Continuous Ultrasonic Devulcanization of NR/SBR Blends

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ABSTRACT: The ultrasonic devulcanization of sulfur-cured natural rubber (NR)/styrene–butadiene rubber (SBR) blends was studied with the goal of understanding the devulcanization of rubber vulcanizates in which two networks of different natures were present. Also, similarities and differences in the devulcanization behaviors of NR, SBR, and their blends were found. During the devulcanization of cured NR/SBR blends, we observed that, as for NR, the ultrasonic power consumption for 75/25 and 50/50 (w/w) NR/SBR blends passed through a maximum at 7.5 μm. For SBR and 25/75 (w/w) NR/SBR blends, the power consumption increased with increasing ultrasonic amplitude. The higher power consumption led to a higher degree of devulcanization. The crosslink densities of the devulcanized 25/75, 50/50, and 75/25 (w/w) NR/SBR blends were lower than those of the devulcanized NR and SBR, possibly because of the reduced degree of unsaturation. The tensile properties of the revulcanized blends were lower than those of the virgin vulcanized blends. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 160–168, 2002

Key words: devulcanization; blends; natural rubber (NR); styrene–butadiene rubber (SBR); curing; mechanical properties; process parameters; ultrasound; rheology

INTRODUCTION

The environmental problems created by waste rubbers and discarded tires have become significant in recent years. Also, the management of waste rubbers has become a growing problem in the rubber industry. Increasing legislation restricting the disposal of waste rubber and used tires has demanded a search for economical and environmentally sound methods of recycling. Therefore, the development of a suitable technology to recycle waste rubbers is an important issue facing the rubber industry.

The vulcanization of rubber leads to the formation of a three-dimensional crosslinked network.

The presence of this network creates a tremendous problem in rubber recycling. A number of methods[1–3] have been developed to find more effective ways of recycling rubber. In recent years, Isayev and coworkers[4–9] have carried out extensive studies on ultrasonic devulcanization. Ultrasonic waves of certain levels in the presence of pressure and heat can break down the three-dimensional network in crosslinked rubber. Devulcanized rubber can be reprocessed in very much the same way as virgin rubber. The process of ultrasonic devulcanization is very fast, occurring in about a second, and may lead to a preferential breakage of sulfidic crosslinks in vulcanized rubbers.

The use of blends of rubbers is almost as old as the synthetic rubber industry and generally stems from an understandable desire to combine the best features, technical or economic, of two rubbers.[10] Today, rubber blends are widely used in industry, primarily in the tire industry, for

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Table I   Recipes for NR/SBR Blends

Compound	Rubber (phr)	Sulfur (phr)	CBS (phr)	ZnO (phr)	Stearic Acid (phr)
Recipe 1	100 (Virgin)	2	1.1	5	1
Recipe 2	100 (Revulcanization)	2	0	5	1

which the major blend components are natural rubber (NR) and styrene–butadiene rubber (SBR). Enhanced properties of polymeric materials are achieved by the development of multicomponent systems in the form of rubber blends composed of two or more homopolymers. This is a useful approach for the preparation of new materials with specially tailored or improved properties, often absent in the single-component rubbers. NR can be blended with synthetic rubbers to improve their mechanical properties, such as tensile strength, resilience, tear strength, fatigue, and fracture.[11] Blends of NR and SBR have been reported to exhibit improved oxidative stability compared with either pure component and to be heterogeneous in the bulk.[12] It has also been reported that the fatigue and the strain energy vary linearly with blend composition in NR/SBR blends.[13]

In this study, the continuous ultrasonic devulcanization of sulfur-cured NR/SBR blends was investigated. One goal was to understand the devulcanization of rubber vulcanizates in which two networks of different natures were present. The other goal was to investigate the similarities and differences in the devulcanization behaviors of NR, SBR, and their blends.

EXPERIMENTAL

Materials

The materials used in these experiments were NR (SMR CV60, Akrochem Co., Akron, OH) and SBR (23.5% bound styrene; Duradene 706, Firestone Co., Akron, OH). The other compounding ingredients were sulfur, zinc oxide (ZnO), stearic acid (Akrochem), and N-cyclohexylbenzothiazole-2-sulfenamide (CBS; Monsanto Inc.). The recipes used are given in Table I.

Preparation of the Vulcanizates

The NR/SBR blends were prepared on a two-roll mill (Dependable Rubber Machinery Co., Cleve-land, OH) at 50°C. The rubbers were added to the nip of the rolls and masticated for 5 min. The ingredients were then slowly added to the rolling bank; this was followed by alternating cuts for 6 min to achieve a homogenization of the rubber constitution. The ratios of the NR/SBR blends were 100/0, 75/25, 50/50, 25/75, and 0/100 (w/w).

The compression molding of slabs (260 mm × 260 mm × 12 mm) was performed with an electrically heated compression-molding press (Wabash, Wabash, IN) at 160°C. According to the cure curve, the cure time was determined on the basis of the maximum torque. After molding, the vulcanized samples were ground with a Nelmor grinding machine (N. Uxbridge, MA).

Ultrasonic Devulcanization

The ground blend vulcanizates were devulcanized in an extruder with an ultrasonic die attachment.[4,5] The temperature of the extruder barrel was set at 120°C. The gap between the die and horn was set at 2.54 mm. The flow rate was 0.63 g/s. Devulcanization was carried out at a frequency of 20 kHz and amplitudes of 5, 7.5, and 10 μm. The ultrasonic power consumption and die entrance pressures were measured at the conditions of devulcanization.

Revulcanization

The devulcanized NR/SBR blends were compounded with curatives (recipe 2) on the two-roll mill. Revulcanization was carried out in the compression-molding press at 160°C in a mold (127 mm × 127 mm × 2 mm), with the cure time based on the maximum torque.

Characterization

A Monsanto oscillating disc rheometer was used to obtain the torque–time curves at 160°C according to ASTM Standard D 2084.

The gel fractions of virgin cured and devulcanized NR/SBR blends were measured by Soxhlet extraction methods with benzene as a solvent.
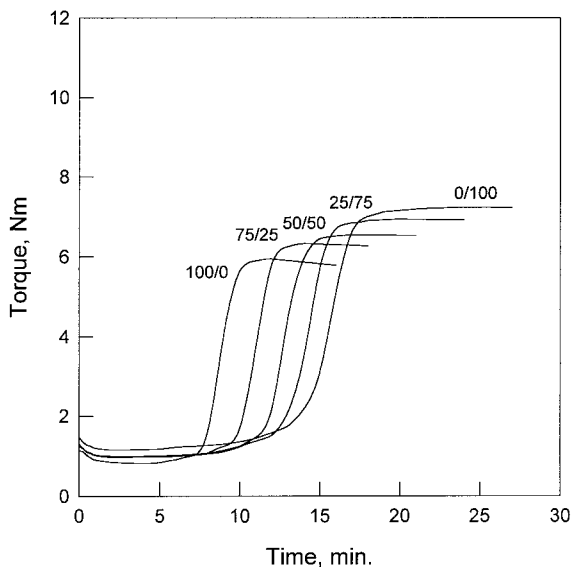
Figure 1 Cure curves for virgin NR, SBR, and NR/SBR blends with recipe 1.

The crosslink densities were characterized by a swelling method with the Flory–Rehner equation.[14]

The rheological behavior of the blends was investigated with a Monsanto processability tester at a temperature of 120°C according to ASTM Standard D 5099.

A Monsanto tensiometer (Flexsys T2000) was used for the tensile property measurement according to ASTM Standard D 412 (type C). All tests were performed at room temperature with a crosshead speed of 500 mm/min.

The thermal stability of the NR/SBR blends was evaluated with a DuPont (Wilmington, DE) 951 thermogravimetric analysis (TGA) instrument at a heating rate of 20°C/min from 50 to 600°C in a nitrogen atmosphere. Each time, a sample of about 15 mg was used.

RESULTS AND DISCUSSIONS

Cure Behavior

Figure 1 shows the cure curves at 120°C for virgin NR/SBR blends (recipe 1). The scorch time and cure time increase with increasing SBR concentration. This can be explained by the fact that, in SBR, the degree of unsaturation is lower than that in NR where the repeating unit is the isoprene monomer.[15,16] Thus, SBR cures slower than NR, and a longer scorch time is observed in SBR.

The maximum torque, which is a measure of the elastic modulus, increases steadily with increasing SBR concentration. Unlike the curing of NR (100/0), no blends (75/25, 50/50, 25/75, or 0/100) show any tendency for reversion.

The revulcanization recipe was optimized to improve the mechanical properties of revulcanized 50/50 (w/w) NR/SBR blends after devulcanization. The amount of ZnO and stearic acid in the revulcanization recipe was kept the same as in the virgin recipe (recipe 1). The amount of sulfur and accelerator (CBS) was varied so that we could study their effect on the revulcanization of the devulcanized blends. As seen from the cure curves in Figure 2, increasing the amount of sulfur increases the degree of revulcanization, and increasing the amount of accelerator increases the rate of revulcanization. Because it showed the best mechanical properties among all the recipes, recipe 2 (see Fig. 12, shown later), which consisted of 2 phr sulfur and 0 phr accelerator, was chosen as the optimized revulcanization recipe for all ratios of NR/SBR blends. It has been reported that ultrasonically devulcanized SBR contains about 85% of the initially added accelerator.[7] Therefore, it seems that some amount of sulfenamides that preexisted in the devulcanized sample gave a satisfactory degree of cure.

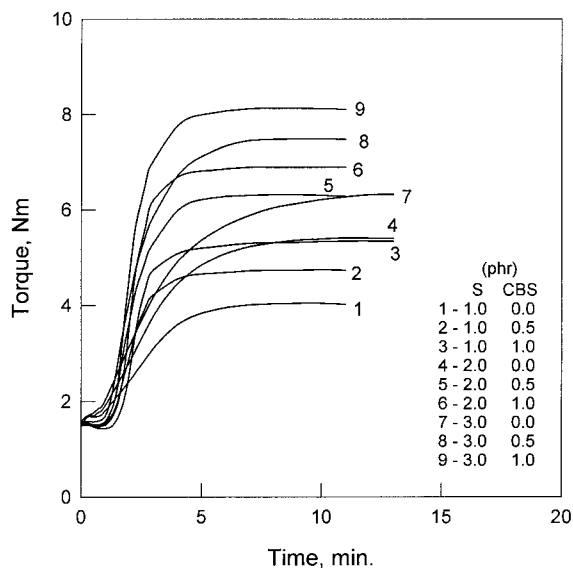The cure curves with recipe 2 for devulcanized 50/50 (w/w) NR/SBR blends obtained at different

Figure 2 Cure curves for 50/50 (w/w) NR/SBR blends ultrasonically devulcanized at an amplitude of 5 μm and compounded with 5 phr ZnO, 1 phr stearic acid, and different amounts of sulfur and accelerator.
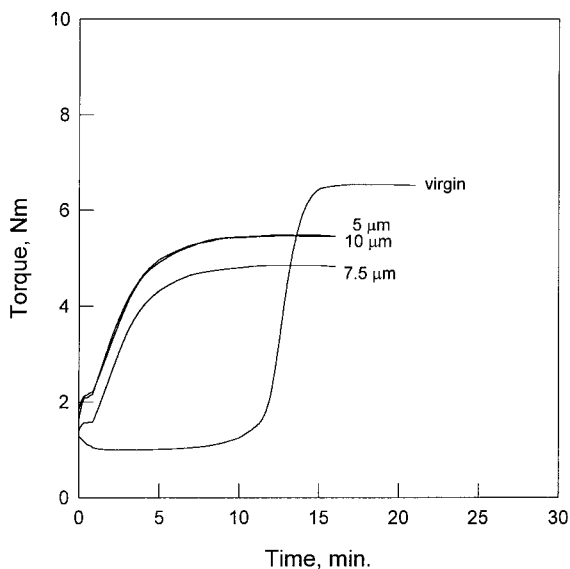
Figure 3 Cure curves for virgin and ultrasonically devulcanized 50/50 (w/w) NR/SBR blends.

amplitudes are seen in Figure 3. The maximum torque, which is related to the crosslink density, of the devulcanized 50/50 (w/w) NR/SBR blend is lower than that of the virgin sample. During the ultrasonic devulcanization of the blends along with the breakup of crosslinks, a possibility exists for the breakup of main chains.[17] Moreover, the maximum torque of the devulcanized 50/50 (w/w) NR/SBR blend shows a minimum at 7.5 μm. Although devulcanization is dominant between 5 and 7.5 μm, some reformation occurs when the ultrasound amplitude is increased from 7.5 to 10 μm. As shown in Figure 3, the cure behavior of virgin and devulcanized blends is significantly different. The shortness or almost absence of the scorch time in the devulcanized sample indicates that the crosslinking reactions may start immediately on heating.[7,17]

Die Characteristics and Power Consumption

Figure 4 represents a dependence of the die entrance pressure on the ultrasonic amplitude during the devulcanization of NR, SBR, and NR/SBR blends. The die pressure decreases substantially with the application of ultrasound, and with increasing amplitude, the pressure decreases further. This has been previously explained as the combined effect of the softening of rubber due to devulcanization in the die gap and the reduction in friction between the particles and die wall due to ultrasonic vibrations.[5] The die pressure of the

NR/SBR blends significantly decreases with increasing SBR concentration in the absence of ultrasound, but the differences are not significant after the application of ultrasound. It is possible that the die pressure in this study can depend on the mechanical strength, viscosity, and degree of devulcanization.

Figure 5 gives the ultrasonic power consumption during the devulcanization of cured NR, SBR, and NR/SBR blends as a function of ultrasonic amplitude. Similar to that for pure NR, the ultrasonic power consumption for the 75/25 and 50/50 (w/w) NR/SBR blends passed through a maximum at 7.5 μm. It has been reported[9] that the reason is the competition between bond breakage and reformation during ultrasonic devulcanization. Although devulcanization is dominant between 5 and 7.5 μm, some revulcanization occurs with increasing intensity when the ultrasound amplitude is increased from 7.5 to 10 μm, which accounts for the reduction in power consumption at 10 μm. For pure SBR and 25/75 (w/w) NR/SBR blends, the power consumption increases with increasing ultrasonic amplitude. In this case, the higher the ultrasonic amplitude is, the more devulcanization there is and the more power is needed to carry it out.[6] Therefore, in the 75/25 and 50/50 (w/w) blends, NR contributes more to devulcanization of the blends, and in the 25/75 (w/w) blend, SBR contributes more to the devulcanization. As shown in Figure 5, the power con-
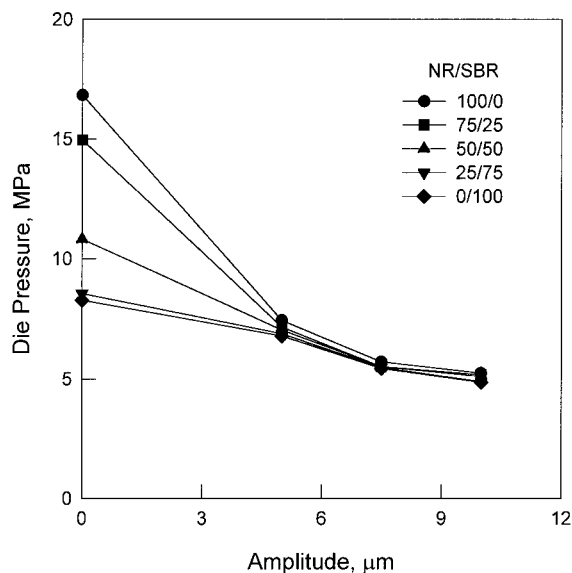

Figure 4 Die pressure as a function of ultrasonic amplitude during devulcanization of cured NR, SBR, and NR/SBR blends.
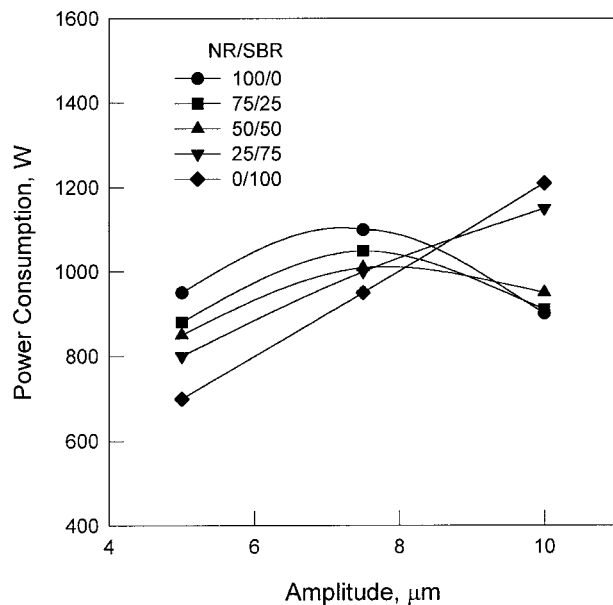
Figure 5 Ultrasonic power consumption as a function of ultrasonic amplitude during devulcanization of cured NR, SBR, and NR/SBR blends.

sumption of NR is higher than that of SBR from 5 to 7.5 μm. The higher power consumption leads to a higher degree of devulcanization. Therefore, it is believed that NR is easier to devulcanize than SBR. The mechanism of the devulcanization of the rubber network is based on ultrasonic cavitation, which is created by high-intensity ultrasonic waves in the presence of pressure and heat.[18] The devulcanization of the rubber network can occur primarily around pulsating cavities because of the highest level of strain produced by the powerful ultrasound. The differences in devulcanization between NR and SBR are due to the different structures of the polymer chains and/or thermal properties.

Thermal Stability

Figure 6 presents TGA traces of virgin NR, 50/50 (w/w) NR/SBR blend, and SBR vulcanizates. Because of the decomposition, at elevated temperatures NR shows inferior thermal stability compared with that of the 50/50 (w/w) NR/SBR blend and SBR. This means that the probability for devulcanization is increased. Therefore, it could be said that NR is easier to devulcanize than SBR. In the devulcanization experiment, temperature buildup due to the dissipation of ultrasonic energy was rapidly removed by water cooling, and ultrasonic devulcanization was very fast and oc-
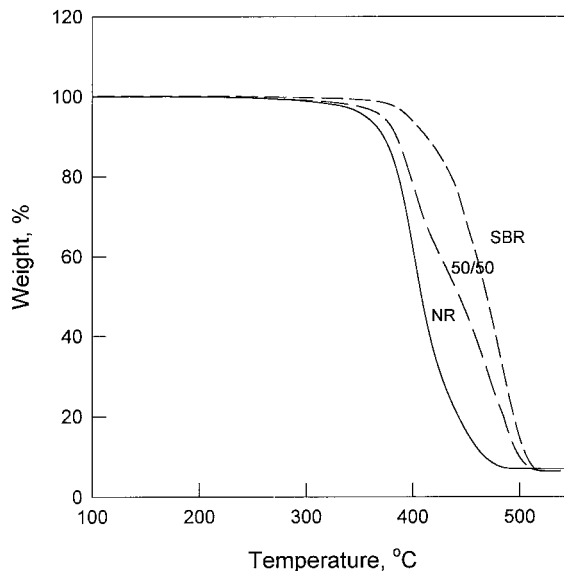

Figure 6 TGA traces of virgin vulcanizates of NR, SBR, and 50/50 (w/w) NR/SBR blends.

curred in about a second. Therefore, it could be expected that thermal degradation was minimized during the ultrasonic treatment.

Rheology

The flow curves for the virgin uncured NR, SBR, and 50/50 (w/w) NR/SBR blend are shown in Figure 7. The viscosity of the virgin uncured SBR is higher than that of the NR. Also, the viscosity of
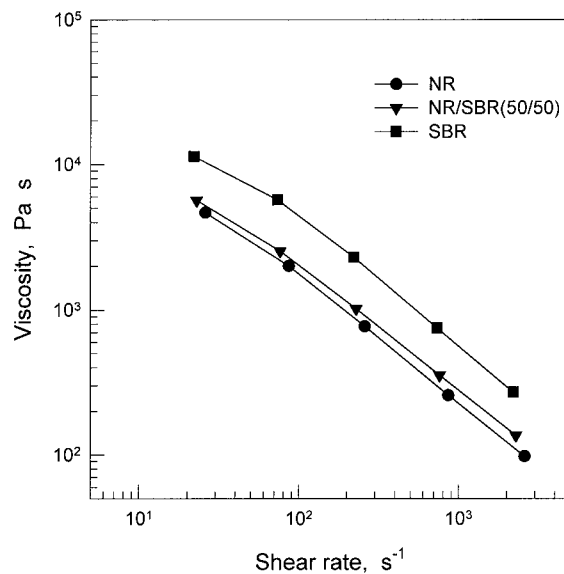

Figure 7 Flow curves for virgin uncured NR, SBR, and 50/50 (w/w) NR/SBR blends.
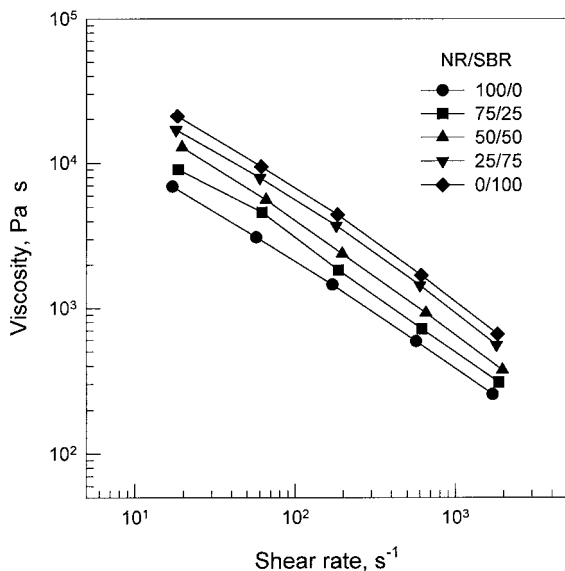
Figure 8 Flow curves for NR, SBR, and NR/SBR blends ultrasonically devulcanized at an amplitude of 5 μm.

Figure 9 Flow curves for ultrasonically devulcanized 50/50 (w/w) NR/SBR blends at various amplitudes.

the blend is much lower than that of the SBR. Figure 8 shows the flow curves for ultrasonically devulcanized NR/SBR blends at an amplitude of 5 μm. The viscosity of the ultrasonically treated blends increases with increasing SBR content. This behavior is similar to that for virgin blends. In Figure 5, we see that the ultrasonic power consumption of NR/SBR blends devulcanized at an amplitude of 5 μm decreases with increasing SBR content. The lower power consumption means a lower degree of devulcanization. Therefore, it is believed that NR is easier to devulcanize than SBR and that a lower degree of devulcanization of the SBR component in the blend causes a higher viscosity in the case of NR/SBR blends in comparison with NR.

Figure 9 gives the flow curves for devulcanized 50/50 (w/w) NR/SBR blends at different amplitudes. The viscosity at 7.5 μm is lower than the viscosity at 5 and 10 μm. This observation is in agreement with the ultrasonic power consumption shown in Figure 5, indicating a higher power consumption at 7.5 μm. It is clear that the higher power consumption leads to a higher degree of devulcanization and lower viscosity.

Gel Fraction and Crosslink Density

Figure 10 presents the gel fraction of virgin vulcanized, devulcanized, and revulcanized NR/SBR blends as a function of SBR concentration. The gel
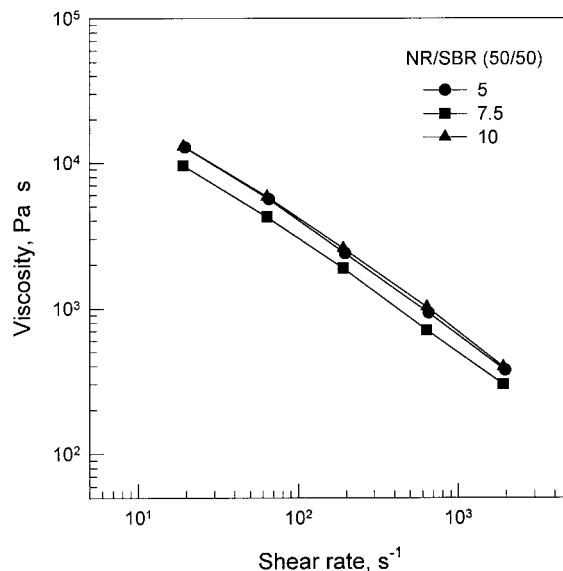
fraction of devulcanized SBR is higher than that of NR. Similar to the fraction in NR, the gel fraction in the devulcanized 75/25 and 50/50 (w/w) NR/SBR blends is the lowest at 7.5 μm. In contrast, for 25/75 (w/w) NR/SBR blends, as for SBR, the gel fraction decreases with increasing ultrasonic amplitude. All these observations agree with the power consumption during the ultra-
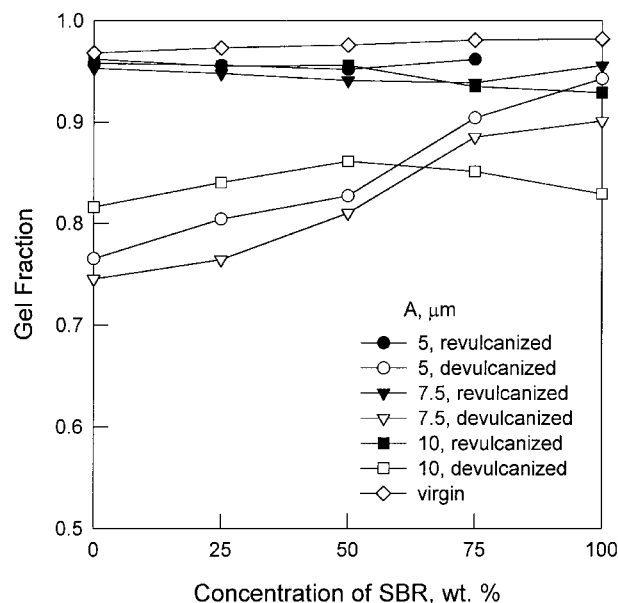

Figure 10 Gel fractions of virgin vulcanized, devulcanized, and revulcanized NR/SBR blends as a function of SBR concentration.
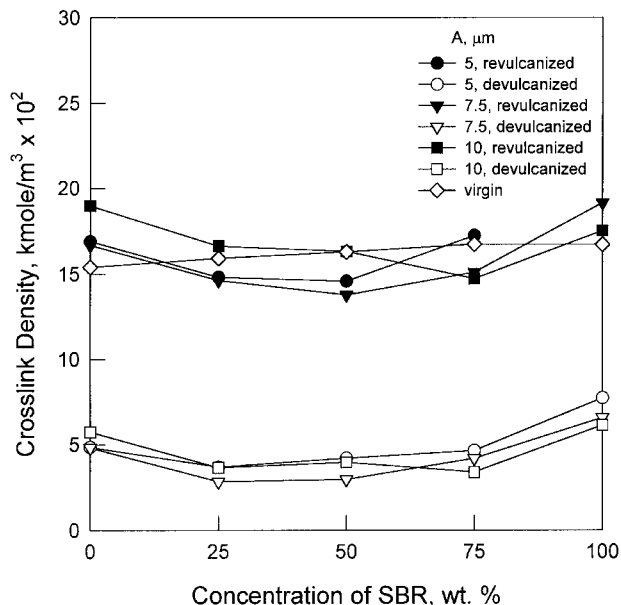
Figure 11 Crosslink density of virgin vulcanized, devulcanized, and revulcanized NR/SBR blends as a function of SBR concentration.

sonic devulcanization of NR/SBR blends and their components. Also, the gel fraction of virgin vulcanized blends is higher than that of revulcanized samples. This is possibly due to the breakup of main chains during ultrasonic treatment.

The crosslink density of virgin vulcanized, devulcanized, and revulcanized NR/SBR blends as a function of SBR concentration is shown in Figure 11. The crosslink densities of the devulcanized and revulcanized 25/75, 50/50, and 75/25 (w/w) NR/SBR blends are lower than those of the devulcanized NR and SBR. It seems possible that the degree of unsaturation in the repeating units of NR and SBR is decreased during ultrasonic treatment. Also, it might be thought that some reactions between networks of NR and SBR had occurred during ultrasonic treatment. However, the reason for the decreased crosslink density during the ultrasonic treatment of the blends is not clear. More detailed experiments are needed to understand the ultrasonic treatment of the blend systems.

Mechanical Properties

Various curing recipes are used to optimize the mechanical properties of 50/50 (w/w) NR/SBR blends. The effect of the variation of the amount of sulfur and accelerator on the mechanical properties of the revulcanized NR/SBR blends is

shown in Figure 12. Recipe 2, containing 2 phr sulfur without any accelerator, gives the best stress–strain curve. Therefore, this recipe was used for the revulcanization of all devulcanized blends.

Figures 13 and 14 give the tensile strength and elongation at break, respectively, of virgin vulcanized and revulcanized blends as a function of SBR concentration. The tensile strength and elongation at break of the blends increase with increasing NR content. Also, the tensile strength and elongation at break of the revulcanized blends are lower than those of the virgin vulcanized blends. The deterioration in tensile properties of the revulcanized sample may be mainly due to main-chain scission during ultrasonic devulcanization. Also, the revulcanization recipe was optimized just for the 50/50 (w/w) blend, not for all blend concentrations. If the revulcanization recipe is optimized for each blend, the tensile properties may possibly improve.

The modulus at 100% strain of virgin and revulcanized blends as a function of SBR concentration is shown in Figure 15. The moduli at 100% strain of revulcanized 25/75, 50/50, and 75/25 (w/w) NR/SBR blends are lower than those of the virgin vulcanized blends. This could be due to a decrease in the degree of unsaturation of NR/SBR blends during the ultrasonic treatment, leading
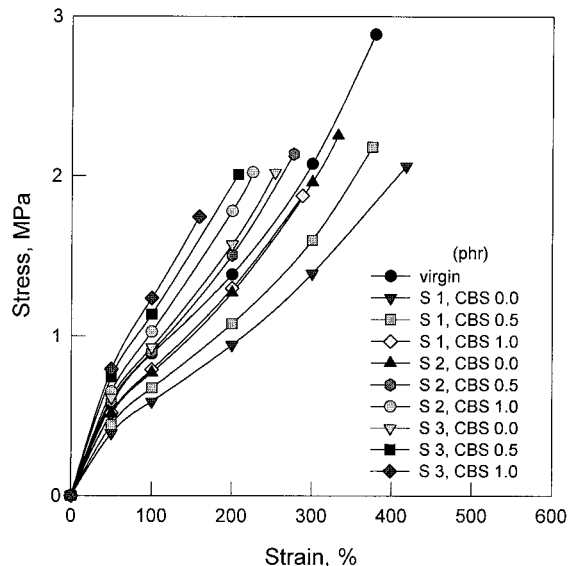

Figure 12 Stress–strain curves for 50/50 (w/w) NR/SBR blends ultrasonically devulcanized at an amplitude of 5 μm and compounded with 5 phr ZnO, 1 phr stearic acid, and different amounts of sulfur and accelerator.
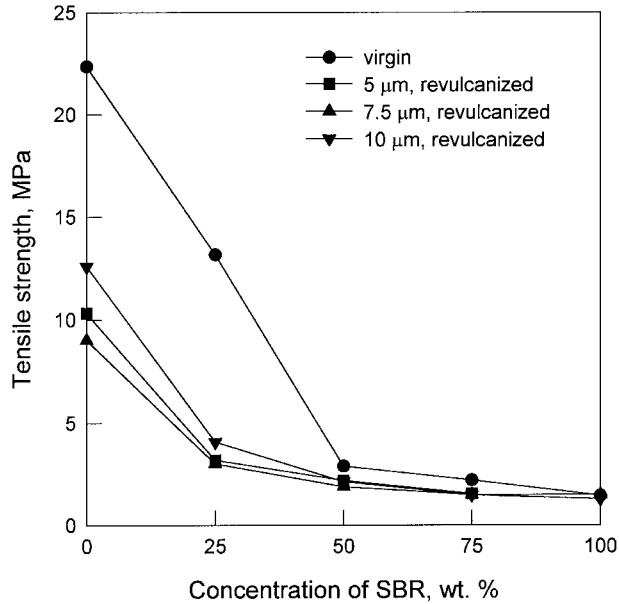
Figure 13 Tensile strength of virgin vulcanized and revulcanized NR/SBR blends as a function of SBR concentration.

to a lower crosslink density in the revulcanized blends.

CONCLUSIONS

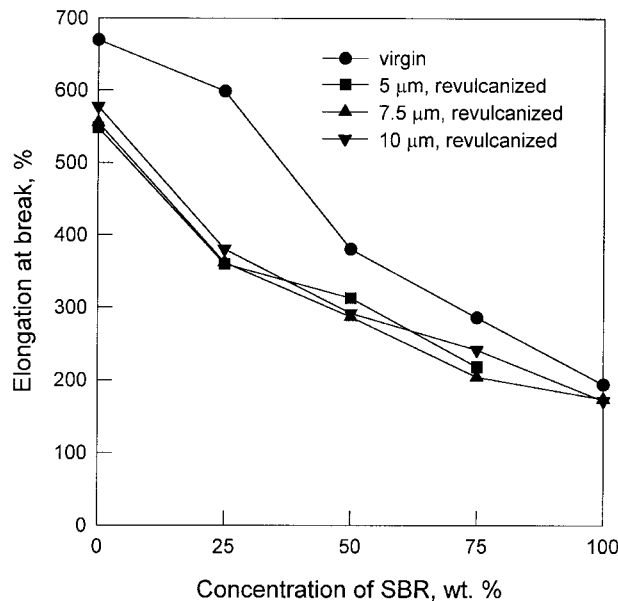In this study, the ultrasonic devulcanization of sulfur-cured NR/SBR blends was investigated.

Figure 14 Elongation at break of virgin vulcanized and revulcanized NR/SBR blends as a function of SBR concentration.
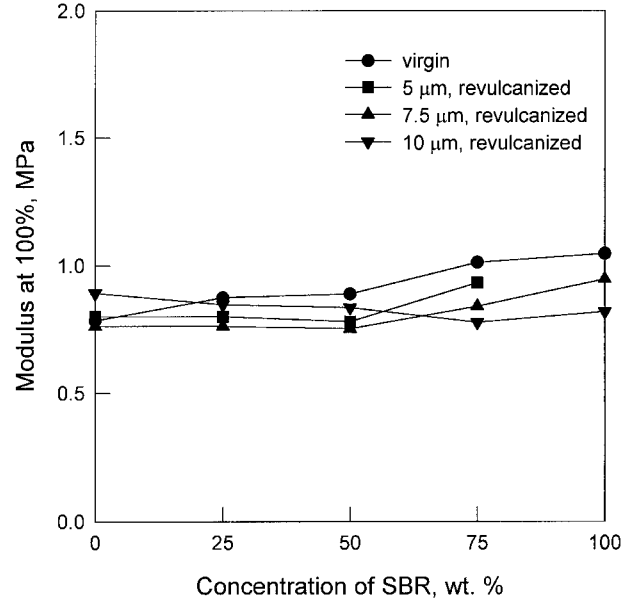

Figure 15 Modulus at 100% strain of virgin vulcanized and revulcanized NR/SBR blends as a function of SBR concentration.

During the devulcanization of cured NR/SBR blends, similar to the consumption for NR, the ultrasonic power consumption for the 75/25 and 50/50 (w/w) NR/SBR blends passed through a maximum at 7.5 μm. For SBR and 25/75 (w/w) NR/SBR blends, the power consumption increased with increasing ultrasonic amplitude. Also, the power consumption for the devulcanization of NR was higher than that for SBR between 5 and 7.5 μm, and the ultrasonic power consumption of NR/SBR blends at 5 μm decreased with increasing SBR content. The higher power consumption led to a higher degree of devulcanization. Therefore, it is believed that NR is easier to devulcanize than SBR. The viscosity of the ultrasonically treated NR/SBR blends increased with increasing SBR content.

To improve the mechanical properties of the revulcanized 50/50 (w/w) NR/SBR blend after ultrasonic devulcanization, we optimized the revulcanization recipe. The crosslink densities of the devulcanized and revulcanized 25/75, 50/50, and 75/25 (w/w) NR/SBR blends were lower than those of the devulcanized NR and SBR. It seems possible that the degree of unsaturation in the repeating units of NR and SBR decreases during ultrasonic treatment. The tensile properties of the revulcanized blends were lower than those of the virgin vulcanized blends.

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