization starts, and the sample becomes a mixture of crumbs and liquid. This resulting mixture restricts the flow of the sample through the die gap, causing the pressure to increase. With a further increase in the amplitude, the sample becomes more liquidlike and, therefore, more easily flowing, and this results in an expected decrease of pressure.

The recorded power consumption is the total power consumption, one part of which is dissipated as heat and another part of which is used for breaking the bonds necessary for devulcanization. However, it is not possible to determine exactly the proportion of power in these two cases. The only thing that can be recorded is the initial power consumption of the system when the horn works without loading, and this loss has to be subtracted from the recorded values of the power consumption to give the values used in Figure 1. Also, for the samples passing through the 2.54-mm gap, at both feed rates, the power consumption increases with the amplitude, indicating that more energy has been transmitted into the rubber as the amplitude is increased. Additionally, the increase in the feed rate for the same gap size leads to an increase in pressure and power consumption that is an indication that greater energy is being transmitted into the rubber at higher feed rates. Similar graphs for the die pressure and power consumption have been observed with the ultrasonic treatment of various other unfilled rubbers such as NR,<sup>24</sup> SBR,<sup>32</sup> silicone rubber,<sup>27</sup> and EPDM.<sup>31</sup> For the 3-mm gap, the power consumption is more or less the same at 5 and 7.5  $\mu\text{m}$ , but it increases when the amplitude is increased to 10  $\mu\text{m}$ . In this gap, devulcanization takes place at only 7.5 and 10  $\mu\text{m}$ .

### Cure behavior

Figure 2(a,b) shows the cure curves of the samples devulcanized at flow rates of 0.63 and 1.26 g/s, respectively, and at different amplitudes and gap sizes. At a feed rate of 1.26 g/s, only the samples devulcanized at 7.5 and 10  $\mu\text{m}$  can be revulcanized as only these samples can form bands on the two-roll mill. Both figures show that with an increase in the amplitude, there is a decrease in the maximum torque value. Also, the devulcanized samples cure at a faster rate than the virgin sample with a substantial lower final torque. The minimum torque values for a particular feed rate and gap size show a decrease with an increase in amplitude. A lower minimum torque indicates a lower viscosity of the devulcanized sample. This fact is further strengthened by the viscosity curves obtained from the APA [shown later in Fig. 4(a,b)]. At



**Figure 2** Cure curves for original and devulcanized PU rubber obtained (a) at a flow rate of 0.63 g/s, a temperature of 120°C, amplitudes of 5, 7.5, and 10 μm, and a gap of 2.54 mm as measured with a Monsanto curometer and (b) at a flow rate of 1.26 g/s, a temperature of 120°C, amplitudes of 7.5 and 10 μm, and gaps of 2.54 and 3 mm as measured using the APA.

higher amplitudes, there is greater devulcanization of the sample, and so the viscosity drops. Another observation from the cure curves is the scorch time of the virgin and devulcanized samples. The devulcanized samples have a lower scorch time than the original sample. The scorch time indicates the onset of crosslinking. With devulcanized samples, there are accelerators, activators, and curing agents (sulfur) remaining in the samples, and so the crosslinking starts earlier. However, at higher feed rates, some of the devulcanized samples show reversion.

**Appearance**

The surfaces of the revulcanized samples have been found to be very smooth and comparable to the surface of the original. However, the color is darker. Generally, devulcanized samples have an inhomoge-

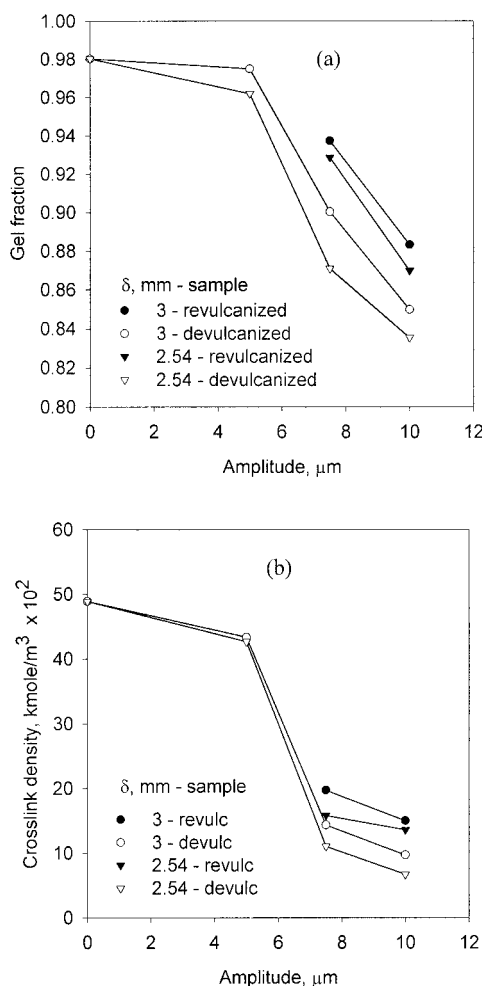
neous nature because they consist of a mixture of gel particles of low crosslink density and sol, almost liquidlike uncrosslinked rubber, but in this case the inhomogeneities are not visible on the surface. However, the inhomogeneities can be observed within the sample by the naked eye when light is allowed to pass through the sample.

**Gel fraction and crosslink density**

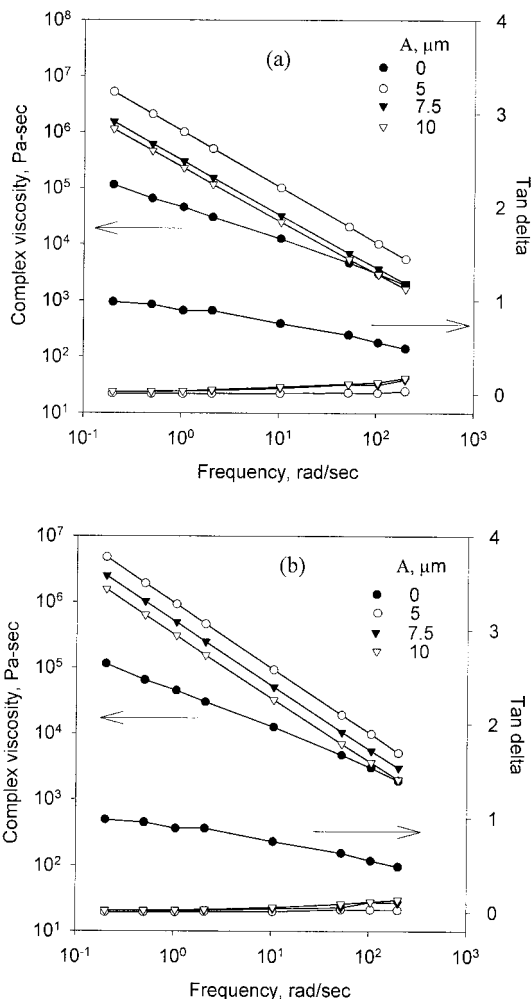
Figure 3(a,b) represents the gel fraction and crosslink densities of the devulcanized and revulcanized samples as a function of the amplitude. The crosslink density of the sample is calculated with the Flory–Rehner equation:<sup>37</sup>

$$n_c = \frac{-\ln(1 - V_r) + V_r + \chi V_r^2}{-V_1(V_r^{1/3} - V_r/2)}$$

where  $n_c$  is the effective number of chains in a real network per unit volume,  $V_1$  is the molar volume of



**Figure 3** (a) Gel fraction and (b) crosslink density versus the amplitude for original, devulcanized, and revulcanized samples at different gap sizes and a flow rate of 1.26 g/s.

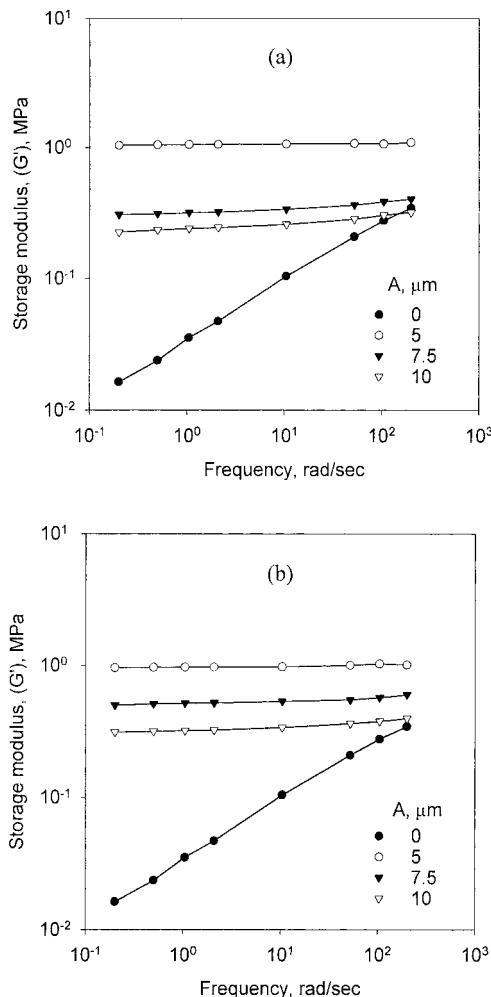


**Figure 4**  $\eta^*$  and  $\tan \delta$  versus the frequency at 120°C for original and devulcanized PU rubber. The conditions of devulcanization are a flow rate of 1.26 g/s, a temperature of 120°C, amplitudes of 5, 7.5, and 10  $\mu\text{m}$ , and gaps of (a) 2.54 and (b) 3 mm.

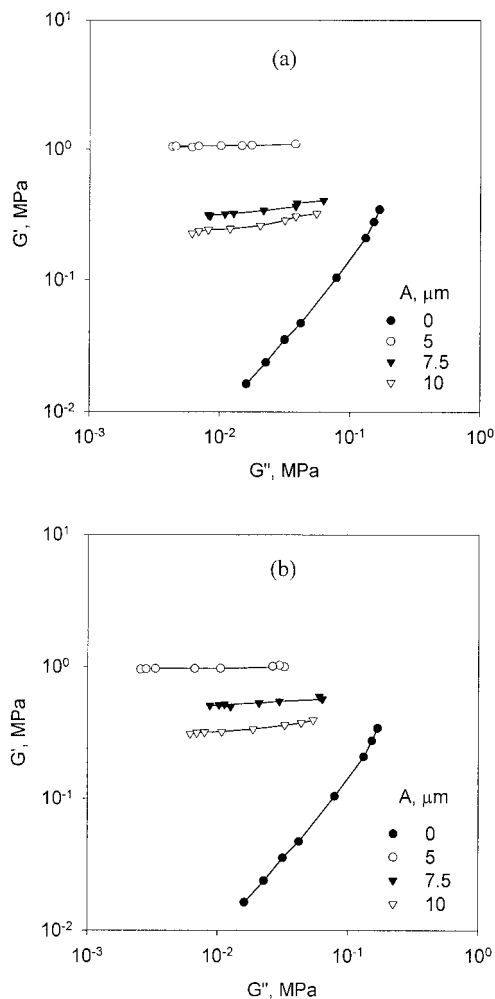
the solvent,  $V_r$  is the volume fraction of the polymer in the swollen network in equilibrium with the pure solvent, and  $\chi$  is the interaction parameter between the solvent and the polymer. THF has been chosen as a suitable solvent for this system, and it has the value of  $V_1 = 81.7 \text{ cc/mol}$ . The specific gravity of the rubber is 1.15, and the interaction parameter has been taken to be 0.39.<sup>38</sup>

In Figure 3(a,b), it can be seen that the gel fraction and crosslink density of both the devulcanized and revulcanized samples for the feed rate of 1.26 g/s decrease with an increase in the amplitude. At an amplitude of 5  $\mu\text{m}$ , the gel fraction of the devulcanized sample is almost the same as that of the original, but there is a sufficient drop from 7.5  $\mu\text{m}$  onward. The crosslink density value of the devulcanized sample at an amplitude of 5  $\mu\text{m}$  is also sufficiently high and shows a sharp drop at higher amplitudes. For both gap sizes, at this amplitude there is very little devul-

canization of the sample taking place, as is evident from the powdery appearance of the sample. Therefore, high values of the gel fraction and crosslink density have been observed. It should be noted that samples obtained at 5  $\mu\text{m}$  cannot be revulcanized, and so the gel fraction and crosslink density of the revulcanized samples at this amplitude cannot be measured. Also, increasing the gap size for the same feed rate and the same amplitude leads to a higher gel fraction and crosslink density. At higher gaps, less devulcanization takes place, and so both the gel fraction and crosslink density are higher. It can also be seen in Figure 3(a,b) that the gel fraction and crosslink density of revulcanized samples are substantially lower than those of virgin vulcanizates. The latter indicates that the devulcanized samples lose a substantial number of unsaturated sites available for revulcanization. This observation of a decrease in the gel fraction and crosslink density of the devulcanized



**Figure 5** Storage modulus versus the frequency at 120°C for original and devulcanized PU rubber. The conditions of devulcanization are a flow rate of 1.26 g/s, a temperature of 120°C, amplitudes of 5, 7.5, and 10  $\mu\text{m}$ , and gaps of (a) 2.54 and (b) 3 mm.



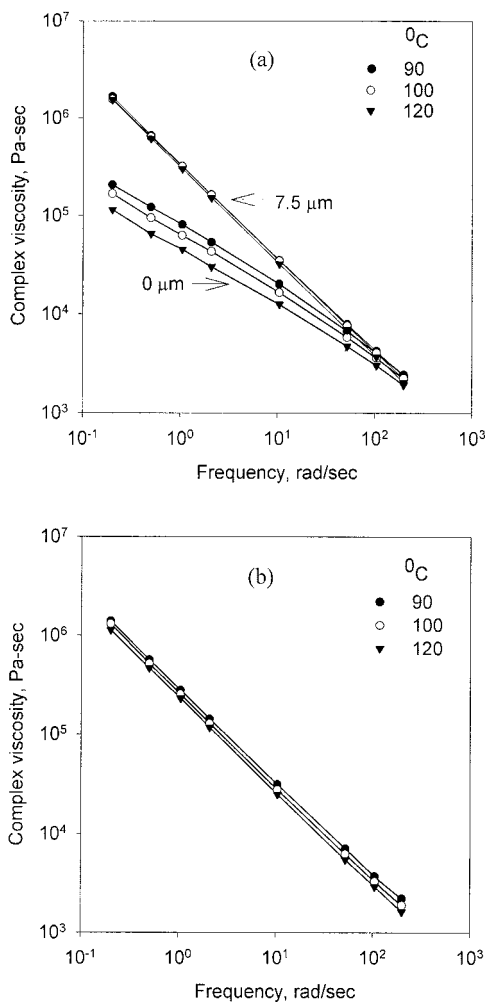
**Figure 6** Storage modulus ( $G'$ ) versus the loss modulus ( $G''$ ) at  $120^\circ\text{C}$  for original and devulcanized PU rubber. The conditions of devulcanization are a flow rate of  $1.26\text{ g/s}$ , a temperature of  $120^\circ\text{C}$ , amplitudes of  $5, 7.5,$  and  $10\ \mu\text{m}$ , and gaps of (a)  $2.54$  and (b)  $3\text{ mm}$ .

samples with an increase in the amplitude has been observed in other unfilled systems such as SBR,<sup>29,32–34</sup> silicone rubber,<sup>27</sup> EPDM,<sup>31</sup> and NR.<sup>24</sup> However, as for SBR<sup>29,32–34</sup> and EPDM,<sup>31</sup> the revulcanized samples show higher values of the gel fraction and crosslink density with respect to the original sample, whereas for NR<sup>24</sup> and silicone rubber,<sup>27</sup> in certain cases, trends similar to those of PU rubber, that is, a decrease in the gel fraction and crosslink density with respect to the original, are observed.

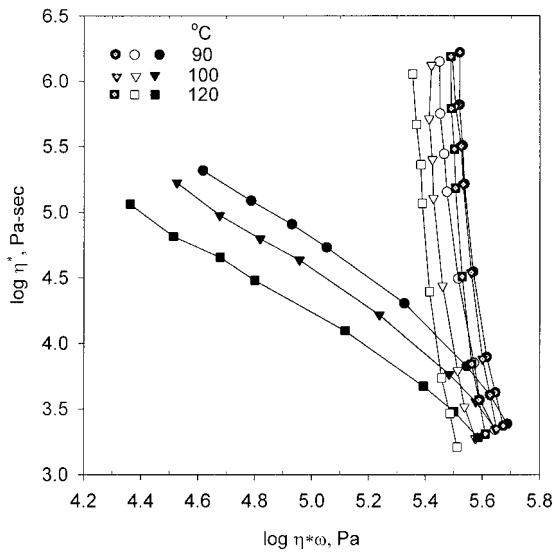
**Viscoelastic properties**

The dynamic viscoelastic properties of the original and devulcanized samples have been measured with the APA 2000. The properties have been measured at a temperature of  $120^\circ\text{C}$ , the temperature at which the rubber is devulcanized, and at  $\gamma_0 = 0.042$  ( $0.3^\circ$ ). The variation of the complex viscosity ( $\eta^*$ ) and  $\tan \delta$  with

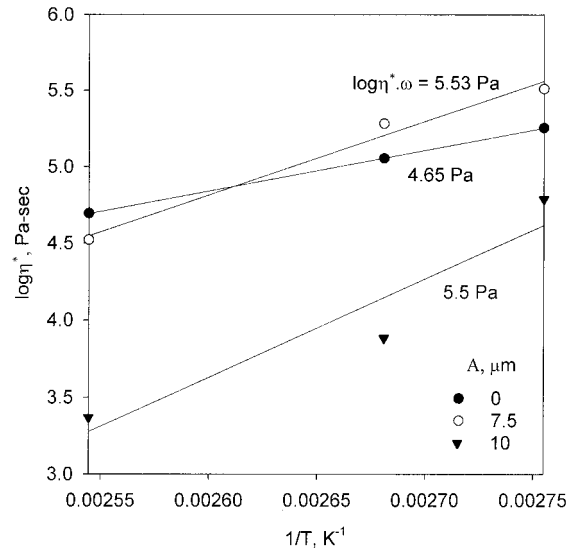
the frequency for samples devulcanized at  $1.26\text{ g/s}$  and at gaps of  $2.54$  and  $3\text{ mm}$  are shown in Figure 4(a,b). The  $\eta^*$  values of the devulcanized samples are higher than those of the original. This is probably due to the high gel content present in the devulcanized samples, as indicated in Figure 3(a). Again, the viscosity shows a decrease with an increase in the amplitude. The viscosity is indirectly related to the degree of devulcanization and degradation, and this decrease in the viscosity implies that greater devulcanization and degradation are occurring at higher amplitudes. The variation of  $\tan \delta$  with the frequency can also be noted in the figure. For the original gum rubber, the value of  $\tan \delta$  shows a marked decrease with an increase in the frequency. However, for the devulcanized samples,  $\tan \delta$  remains virtually unchanged at  $5\ \mu\text{m}$  at all frequencies but increases with the frequency at higher amplitudes. The value of  $\tan \delta$  can give an idea of the elasticity of a sample. A lower value of  $\tan \delta$  indicates



**Figure 7**  $\eta^*$  versus the frequency at different temperatures for gum and devulcanized PU rubber. The conditions of devulcanization are a flow rate of  $1.26\text{ g/s}$ , a temperature of  $120^\circ\text{C}$ , amplitudes of (a)  $7.5$  and (b)  $10\ \mu\text{m}$ , and a gap of  $2.54\text{ mm}$ .



**Figure 8**  $\eta^*$  versus  $\eta^*\omega$  for virgin (solid symbols) and devulcanized samples. The conditions of devulcanization are a flow rate of 1.26 g/s, a temperature of 120°C, amplitudes of 7.5 (open dotted symbols) and 10  $\mu\text{m}$  (open symbols), and a gap of 2.54 mm.



**Figure 9**  $\log \eta^*$  versus  $1/T$  for gum and devulcanized samples at constant values of  $\log \eta^*\omega$ . The conditions of devulcanization are a flow rate of 1.26 g/s, a temperature of 120°C, a gap of 2.54 mm, and various amplitudes.

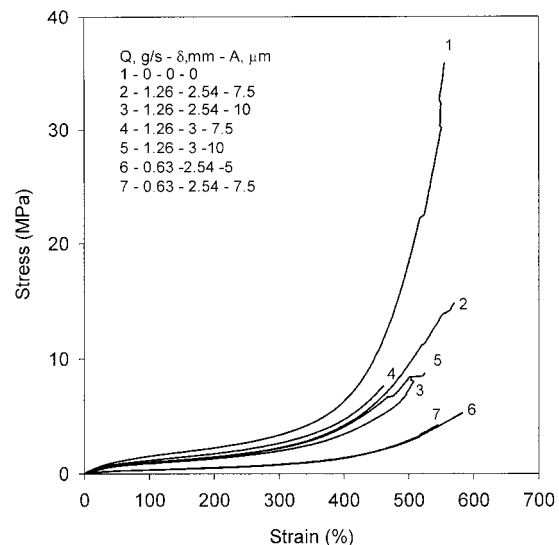
a more elastic sample. The devulcanized samples, because of the presence of a gel, are more elastic than the gum rubber. For the devulcanized samples, the storage modulus becomes more or less independent of frequency, and this is indicated in Figure 5(a,b), which shows the variation of the storage modulus with the frequency. Clearly, the values of the storage modulus of the devulcanized samples are much higher than that of the original gum. Figure 6(a,b) shows a plot of the storage modulus versus the loss modulus. For the same value of the loss modulus, at all frequencies, the storage modulus is always higher for the devulcanized samples. This is also an indication of the higher elasticity of the devulcanized material. Figure 7(a,b) shows the variation of the viscosity of the gum rubber and the devulcanized rubber at different temperatures. As expected, the viscosity decreases with an increase in the temperature in all cases, but this decrease in the viscosity is more pronounced in the gum rubber than in the devulcanized samples. Also, the power-law index of the devulcanized rubber is substantially lower than that of the virgin rubber.

Another important observation can be made in terms of the activation energies of the viscous flows. Figure 8 shows the log-log plots of  $\eta^*$  versus  $\eta^*\omega$ . The

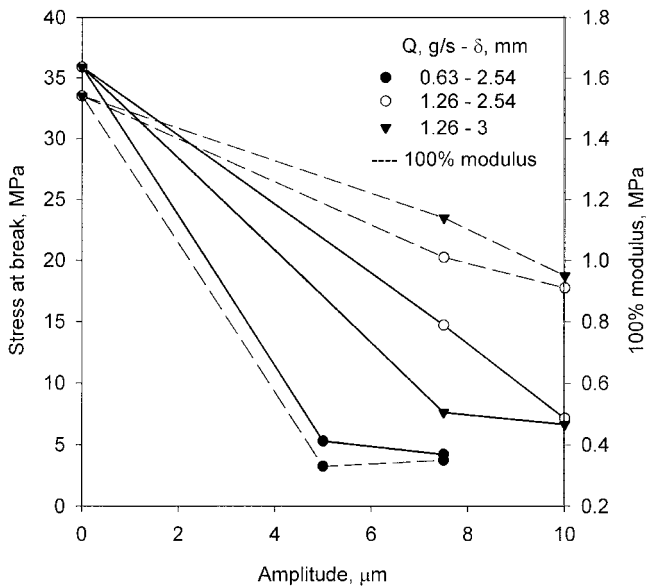
slopes of the viscosity curves of the devulcanized samples are much higher than that of the virgin sample. This is an indication that the devulcanized samples exhibit higher activation energies than the original. This effect is more pronounced at lower stress values. The value of the activation energy is affected by factors related to the flexibility of the macromolecules, one of which is branching. It is well known from a comparison of the activation energies of the viscous flows of linear and branched polymers that linear polymers have a lower value than branched polymers.<sup>39</sup> Therefore, a higher value of the activation

**TABLE I**  
Temperature Sensitivity Values of Viscosity

Sample	$T_{br}$ (K)
Virgin gum PU	2660
1.26 g/s - 2.54-mm gap - 7.5 $\mu\text{m}$	4820
1.26 g/s - 2.54-mm gap - 10 $\mu\text{m}$	6380



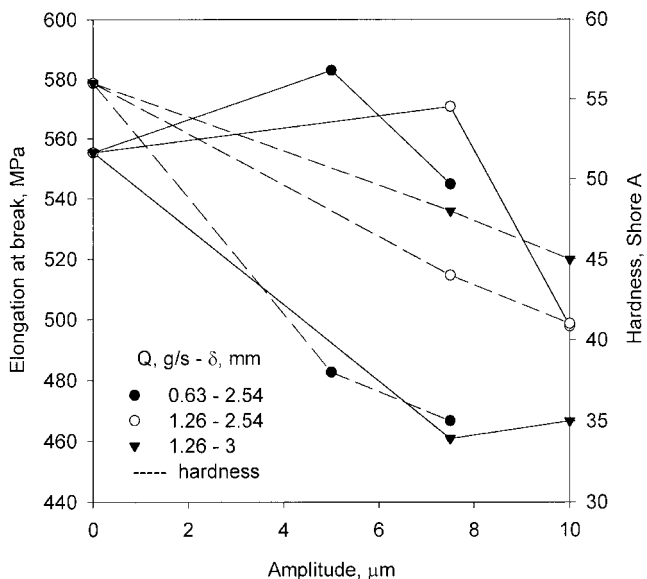
**Figure 10** Stress-strain curves for revulcanized samples prepared from devulcanized samples at different feed rates, gap sizes, and amplitudes.



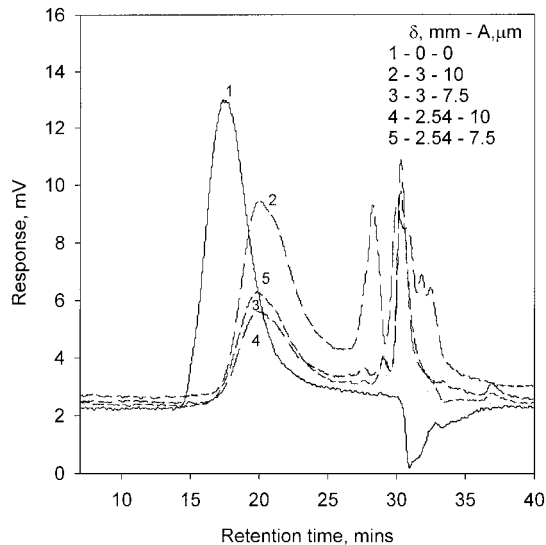
**Figure 11** Stress at break and 100% modulus versus the amplitude for revulcanized PU samples prepared from devulcanized samples at different feed rates, gap sizes, and amplitudes.

energy for the devulcanized samples is possibly an indirect indication of branching taking place after devulcanization. Table I shows the values of  $T_b$ , which is equal to  $E/R$  (where  $E$  is the activation energy and  $R$  is the universal gas constant). It is a measure of the temperature sensitivity of  $\eta^*$  and is given by an Arrhenius-type equation:<sup>40</sup>

$$\eta^* = B \exp(T_b/T) \quad (2)$$



**Figure 12** Elongation at break and hardness versus the amplitude for revulcanized PU samples prepared from devulcanized samples at different feed rates, gap sizes, and amplitudes.



**Figure 13** GPC data showing the reduction in the molecular weight in devulcanized samples in comparison with gum rubber. The conditions of devulcanization are a flow rate of 1.26 g/s, a temperature of 120°C, amplitudes of 7.5 and 10  $\mu\text{m}$ , and gaps of 2.54 and 3 mm.

where  $B$  is a pre-exponent. From the table, it is clear that the devulcanized samples exhibit higher activation energies than the untreated gum sample. Figure 9 shows a plot of  $\log \eta^*$  versus  $1/T$  at constant values of  $\log \eta^* \omega$ , from which the value of  $T_b$  has been calculated.

When the ultrasonic waves act on the crosslinked rubber, not only are the sulfur bonds broken, but portions of the main chain are broken as well. These remnants of the network chain remain attached to the ruptured main chain and lead to a branched structure. This reduces the flexibility of the chains and consequently raises the activation energy.

**Mechanical properties**

Figure 10 shows the stress-strain curves of the revulcanized samples. It seems that the processing conditions or the conditions of devulcanization have a strong effect on the mechanical properties of the final sample. For the same gap size, the samples devulcanized at a lower feed rate show properties inferior to those of the samples devulcanized at a higher feed rate. This is also evident from Figure 11. The reason for this is probably the tremendous degradation of the main chains that occurs during devulcanization at lower feed rates (higher residence time) and, therefore, under more severe conditions. Once the main chains have been broken along with the crosslinks, it is not possible to obtain revulcanized samples with the aim of getting properties comparable to those of the original. Therefore, the samples devulcanized at the feed rate of 0.63 g/s and high amplitudes have been



TABLE II  
Molecular Weight Data of Gum and Devulcanized Samples as Obtained from GPC

Sample	$M_n$	MP	$M_w$	$M_z$	PDI of main peak
Gum	42,300	98,500	65,100	84,700	1.54
1.26 g/s - 3-mm gap - 7.5 $\mu\text{m}$ (sol part)	21,300	23,200	29,600	42,200	1.39
1.26 g/s - 3-mm gap - 10 $\mu\text{m}$ (sol part)	20,300	21,500	27,400	37,900	1.34
1.26 g/s - 2.54-mm gap - 7.5 $\mu\text{m}$ (sol part)	22,000	23,200	31,600	46,700	1.44
1.26 g/s - 2.54-mm gap - 10 $\mu\text{m}$ (sol part)	22,500	23,000	32,600	48,000	1.45

MP = molecular weight at peak;  $M_z$  = z average molecular weight; PDI = polydispersity index.

discarded from further discussion, and more attention has been given to the samples obtained at the higher feed rate of 1.26 g/s, as they show much better mechanical properties. An interesting observation can be made from Figure 12, which shows that under certain conditions, the elongation at break can be even greater than that of the original.

At the same feed rate and gap size, samples devulcanized at lower amplitudes exhibit better mechanical properties. This is quite natural, as at higher amplitudes, a significant amount of degradation will also come into play. Also, although the sample devulcanized at 3-mm gap and 7.5  $\mu\text{m}$  shows a higher modulus and a higher torque value, it also shows greater reversion. The sample devulcanized at 2.54-mm gap and 7.5  $\mu\text{m}$  shows the best mechanical properties.

The modulus (Fig. 11) and hardness (Fig. 12) of the revulcanized samples show substantially lower values than those of the original unfilled sample. There is a substantial difference between the samples obtained at different processing conditions. In agreement with the modulus values, higher values of hardness have been obtained at lower amplitudes.

### Molecular weight

Figure 13 shows the molecular weight data obtained from gel permeation chromatography (GPC). The molecular weight values are given in Table II. The  $M_w$  value of the gum corresponds to about 65,000, which agrees with the value supplied by Uniroyal (~70,000). As evident from the number-average molecular weight ( $M_n$ ) and  $M_w$  values, there is substantial molecular weight degradation in the case of the devulcanized samples. Also, additional peaks are obtained at lower molecular weight values, but these are probably due to the presence of the compounding and curing agents. GPC runs made on the extracted portion of the virgin cured sample also indicate the presence of similar peaks corresponding to lower molecular weight substances in the same region of retention time. The molecular weights of the devulcanized samples have been obtained only from the extracted sol, which, in turn, constitutes only 10–15% of the devulcanized samples. However, these molecular weight data fur-

ther strengthen the results obtained from the curing curves and mechanical property figures, which have shown devulcanization and degradation of the samples after the application of ultrasound.

### CONCLUSIONS

This investigation has proven that polyester-type PU rubber can be successfully recycled with the coaxial ultrasonic reactor developed in our laboratory. Optimum processing conditions for devulcanization have been established. The devulcanized samples have been revulcanized by a certain modification of the curing recipe. During curing, some of the devulcanized samples show a reversion. After revulcanization, the surfaces of the samples show no change from the original in terms of smoothness; the only difference is that the color is darker. The revulcanized samples retain their elongation at break, although the modulus and tensile strength are much lower. Dynamic properties indicate that the devulcanized samples have greater elasticity than the original gum rubber. The hardness of the revulcanized samples is lower. The activation energy of the viscous flow of the devulcanized samples is higher than that of the virgin gum. This is an indirect indication that the devulcanized samples possibly consist of branched structures. Molecular weight data obtained from GPC experiments strengthen the results obtained from cure curves and mechanical property data. GPC shows a reduction in the molecular weights of the devulcanized samples by more than half, indicating devulcanization and degradation of the samples upon the application of ultrasound. As a result, the revulcanized samples exhibit lower mechanical properties.

Further work needs to be done on the blending of devulcanized samples with original samples in various proportions. Initial investigations have shown promising results, but detailed investigations are being carried out.

The authors are grateful to the late Dr. Emmanuel Kontos of Uniroyal Chemicals for providing the Vibrathane 5008.

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