

Comparative Analysis of Ultrasonically Devulcanized Unfilled SBR, NR, and EPDM Rubbers

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ABSTRACT: The comparative study of the continuous ultrasonic devulcanization of various unfilled rubbers [natural rubber, styrene-butadiene rubber (SBR), ethylene-propylene-diene rubber (EPDM)] is carried out by means of a ultrasonic reactor. The power consumption, gel fraction, crosslink density, cure behavior, and physical properties of devulcanized rubbers were measured. The glass transition temperatures of virgin, vulcanized, and devulcanized rubbers were determined in order to characterize the difference in the mobility of rubber molecules for each rubber before and after devulcanization. Thermogravimetric analysis was

also used to determine thermal stability of the various rubbers. A unique correlation between gel fraction and crosslink density indicated significant differences in the efficiency of devulcanization of various rubbers. Under certain devulcanization conditions, the mechanical properties of devulcanized SBR and EPDM rubbers were found to improve compared to those of the original rubbers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 434–441, 2003

Key words: devulcanization; natural rubber; styrene-butadiene rubber; ethylene-propylene-diene rubber; ultrasound

INTRODUCTION

The direct reprocessing and recycling of waste tires and vulcanized rubbers that have three-dimensional networks are impossible. These cause environmental problems that have become significant in the 21st century. Increasing legislative restriction of the disposal of waste tires and waste rubber has demanded a search for environmentally and economically sound methods of recycling. Therefore, the development of a suitable recycling technology is an important issue facing the industry. So far, several techniques have been proposed for recycling waste rubbers, including fuel source with scrap,¹ chemical,^{2–5} mechanical,^{6–9} biotechnological,^{10,11} microwave process,¹² and solid-state shear pulverization.¹³ Each technique possesses certain disadvantages concerning recycled product quality as well as processing time and cost. Recently, reviews by Warner,¹⁴ Adhikari et al.,¹⁵ and Isayev¹⁶ provided the description of existing technology on rubber recycling.

The ultrasonic devulcanization of rubber is the most recent approach. It is now considered as one of the most promising recycling methods of rubbers.^{15,17} Extensive studies of various types of rubbers, including

ground rubber tire (GRT),^{18–20} styrene-butadiene rubber (SBR),^{21,22} natural rubber (NR),^{23,24} and silicone rubber,^{25,26} have been conducted. These studies have shown that ultrasonic waves, at a certain level of pressure and temperature, can rapidly break down the three-dimensional rubber network. As the most desirable consequence, the ultrasonically devulcanized rubber can be reprocessed and devulcanized in a manner similar to that employed with unvulcanized elastomers. Ultrasonic devulcanization of rubbers is a continuous process with no chemicals involved, which makes it attractive to the rubber industry.

Natural rubber, styrene-butadiene rubber, and ethylene-propylene-diene rubber (EPDM) have been widely used in tires and a variety of industrial and engineering applications. This article provides a comparative analysis of the continuous ultrasonic devulcanization of unfilled NR, SBR, and EPDM rubbers. The investigation of the recyclability of various rubbers using the continuous ultrasonic reactor is carried out. The unique correlation found between gel fraction and crosslink density is used to establish differences in the efficiency of devulcanization. Also, a possible correlation between the thermal stability and the ultrasonic devulcanization of rubbers will be discussed.

EXPERIMENTAL

Materials

NR (SMR CV60) was obtained from Akrochem and SBR (Duranene 706) was solution-polymerized styrene-butadiene rubber manufactured by Firestone

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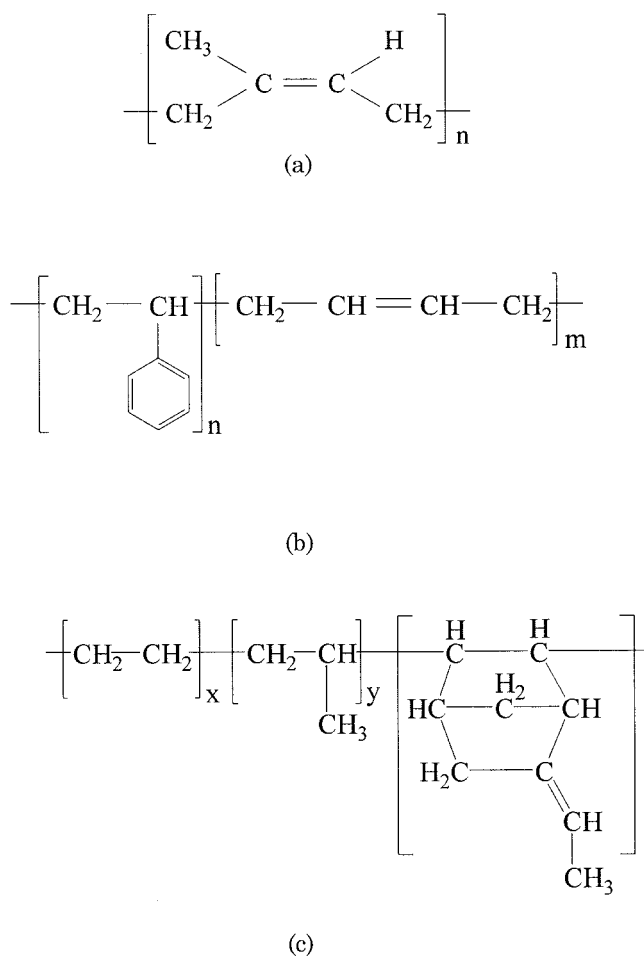


Figure 1 Chemical structure of (a) NR, (b) SBR, and (c) EPDM rubbers.

Co. SBR consisted of 23.5 wt % bound styrene and 76.5 wt % butadiene. EPDM (Keltan 2506) was obtained from DSM Elastomers. Comonomer (ENB) content was 4.5 wt % and ethylene content was 56 wt %.

The chemical structures of these rubbers are shown in Figure 1. The other compounding ingredients were sulfur, zinc oxide (ZnO), stearic acid, tetramethylthiuram disulfide (TMTD), 2-mercaptobenzothiazole (MBT; Akrochem), and *N*-cyclohexylbenzothiazole-2-sulphenamide (CBS; Monsanto). The cure recipes are shown in

Table I, where virgin 1 and virgin 2 are the original cure recipe used to prepare virgin vulcanizates. In comparison with virgin 1, virgin 2 contains twice the amount of curatives. This is done in order to compare the physical properties of revulcanizates prepared from devulcanized rubbers that were cured using same amount of curative as virgin.

Preparation of vulcanizates

The NR and SBR vulcanizates were prepared on a laboratory two-roll mill (Dependable Rubber Machinery, Cleveland, OH) at 50°C. The rubbers were added to nip of the rolls and masticated for 5 min. The ingredients were then slowly added to the rolling bank. On the other hand, EPDM rubber was compounded in a two-step process that included preparation of a master batch in a Banbury mixer (Moriyama) by adding zinc oxide and stearic acid. Then the other ingredients (sulfur and accelerator) were added to the master batches prepared by the Banbury mixer. Total mixing time was 5 min. Finally, the compounds were homogenized on two-roll mill for 2 min. The total mixing time was 11.5 min. These procedures are based on ASTM D3568.

The compression molding of slabs (260 mm × 260 mm × 12 mm) was performed by means of electrically heated compression-molding press (Wabash, Wabash, IN) at 160°C and a pressure of 13.8 MPa. Cure time corresponded to the time required to achieve 90% of maximum torque on the cure curve. After molding, the vulcanized samples were ground using a Nelmor grinding machine (N. Uxbridge, MA) having a screen with holes of 5 mm in diameter.

Ultrasonic devulcanization

The ground rubber vulcanizates were devulcanized in a 38.1 mm rubber extruder with a coaxial ultrasonic die attachment.^{18,19} The extruder was preheated to 120°C. The temperature was kept uniform for all barrel zones. The ground rubber vulcanizates were loaded into the hopper. The feeder, providing starved

TABLE I
Vulcanization Recipes for Various Rubbers

	Rubbers	Sulfur	CBS	ZnO	Stearic Acid	TMTD	MBT
Virgin 1	NR	2	1	5	1		
	SBR	2	1.3				
	EPDM	1.5		5	1	1	0.5
Virgin 2	NR	4	1	7.5	1.5		
	SBR	4	2.6				
	EPDM	3		10	2	2	1
Revulcanization recipes	NR	2		2.5	0.5		
	SBR	2	1.3				
	EPDM	1.5		5	1	1	0.5

feed to the extruder, controlled the output. In the extruder, rubber vulcanizates were compressed and conveyed by the screw to the devulcanization zone. The ultrasonic devulcanization of the rubbers occurred in the gap between the horn and the die plate in the reactor. After reaching the steady-state conditions indicated by the pressure transducer and ultrasonic power wattmeter, ultrasonically devulcanized rubbers were collected. The die pressure and temperature of devulcanization zone and the ultrasonic power consumption were measured. The rubber flow rate in the process was 0.63 g/s. A die of uniform gaps of 1.01, 1.38, 1.52, 2.03, and 2.54 mm with a radial length of 19 mm was used to find the optimal devulcanization conditions of various rubbers. For example, optimal gaps were 2.54 mm for NR, 1.52 mm for SBR, and 1.01 mm for EPDM devulcanization. Also, gaps of 1.52 mm and 2.03 mm for NR and SBR, 1.38 mm and 2.03 mm for EPDM were used to carry out experiments for the comparative studies.

Re vulcanization

Prior to revulcanization of ultrasonically devulcanized rubbers, the samples were compounded with curatives using a two-roll mill. The cure recipes for revulcanization are shown in Table I. The revulcanization was carried out by using a compression molding press at 160°C and a pressure of 13.8 MPa. Cure time corresponded to the time required to achieve 90% of maximum torque on the cure curve. Revulcanized sheets with dimensions of 127 × 127 × 2 mm³ were obtained and used for mechanical testing.

Characterizations

A Monsanto oscillating-disk rheometer was used to obtain the torque–time curve at a temperature of 160°C according to ASTM D2084.

The gel fraction of virgin vulcanizates, ultrasonically devulcanized rubbers, and revulcanizates was measured by the soxhlet extraction method using benzene as a solvent. The crosslink density of the gel in their rubbers was measured by the swelling technique using benzene as a solvent. The crosslink density was determined using the Flory–Rehner equation.²⁷

Gel fractions and crosslink densities of original vulcanizates were 0.95 and 14.1×10^{-2} kmol/m³ for EPDM, 0.96 and 12.0×10^{-2} kmol/m³ for SBR, 0.96 and 15.7×10^{-2} kmol/m³ for NR, respectively.

Stress–strain measurements were performed at room temperature according to ASTM D412 (type C) at a crosshead speed of 500 mm/min using Instron Tensile Tester (model 5567).

In order to determine the glass transition temperatures of various rubbers, the Dupont 990 Differential Scanning Calorimeter under nitrogen gas was used.

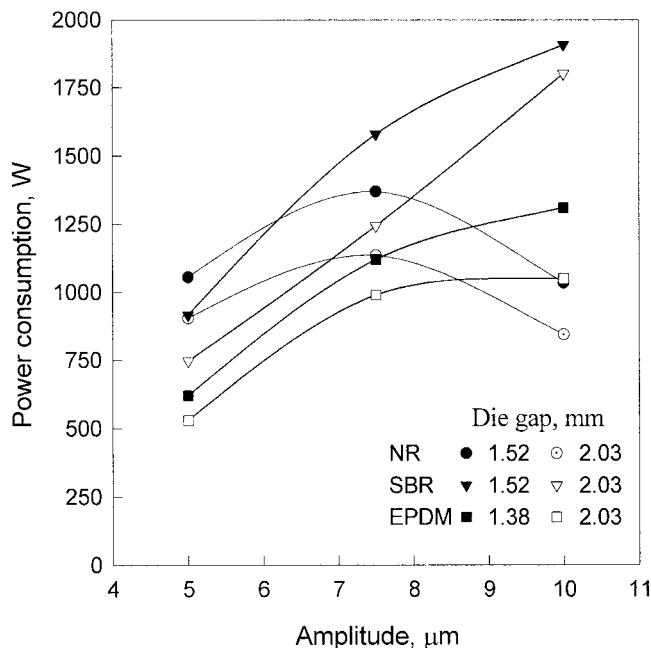


Figure 2 Ultrasound power consumption versus amplitude for various rubbers during devulcanization at various die gaps.

The instrument was calibrated with indium. The heating rate was 20°C/min and the temperature range was –100 to 30°C. The samples were taken from each rubber obtained at various conditions and cut into about 10 mg pieces for DSC measurements. The sample's pieces were sealed in an aluminum pan and an empty pan was used as an inert reference at the same conditions. For the glass transition temperature measurement, the DSC was cooled down to the desired temperature using liquid nitrogen.

In order to measure the thermal stability of rubbers, the Dupont 990 Thermal Gravimetric Analyzer (TGA) under nitrogen gas was used. The temperature was calibrated with zinc. The scanning rate of 20°C/min and temperature range of 40–600°C was used. About 10 mg pieces cut out from the samples were used.

RESULTS AND DISCUSSION

Ultrasonic power consumption

Figure 2 shows the comparison of ultrasonic power consumption versus ultrasonic amplitude for various rubbers during the devulcanization at various die gaps. Ultrasonic energy loss and breakage of bonds leading to devulcanization is the main expenditure for the measured ultrasonic power. One cannot estimate experimentally what part of the power is consumed by devulcanization alone. In addition, the power expended on heat dissipation in the rubber and the power transmitted by the traveling wave through the rubber cannot be separated. The only measurable

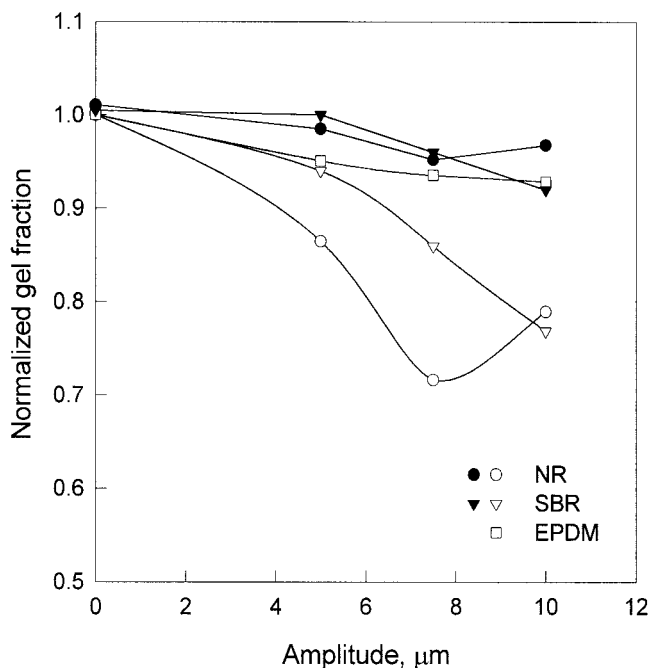


Figure 3 Normalized gel fraction versus amplitude for various devulcanized (open symbols) and revulcanized (solid symbols) rubbers obtained at a gap of 2.03 mm.

losses are initial power consumption of the acoustic system when the horn works without loading. In obtaining Figure 2, these losses are subtracted from the total power consumption.

In case of SBR and EPDM rubber, ultrasonic power consumption is increased with amplitude of ultrasound. In contrast, in case of NR, ultrasonic power consumption shows a maximum value at 7.5 μm . This indicated that more energy was transmitted into the rubber material with an increase of amplitude during devulcanization of SBR and EPDM rubbers. For NR, however, it is believed that imposition of ultrasonic waves leads to simultaneous bond breakage and reformation in the material.²³ In this case, while devulcanization is the dominant phenomenon between 5 and 7.5 μm , some revulcanization occurred with increasing ultrasound intensity when amplitude is increased from 7.5 to 10 μm . The latter accounts for the reduction in power consumption at 10 μm .

At the same processing conditions, the higher ultrasonic power consumption leads to a higher degree of devulcanization. Based on a comparison of the power consumption values of SBR and EPDM, it is inferred that SBR is easier to devulcanize than EPDM. The differences in devulcanization among NR, SBR, and EPDM are possibly due to the different chemical structure of the polymer chains and the thermomechanical stability, which will be discussed later. In addition, decreasing gap size leads to higher ultrasonic power consumption, which is evidently related to the higher degree of devulcanization.

Normalized gel fraction and normalized crosslink density

Figures 3 and 4 represent the normalized gel fraction and normalized crosslink density of devulcanized and revulcanized rubbers as a function of ultrasonic amplitude at a constant gap of 2.03 mm. The normalized gel fraction and normalized crosslink were calculated by the ratio of the corresponding measured values for devulcanized samples obtained at various conditions and the measured values of original vulcanizates based on recipe 1. Filled symbols at the ordinates indicate values of the gel fraction and crosslink density obtained using virgin rubber mixed with twice the amount of curatives referred to as virgin 2 in Table I. Filled symbols at various amplitudes corresponded to revulcanization recipes in Table I. Also, it is noted that the devulcanized EPDM rubbers obtained at a gap of 2.03 mm were not millable and reprocessable because of high gel content. Thus, revulcanized EPDM rubbers could not be obtained at this gap. Both the normalized gel fraction and normalized crosslink density decrease substantially during the ultrasonic devulcanization of NR and SBR. Since the curative level is the same in all the samples, the devulcanized SBR and NR rubbers having higher gel fraction and crosslink density have a correspondingly higher gel fraction and crosslink density on revulcanization. In fact, the total crosslink density of revulcanized rubber seems to be close to the sum of the crosslink density of devulcanized rubber and the crosslink density of the original virgin vulcanizate. In addition, normalized gel fraction and

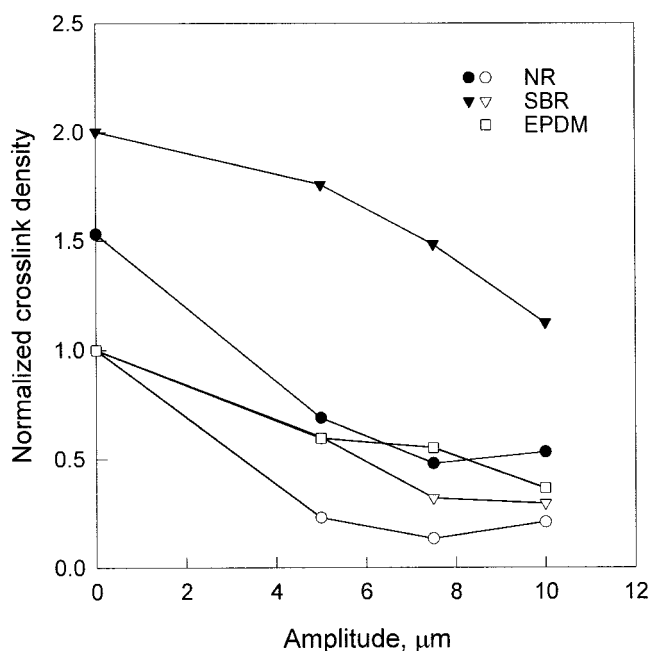


Figure 4 Normalized crosslink density versus amplitude for various devulcanized (open symbols) and revulcanized (solid symbols) rubbers obtained at a gap of 2.03 mm.

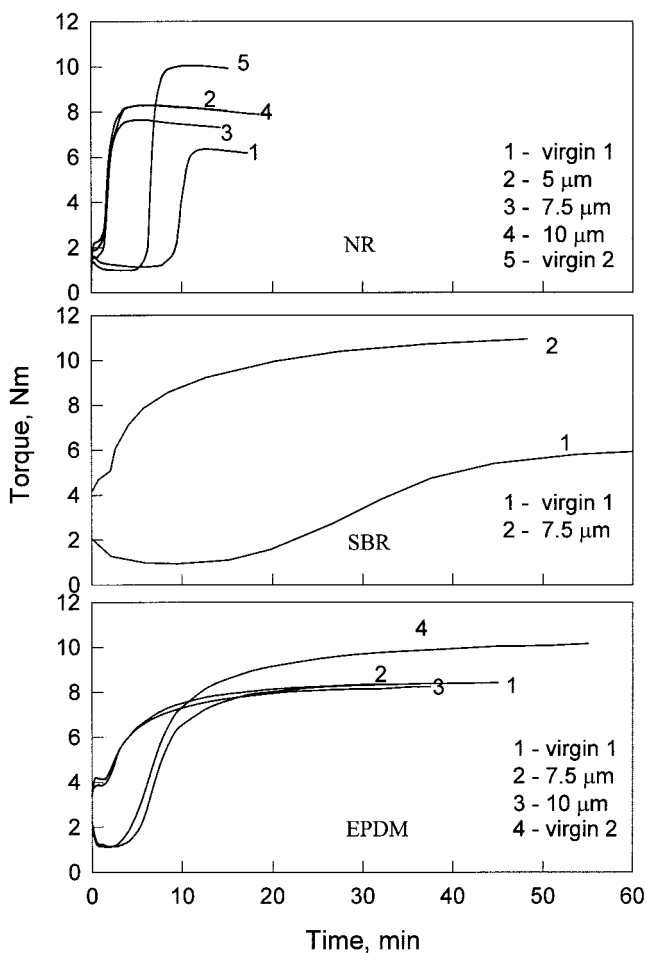


Figure 5 Cure curves for virgin rubber and devulcanized rubbers obtained at different amplitudes.

crosslink density of devulcanized samples according to the ranking of the degree of devulcanization defined by normalized values was NR > SBR > EPDM at the same gap size and ultrasonic amplitude. In particular, devulcanized EPDM rubbers have the highest gel fraction and crosslink density at this experimental condition. This can be explained by the characteristic of rubber chemical structure. The polymer main chains of EPDM rubber are almost saturated (nonconjugated), while those of SBR and NR have double bonds (conjugated). Therefore, it is believed that the degree of devulcanization has a certain order according to the type of rubber. This is related to the chemical structure of rubber shown in Figure 1. In other words, the rubber containing higher concentration of double bonds is possibly easier to devulcanize.

Cure behavior

Figure 5 gives the cure curves of virgin and devulcanized rubbers obtained at various amplitudes and gap sizes at a flow rate of 0.63 g/s and a cure temperature of 160°C. These curves were obtained for the devulca-

nized samples that had the best millability and reprocessability. Gap size during devulcanization is different for different rubbers. Gap size for NR, SBR, and EPDM was 2.54, 1.52, and 1.01 mm, respectively. This is also the indirect indication of the degree of devulcanization because a higher gap size reflects the ease of devulcanization. One can observe that the devulcanized rubbers cure faster than virgin rubbers. The shortness or absence of the induction period indicates that crosslinking reactions start immediately upon heating. This can be explained by the presence of residual curative in the devulcanized sample, which is a typical characteristic of reclaimed rubber.²⁸

Mechanical properties

Processing parameters during devulcanization are found to have a strong effect on the mechanical properties of revulcanized rubbers. Depending on the degree of devulcanization, the tensile strength, σ_b , and elongation at break, ϵ_b , of the revulcanized rubber vary.

Figure 6 presents the stress-strain curves of virgin vulcanizates and revulcanized NR, SBR, and EPDM obtained from devulcanized rubbers prepared at various values of amplitudes. In the stress-strain curves of NR, stress-induced crystallization is observed in all the revulcanized samples. The best tensile properties of revulcanized NR obtained at amplitude of 5 μm are $\sigma_b = 13.9$ MPa and $\epsilon_b = 682\%$, compared to virgin 1 having $\sigma_b = 19.3$ MPa and $\epsilon_b = 700\%$. One can see only 28% and 2.6% reduction in the tensile strength and the elongation at break, respectively. On the other hand, the revulcanized SBR and EPDM show superior tensile properties than virgin vulcanizates. This is in contrast to the usual findings that the mechanical properties of reclaimed rubbers obtained using different techniques are inferior to those of virgin vulcanizates. The best tensile properties of revulcanized SBR are obtained at amplitude of 5 μm . For this sample, $\sigma_b = 1.94$ MPa and $\epsilon_b = 199\%$, compared to virgin 1 $\sigma_b = 1.23$ MPa and $\epsilon_b = 217\%$. For revulcanized SBR rubber, 58% increase in tensile strength at break and 8.3% decrease in elongation at break in comparison with virgin vulcanizate are observed. The best tensile properties of revulcanized EPDM are obtained at amplitude of 10 μm . For this sample, $\sigma_b = 3.8$ MPa and $\epsilon_b = 207\%$, compared to virgin 1 $\sigma_b = 1.9$ MPa and $\epsilon_b = 244\%$. The 100% increase in the tensile strength and 15% decrease in the elongation at break of revulcanized EPDM rubber are observed. Therefore, the tensile strength of revulcanized SBR and EPDM rubbers exceeds that of virgin vulcanizates significantly, while the elongation at break is practically intact. The stress-strain characteristics of the revulcanized samples exhibit an S-shaped curve, which is typical of a rubber crystallizable under strain. However such a stress-

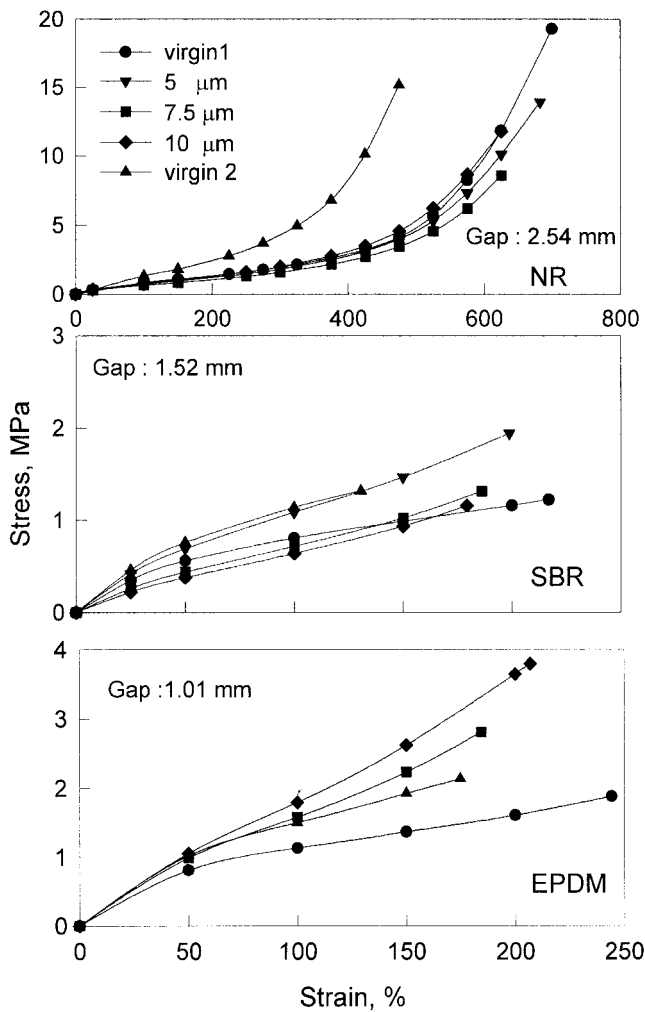


Figure 6 Stress–strain curves of virgin rubbers and revulcanized rubbers obtained at various amplitudes and gaps.

strain behavior cannot be explained by the possibility of strain-induced crystallization in the SBR and EPDM rubber networks.

The ultrasound treatment of rubber leads to an increase in sol fraction and reduction in gel fraction. The sol and gel fraction strongly depend on the condition of ultrasound treatment that is related to the degree of devulcanization. This means that the revulcanization reaction takes places in a heterogeneous system (in both the sol and in the gel). It is reasonable to suggest that the crosslink density of the revulcanized gel should be much higher than that of the revulcanized sol in revulcanized SBR²² and EPDM rubber. Thus, revulcanized SBR and EPDM can be assumed to have a bimodal network as shown schematically in Figure 7 in contrast to the unimodal network in virgin SBR and EPDM. It is well known that a bimodal network typically shows exceptional mechanical properties.^{29,30}

Thermal properties

Figure 8 shows glass transition temperature (T_g) of the devulcanized rubbers versus amplitude at various

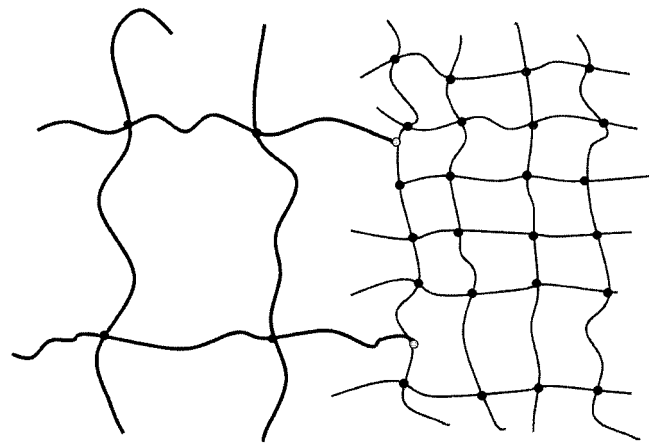


Figure 7 Schematics of bimodal network in revulcanized rubber obtained from ultrasonically devulcanized rubber.

gaps. In the ordinate of Figure 8, open symbols represent T_g of uncured rubber gums and solid symbols represent T_g of original vulcanizates. It is clearly observed that the glass transition temperature of uncured gums is lower than that of vulcanizates for three rubbers. The glass transition temperature of EPDM vulcanizate cured by recipe virgin 2 shows higher T_g than that of original vulcanizate cured by recipe virgin 1 and uncured gum. Clearly, one can conclude that the glass transition temperatures of rubbers are increased with crosslink density due to a reduced mobility of chains upon crosslinking.

However, it is shown that the T_g of devulcanized NR and SBR exceeds that of the virgin NR and SBR vulcanizates, while that of devulcanized EPDM is lower than that of the virgin EPDM vulcanizate. An increase in the T_g value of devulcanized NR and SBR containing lower amount of crosslinks was possibly

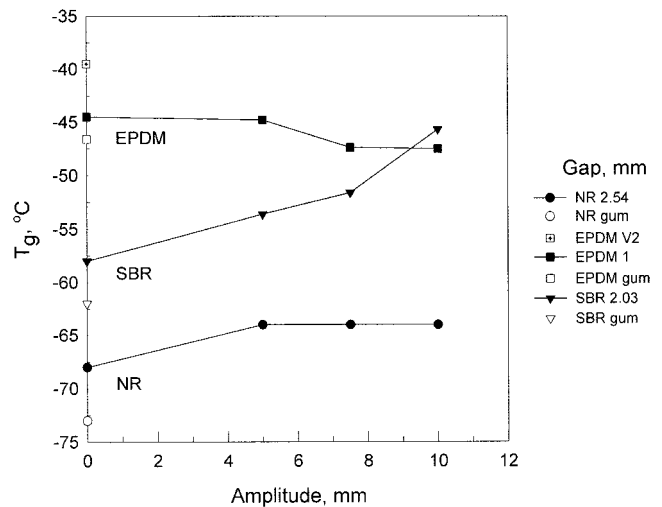


Figure 8 Glass transition temperature of the virgin gums, virgin vulcanizates, and devulcanized rubbers versus amplitude at various gaps. V2 denotes virgin vulcanizate cured by virgin 2 recipe.

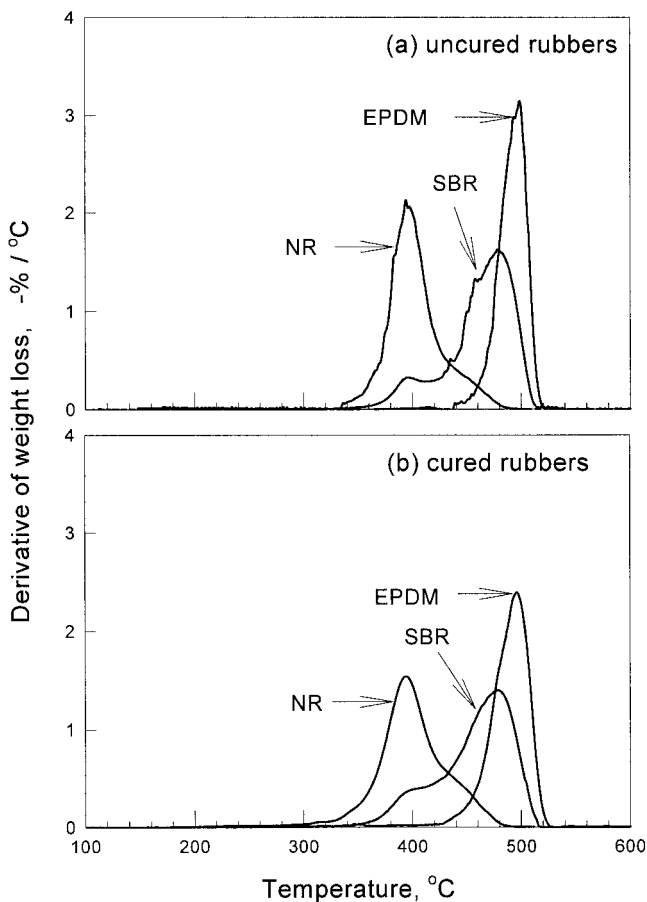


Figure 9 Derivative of weight loss versus temperature for various uncured (a) and cured (b) virgin rubbers in nitrogen environment.

attributed to the transformation during ultrasonic treatment of polysulfidic crosslinks into cyclic sulfidic structures chemically linked to the backbone chain.²¹ In the case of NR and SBR, transformations of polysulfidic crosslinks into cyclic structures led to a decrease in the mobility of chains. However, the results of EPDM indicated an opposite effect. Therefore, in the case of EPDM, no transformation of polysulfidic crosslinks into cyclic structure possibly took place due to the presence of bulky diene (ENB) group in polymer backbone as shown in Figure 1(c).

Figure 9 shows the thermal stability of uncured and cured rubbers under nitrogen atmosphere. It is seen here that the temperature corresponding to the maximum derivative of weight loss of both uncured and cured rubbers showed the following order, NR < SBR < EPDM. In fact, it is the same as the above-obtained order of the degree of devulcanization of various rubbers at the same devulcanization condition. Therefore, it is believed that the thermal stability of various rubbers could be related to the degree of devulcanization.

Unique characteristics of devulcanized rubbers

As has been described before,¹⁹ the normalized crosslink density and normalized gel fraction for ultrasonically devulcanized rubber can be correlated by a universal master curve that is independent of the processing conditions (such as ultrasonic amplitude, pressure, and gap size). As shown in Figure 10, this curve is unique for each elastomer due to its unique chemical structure. Based on these universal master curves, the efficiency of devulcanization of various rubbers can be predicted. Thus, at the same crosslink density, the higher gel fraction would indicate less devulcanization. For example, NR shows higher gel fraction at the same level of crosslink density than SBR. The latter is possibly due to a competitive reaction (devulcanization and redevulcanization) during devulcanization of NR. However, EPDM has higher gel fraction than SBR at the same level of crosslink density. It clearly indicates that it is more difficult to devulcanize EPDM than NR and SBR.

CONCLUSIONS

Gel fraction and crosslink density show that ranking of the degree of devulcanization is NR > SBR > EPDM, which is similar to ranking of the thermal stability. For SBR and EPDM, both crosslink density and gel fraction continuously decrease with amplitude, while for NR, crosslink density and gel fraction pass through a minimum of 7.5 μm and increase at 10 μm due to a predominant effect of redevulcanization over devulcanization during ultrasonic treatment.

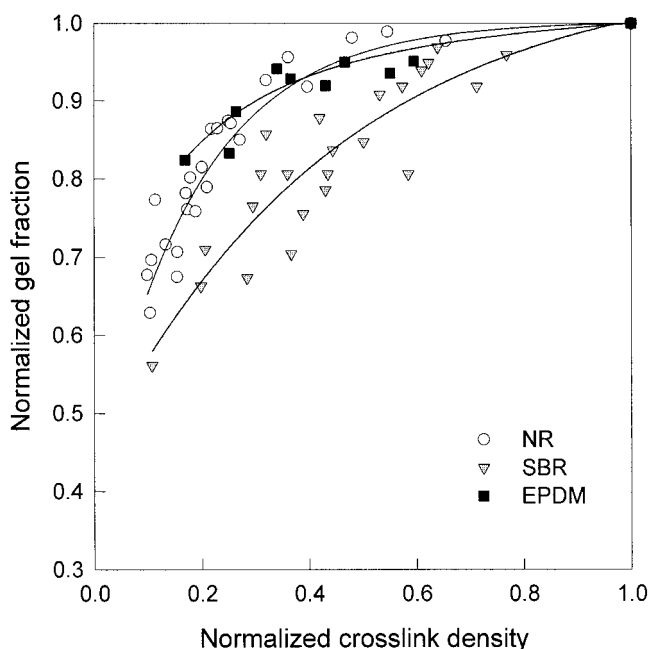


Figure 10 Normalized gel fraction versus normalized crosslink density for various rubbers.

Unique correlations between gel fraction and crosslink density are obtained for various rubbers. In comparison with virgin vulcanizates, for devulcanized SBR and NR, the glass transition temperature increases with amplitude but decreases for devulcanized EPDM. Decrease of molecular mobility of devulcanized SBR and NR is possibly due to a transformation of polysulfidic crosslinks to cyclic sulfidic structures along their macromolecular chains during ultrasonic devulcanization. Increase of molecular mobility of devulcanized EPDM is possibly due to a breakdown of rubber network without creation of cyclic sulfidic structures. The improvement in the mechanical properties of revulcanized SBR and EPDM is possibly due to the extent of nonaffine deformation of bimodal network, which is likely to appear in the process of revulcanization of ultrasonically devulcanized rubbers.

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