Ultrasonic Devulcanization of Carbon Black–Filled Ethylene Propylene Diene Monomer Rubber

J. Yun, V. V. Yashin, A. I. Isayev

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

ABSTRACT: The recycling of carbon black (CB)–filled ethylene propylene diene monomer (EPDM) rubber was carried out by using a newly built continuous ultrasonic grooved-barrel reactor. Using this reactor, it was possible to increase by two times the output of devulcanized rubber in comparison with the coaxial reactor built earlier. The dynamic viscoelastic properties of virgin vulcanizates, devulcanized, and revulcanized EPDM rubbers were measured. The cure behavior of virgin and devulcanized rubbers was measured. The gel fraction and crosslink density of virgin vulcanizate and devulcanized EPDM rubbers, and the mechanical properties of virgin vulcanizates and revulcanized rubbers were determined. Similar to our previous findings using the co-axial reactor, the revulcanizates of unfilled EPDM rubbers of the present study showed higher mechanical properties than those of the virgin unfilled vulcanizates. However, a progressive decrease in the mechanical properties of CB-filled EPDM revulcanizates with an increase of filler concentration, attributed to partial deactivation of filler, was observed. An improvement of mechanical properties of vulcanizates was achieved upon blending the devulcanized and virgin filled rubbers. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1646–1656, 2004

Key words: recycling; EPDM rubber; rheology; mechanical properties; ultrasound

INTRODUCTION

The recycling of used tires and waste rubbers has become a growing problem facing the rubber industry. In fact, the direct reprocessing and recycling of waste tires and vulcanized rubbers are impossible because of the presence of three-dimensional crosslink networks. So far, numerous techniques have been proposed for recycling waste rubbers, including catalysis,[1] mechanical,[2–4] thermomechanical,[5] and microwave[6] methods. Recently, extruder-type processes such as twin-screw extruder[7] and solid-state shear pulverization[8,9] have been used. However, none of the methods is predominantly related to the devulcanization of the elastomers. Each technique possesses certain disadvantages with respect to the recycled product quality, processing time, and cost. Review articles on rubber recycling were published by Warner,[10] Adhikari et al.,[11] and Isayev.[12]

The application of powerful ultrasound for the continuous devulcanization of rubber is the most recent approach.[13,14] It is now considered as one of the most promising rubber recycling methods.[11,15] The experiments using ultrasound have been conducted on various types of rubbers including ground rubber tire (GRT),[13,14,16] styrene butadiene rubber (SBR),[17] natural rubber (NR),[18] silicone rubber,[19,20] and unfilled ethylene propylene diene monomer (EPDM) rubber.[21] These studies have shown that ultrasonic waves, at a certain level of pressure and temperature, can rapidly break up the three-dimensional rubber networks. As the most desirable results, the ultrasonically treated rubber can be reprocessed and revulcanized in a manner similar to that used with unvulcanized elastomers. Ultrasonic devulcanization of rubber is a continuous and environmentally friendly process with no chemicals involved, which makes it attractive to the rubber industry. To increase the output and efficiency of a devulcanization reactor, a comparative study of GRT devulcanization in the so-called coaxial and barrel reactors was carried out.[16] However, the power consumption density of ultrasound during the devulcanization process in the barrel reactor was found to be higher because of a high friction in the seal area located between the ultrasound horn and barrel.

About two thirds of the rubbers used in vehicles are in tires. The classification of the remaining rubber components into polymer types reveals that about half are made of EPDM rubbers,[22] which are widely used in automobile tire sidewalls, automotive tubes, and window sealings in cars because of the excellent weatherability of EPDM rubbers.[23] In industrial and mechanical products, the largest single use of EPDM rubbers is in roofing.[24,25] Other applications include gaskets, conveyer belts, and appliance parts. For the recycling of EPDM rubbers, a twin-screw extruder,[7]

TABLE I
Particle Size Distribution of Ground EPDM Vulcanizate Containing 30 phr of Carbon Black

Particle size (microns)	Mesh	Distribution (%)
$x > 1700$	12	60
$1700 > x > 850$	20	31.4
$850 > x > 600$	30	4.1
$600 > x > 425$	40	2.2
$425 > x > 355$	45	0.9
$355 > x > 300$	50	0.7
$300 > x$	—	0.7

microwave methods,[6] and diphenyldisulfide as a catalyst[26] have been used. Up to now, studies on recycling of rubber using ultrasound have concentrated on other types of elastomers.[15–20]

The present article describes the results of our recent experiments on the recycling of CB-filled EPDM rubber by means of ultrasonic devulcanization with a newly developed ultrasonic reactor (called grooved-barrel reactor). This study shows the possibility of increasing the efficiency of recycling of CB-filled rubber. Rheology and curing behavior of devulcanized rubbers, and mechanical properties of revulcanized rubbers have constituted the main focus of investigation. To improve the mechanical properties of the revulcanized rubbers, the devulcanized and virgin filled rubbers were blended in various proportions. This study using a grooved-barrel reactor complements our earlier study[21] of devulcanization of unfilled EPDM rubber using a coaxial ultrasonic reactor.

EXPERIMENTAL

Materials

EPDM (Keltan 2506) used in our experiments was obtained from DSM Copolymer (Leminster, MA) [comonomer (ENB) content ~ 4.5 wt %; ethylene content 56 wt %; Mooney viscosity 28 (ML$_{(1+4)}$ 125°C)]. The other compounding ingredients were zinc oxide, stearic acid, sulfur, TMTD (tetramethylthiuram disulfide), MBT (2-mercaptobenzothiazole; Akrochem Corp., Akron, OH), and carbon black (HAF N330, Huber Engineered Carbons, Atlanta, GA). Although industrial EPDM formulations typically contain oil, the above recipe does not include oil. This was done to study the ultrasound devulcanization without an additional effect arising from the interaction of oil with EPDM rubber.

Preparation of vulcanizates

The CB-filled compounds were mixed using the Banbury mixer (Farrel, Ansonia, CT). To improve the mix-

ing quality and to prevent prevulcanization, a two-stage mixing process was applied. First, the EPDM was premixed with zinc oxide, stearic acid, and carbon black in a Banbury mixer at a starting temperature of 80°C for 5 min. After the first mixing, a two-roll mill (Dependable Rubber Machinery Co., Cleveland, OH) was used at 50°C to prevent any scorch problem during the incorporation of curatives. Nip of the two-roll mill was 2–5 mm and speed was 40 rpm. One minute was required to soften the compounds. After softening, sulfur and accelerators were added together. The total mixing time was 5 min. The compounds without carbon black were prepared using the same procedures. The concentration of CB varied from 0 to 60 phr. The compression molding of slabs (260 × 260 × 12 mm) was performed by means of an electrically heated compression-molding press (Wabash, Wabash, IN) at 160°C and a pressure of 13.8 MPa. The cure time corresponded to the time required to achieve 90% of the 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. The particle size distribution of ground 30 phr CB-filled EPDM is given in Table I. The cure recipe for virgin vulcanizates was 5 phr of zinc oxide, 1 phr of stearic acid, 1.5 phr of sulfur, 1 phr of TMTD, and 0.5 phr of MBT. This recipe was based on ASTM D3568.

Ultrasonic reactor

In the grooved-barrel reactor (Fig. 1), two ultrasonic water-cooled horns of rectangular cross sections (38.1 × 38.1 mm^2) were inserted into the barrel through two ports. Instead of two restrictors in the barrel reactor,[16] in the grooved-barrel reactor two helical channels were made on the barrel surface (grooved barrel). In this reactor, rubber flows in the helical channels through the gap created between the rotating screw and the tips of the horns. The gap could be controlled similarly as in the barrel reactor.[16] The clearances between the horns and the ports of the barrel were
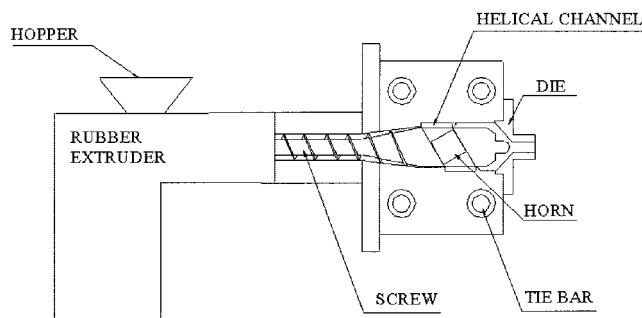

Figure 1 Schematic drawing of the grooved-barrel ultrasonic reactor.

sealed by two Vespel gaskets. Vespel was 40 wt % graphite–filled polyimide that provided an enhanced resistance to wear and a low friction as well as an improved dimensional and oxidative stability. Compared to Teflon, which was used for the sealing of the barrel reactor,[16] Vespel exhibited a higher stiffness and a lower friction coefficient to endure ultrasound waves and to prevent the leakage of rubber during devulcanization and metal-to-metal contact between the horn and the barrel.

In the devulcanization section, the screw diameter (50.8 mm) was the same as that in the barrel reactor.[16] The screw diameter before the devulcanization zone was 38.1 mm. This smaller diameter was provided for the converging flow of the rubber to the devulcanization zone. The latter typically enhanced the devulcanization process. After devulcanization, the devulcanized samples were quenched to prevent thermal degradation. A circular die ($D = 4$ cm) was attached to the extruder at the exit from the devulcanization zone.

Ultrasonic devulcanization

The extruder was preheated to 120°C. The temperature was kept uniform for all barrel zones. The gap between the rotating shaft and the horn, and the amplitude of ultrasound were adjusted to the chosen values. The particles of EPDM rubber were loaded into the hopper. The feeder, providing "starved feed" to the extruder, controlled the output. In the extruder, the EPDM vulcanizate was compressed and conveyed by the screw to the devulcanization zone. The ultrasonic treatment of the rubber occurred in the gap between the horn and the rotating shaft of the screw of the reactor. After reaching the steady-state conditions indicated by the pressure transducer and ultrasonic power wattmeter, ultrasonically treated samples were collected. The entrance pressure before the ultrasonic treatment zone, the temperature in the rubber after the ultrasonic treatment zone, and the ultrasonic power consumption were measured. The gap size between the horn and screw was 1.02 mm for EPDM rubber containing up to 45 phr CB. However, it was found that the ultrasonic unit was overloaded because of the high pressure generated from 60 phr filled EPDM rubber and a flow rate of 1.26 g/s. Therefore, to reduce the pressure, a gap size of 2.03 mm was used for 60 phr CB-filled EPDM rubbers and a flow rate of 1.26 g/s. The ultrasonic amplitudes used were 5, 7.5, and 10 μm and the feed rate of rubber was 0.63 and 1.26 g/s.

Revulcanization

Before vulcanization of devulcanized samples, the samples were compounded with curatives using a two-roll mill, whose nip was 2 mm and roll speed was 40 rpm. The mixing time of the curative using a two-roll mill was 5 min. In most cases, after devulcanization the samples changed to soft and sticky materials, which could be easily milled to form a smooth, continuous sheet. However, some devulcanized samples could not be milled because of a low degree of devulcanization and accordingly a high content of gel.

For the preparation of blends of devulcanized and virgin rubbers, a two-roll mill was used. The mixing time was 5 min. The cure recipe for revulcanization of 100% devulcanized rubber and blends was the same as the cure recipe for virgin vulcanizates.

Molding

The vulcanization was carried out by using a compression-molding press at 160°C and by applying a pressure of 13.8 MPa for about 20 min. This time corresponded to the time required to achieve 90% of the maximum torque on the cure curve. Vulcanized sheets with dimensions of $127 \times 127 \times 2$ mm^3 were obtained and used for mechanical testing.

Characterizations

An Advanced Polymer Analyzer (APA 2000, Alpha Technology, Akron, OH) was used to obtain the torque–time curve at a temperature of 160°C.[27] The dynamic behavior of virgin, devulcanized, and vulcanized EPDM rubbers was also investigated at a temperature of 100 and 80°C, respectively, using this instrument.

The gel fraction of virgin vulcanizates and devulcanized EPDM was measured by the Soxhlet extraction method using benzene as a solvent. The crosslink density of the gel of these rubbers was measured by the swelling technique using benzene as a solvent. The crosslink density was determined using the Flory–Rehner equation[28] with the Kraus correction.[29] For the EPDM–benzene system, the interaction parameter χ in the Flory–Rehner equation was taken as $0.488 + 0.271 V_r$,[30] where V_r is the fraction of the polymer in the swollen network in equilibrium with pure solvent. The value of C, being a universal constant for a given filler in the Kraus correction, was taken as 1.17 for HAF carbon black (the BET surface is 75.1 m^2/g).[29] The stress–strain measurements were acquired at room temperature according to ASTM D412 (type C) at a crosshead speed of 500 mm/min using an Instron tensile tester (Model 5567; Instron, Canton, MA).

RESULTS AND DISCUSSION

Characterization of virgin EPDM

Figure 2(a), which shows the cure curves at 160°C for virgin CB-filled EPDM, indicates that the addition of
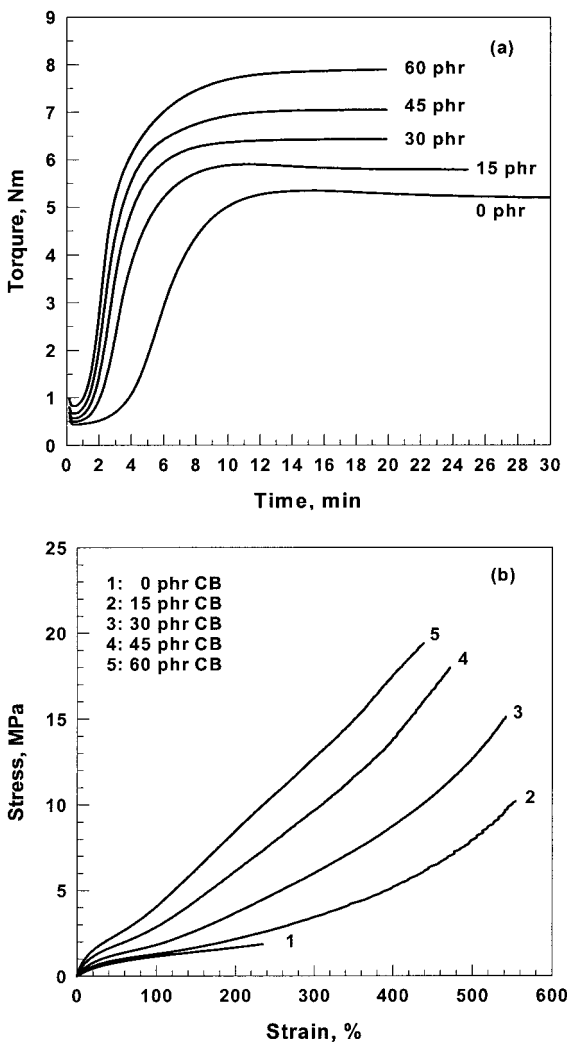
Figure 2 (a) Cure curves of CB-filled EPDM compounds. (b) Stress–strain curves of corresponding vulcanizates.

CB to EPDM leads to a progressive increase in the rate of cure and maximum torque and a decrease of the induction time as typically observed in CB-filled rubbers.[31] The stress–strain curves for CB-filled EPDM are shown in Figure 2(b). Because of the reinforcement by CB, the tensile strength and modulus increase with CB contents. The elongation at break passes through a maximum at 15 phr CB-filled EPDM vulcanizates. The tensile properties versus concentration of CB are summarized in Figure 3(a). The gel fraction and crosslink density of virgin EPDM vulcanizates as a function of CB content are shown in Figure 3(b), which indicates that the gel fraction is not significantly affected by increasing the CB content, but the crosslink density is increased with CB content. Even though the Kraus correction[29] was made in the calculation of the crosslink density, an increase in the CB content increased the crosslink density of EPDM vulcanizates because of the formation of physical bonds between EPDM chains and CB.[32,33] In particular, this result

correlates with an increase of the final torque in cure curves with an increase of CB contents as depicted in Figure 2(a).

Ultrasonic devulcanization

The pressure before the devulcanization zone and the ultrasonic power consumption versus ultrasonic amplitude are shown in Figure 4. The pressure before the devulcanization zone is substantially reduced as the amplitude of ultrasound is increased. The same trend is observed in different devulcanization reactors.[16] The ultrasound facilitates the flow of rubber through the gap because of devulcanization occurring as packed rubber crumbs enter the ultrasonic treatment zone. The pressure increases with the concentration of CB.

The measured ultrasonic power consumption was expended because of dissipation losses and breakage of the bonds leading to devulcanization. It could not
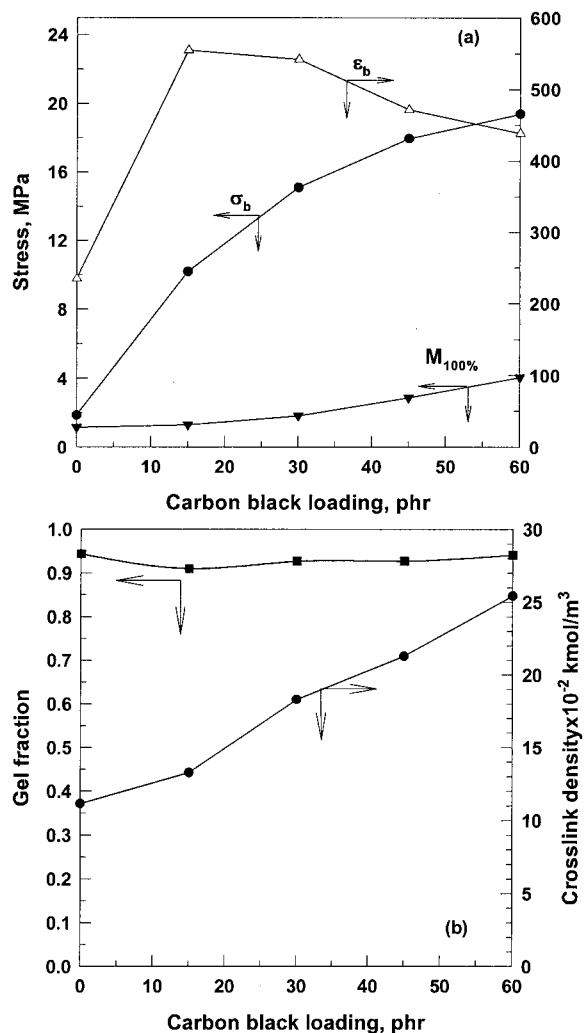

Figure 3 Tensile properties: (a) gel fraction and (b) crosslink density of virgin CB-filled EPDM vulcanizates.
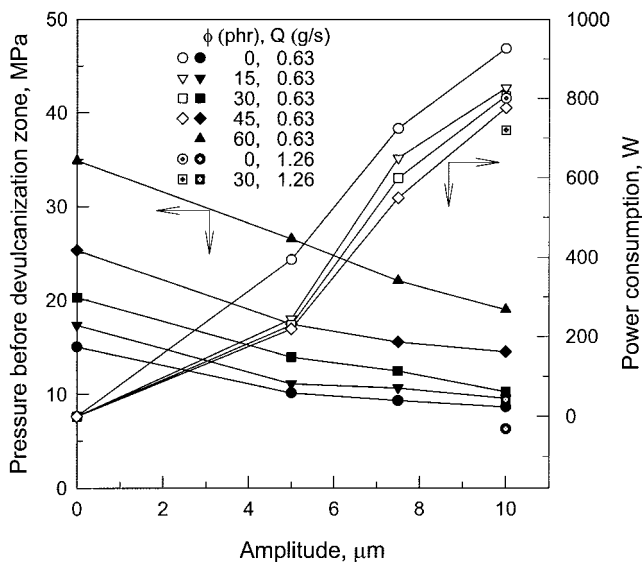
Figure 4 Pressure before devulcanization zone (solid symbols) and power consumption (open symbols) as a function of ultrasonic amplitude during the devulcanization of EPDM vulcanizates at various CB loadings and flow rates.

be estimated experimentally what part of the power was consumed by devulcanization alone. The power expended on heat dissipation in the material and the power transmitted by the traveling wave through the rubber could not be separated. The only measurable losses were the initial power consumption of the acoustic system when the horn worked without loading. In obtaining Figure 4, these losses were subtracted from the total power consumption. Ultrasonic power consumption increased with an increase of ultrasonic amplitudes, which indicates that more energy was transmitted into the rubber material with an increase of amplitude. It is clear that the higher power consumption leads to a higher degree of devulcanization; increasing the CB content leads to a lower ultrasonic power consumption at various ultrasonic amplitudes. This is in spite of the fact that higher pressure is developed in EPDM rubbers of higher CB contents. Typically, an increase of pressure causes an increase in power consumption.

Here we see an opposite effect. Apparently, in CB-filled EPDM rubbers, it may be easier to break both chemical bonds between EPDM chains and physical bonds between EPDM chains and carbon black because of the restricted mobility of chains upon the incorporation of a filler. Therefore, there are two competitive factors affecting the behavior of power consumption. On one hand, more energy is consumed because of an increase in pressure; on the other hand, energy is also consumed to break the chemical bonds of CB-filled EPDM rubbers, which are easier to break because of the reduced molecular mobility of rubber chains in the presence of CB. The latter may contribute

to the observed reduction of ultrasonic power consumption with an increase of CB contents up to 45 phr. However, in the case of 60 phr CB-filled EPDM rubber at a flow rate of 0.63 g/s, and in the case of 0 and 30 phr CB-filled EPDM rubber at a flow rate of 1.26 g/s, an overload of an ultrasonic unit occurred at a gap size of 1.02 mm because of an excessive increase of pressure. When the gap size was increased to 2.03 mm, the power consumption and pressure of 0 and 30 phr CB-filled EPDM rubbers at a flow rate of 1.26 g/s became lower than those of rubbers at a flow rate of 0.63 g/s and a gap size of 1.02 mm (Fig. 4). With an increase of gap, the power consumption was reduced because of reduction of the strain amplitude experienced by the rubber at the same ultrasound amplitude. Also, the pressure was reduced because of less resistance of the rubber to flow at a larger gap. In general, as the flow rate increases, the power consumption and pressure increase at the same gap size.

The mean residence time of the grooved-barrel and coaxial[14] reactors at the flow rate of 0.63 g/s and a gap size of 1.02 mm was calculated to be 5 and 6.2 s, respectively. However, in the grooved-barrel reactor it is possible to achieve devulcanization at the flow rate up to 1.26 g/s (Fig. 4). Devulcanization in a coaxial reactor is not possible to achieve at a flow rate of 1.26 g/s because of an overload of an ultrasound unit. At a flow rate of 1.26 g/s, the mean residence time of the grooved-barrel reactor is 2.5 s. Therefore, by using the grooved-barrel reactor, devulcanization can be achieved at a significantly reduced mean residence time with an increased output.
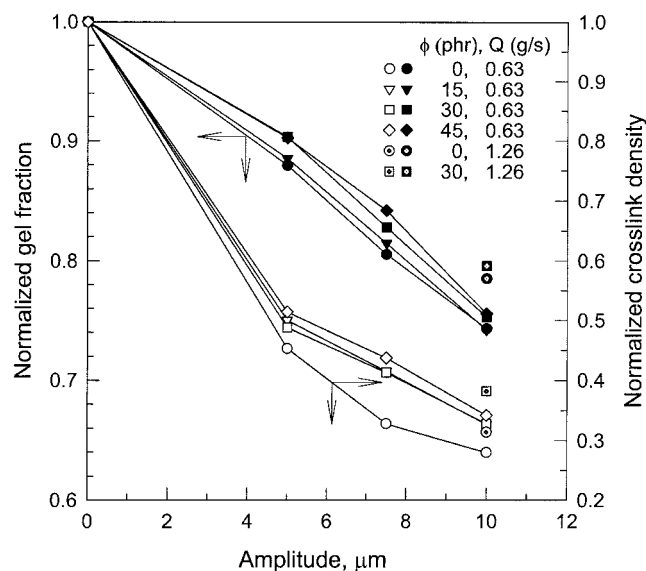

Figure 5 Normalized gel fraction (solid symbols) and normalized crosslink density (open symbols) versus ultrasonic amplitude for devulcanized EPDM rubbers at various CB loadings and various flow rates.

Gel fraction and crosslink density

Figure 5 represents the normalized gel fraction and normalized crosslink density of devulcanized EPDM rubber with various amounts of CB as a function of ultrasonic amplitude. This normalization of gel fraction and crosslink density was made because the values of virgin vulcanizates are affected by the level of CB loading. The normalized values were obtained as a ratio of the gel fraction and crosslink density of devulcanized EPDM rubber to those of virgin vulcanizates, as shown in Figure 3(b). The normalized gel fraction and crosslink density at various concentrations of CB decreased with ultrasonic amplitude. At a constant amplitude, the devulcanized rubber containing a lower amount of CB gave a lower normalized gel fraction and crosslink density, which indicated a higher degree of devulcanization in the case of lower concentration of CB. The latter is supported by an observed increase of power consumption with a decrease of CB concentration, as depicted in Figure 4. In other words, the greater power consumption led to a higher degree of devulcanization. However, it seemingly contradicts with the statement made earlier concerning the ease of devulcanization in CB-filled rubber even at a lesser power consumption than that in the unfilled rubber. This contradiction can be explained by the observation of a significant increase of the crosslink density with CB concentration [Fig. 3(b)]. It means that more bonds are broken at a higher content of CB. As the flow rate increases, the gel fraction and crosslink density of devulcanized rubbers increase because of a lower mean residence time discussed earlier. One may suggest that the effect of CB level on devulcanization efficiency is similar to the strain amplification concept introduced in rheology of filled rubbers. Certainly, at the same ultrasonic energy in the case of filled rubbers a lesser volume of rubber is subjected to devulcanization. However, this analogy is not necessarily appropriate in the case of ultrasonic devulcanization, given that power consumption is a result of the complex interaction of effects of the pressure, flow rate, behavior of rubber–filler interfaces during ultrasonic waves propagation, and loss modulus of rubbers at ultrasonic frequency and amplitude applied.

The experimental data on the dependency of gel fraction in devulcanized SBR and GRT on crosslink density in the gel were simulated numerically using the percolation concept and the Monte Carlo technique.[34,35] The experimental data were also successfully interpreted based on the Dobson–Gordon theory [36,37] of rubber networks statistics.[21,38] In the latter studies, the data on unfilled devulcanized EPDM, SBR, and silicone rubber were simulated using this theoretical approach. It was demonstrated that the assumption of spatiotemporal randomness of rubber
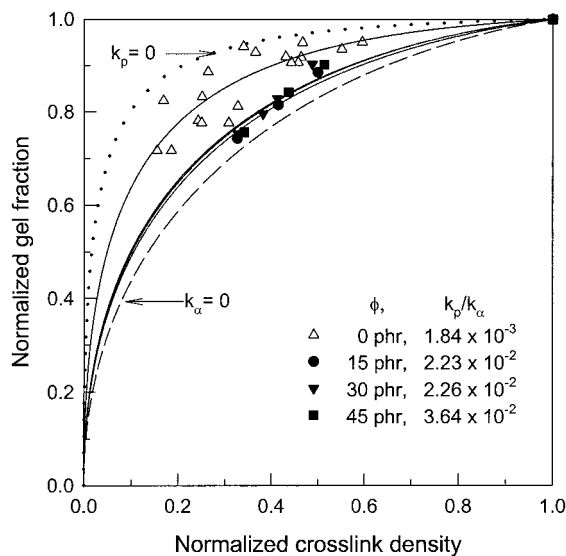

Figure 6 Normalized gel fraction versus normalized crosslink density of devulcanized unfilled (open symbols) and CB-filled EPDM (solid symbols) rubbers. The experimental data are represented by symbols. The dashed and dotted lines correspond to the limiting conditions of $k_\alpha = 0$ (dashed lines) and $k_p = 0$ (dotted lines).

degradation allows achieving a fairly good agreement between experimental and theoretical data. The process of rubber degradation is characterized by the rate constants of main chain and crosslink scission (k_p and k_α, respectively).

Figure 6 shows the change of the normalized gel fraction versus the normalized crosslink density of unfilled and filled EPDM rubbers devulcanized at various conditions. In all cases, the normalized crosslink density of unfilled EPDM networks is lower than that of CB-filled EPDM networks at a given gel fraction. There are two extreme curves in Figure 6, one of which corresponds to the situation where only crosslinks rupture (rate constant $k_p = 0$, dotted curve) and the other, that only rubber main chains are subjected to breakage (rate constant $k_\alpha = 0$, dashed curve). In the latter case, the curve shifts to the right in the plot of the normalized gel fraction versus the normalized crosslink density. Figure 6 indicates that data points for unfilled EPDM rubber are close to the former curve (crosslinks rupture), whereas for CB-filled EPDM rubber they approach the latter curve (main chains rupture). The solid lines represent results of calculations of unfilled and CB-filled EPDM rubbers. At each CB concentration, the corresponding values of k_p/k_α were determined and are shown in Figure 6. The values of k_p/k_α with an increase of CB concentration increase. The value of k_p/k_α of unfilled EPDM rubber is also smaller than that of CB-filled EPDM rubber. This implies that more main chains are severed because of the presence of the physical and chemical crosslinks between EPDM chains and CB
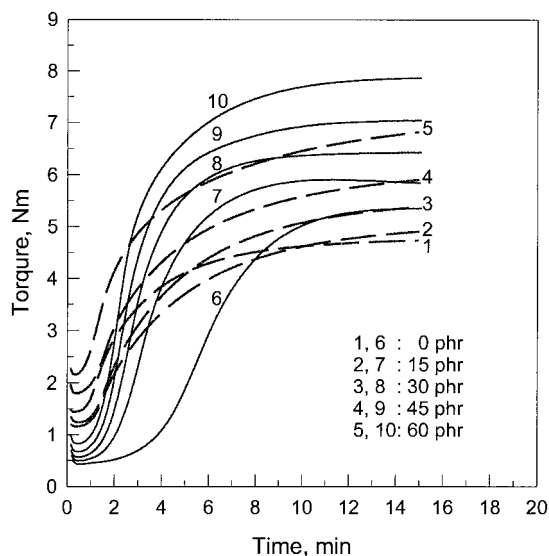
Figure 7 Cure curves for virgin compounds (solid curves, 6–10) and devulcanized EPDM (dashed curves, 1–5) at 160°C devulcanized at a flow rate of 0.63 g/s and an amplitude of 10 μm.

filler surface and because of a decreased mobility of EPDM chains upon CB filling. A similar effect was found and reported for silica-filled PDMS rubber.[20]

Cure behavior

Figure 7 shows the cure curves for virgin gums and devulcanized EPDM at a cure temperature of 160°C. As the filler content increases, the maximum torque increases because of the reinforcement of EPDM upon
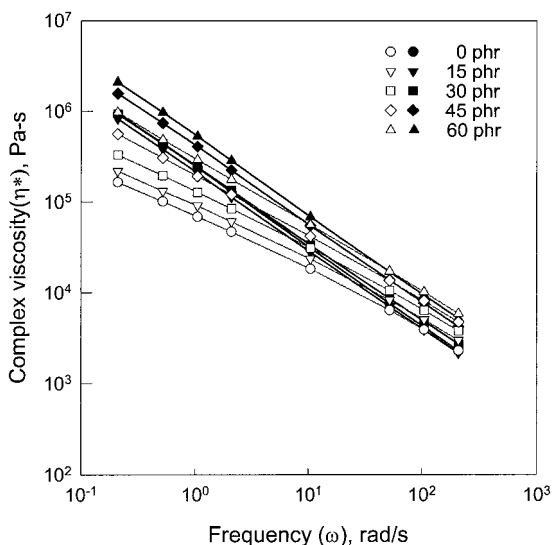

Figure 8 Complex viscosity versus frequency for uncured virgin compounds (open symbols) and devulcanized EPDM rubbers (solid symbols) devulcanized at an amplitude of 10 μm and a flow rate of 0.63 g/s.
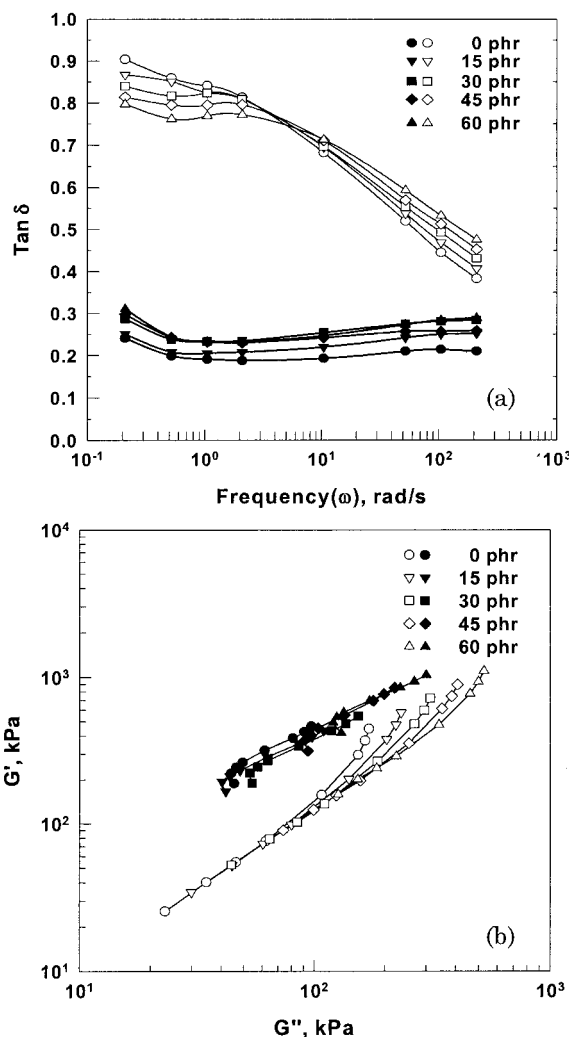

Figure 9 Plots of (a) tan δ versus frequency and (b) G' versus G'' for uncured virgin compounds (open symbols) and devulcanized EPDM rubbers (solid symbols) devulcanized at an amplitude of 10 μm and a flow rate of 0.63 g/s.

addition of CB. The rate of vulcanization of rubber is also increased by adding CB. This is attributed to the ability of CB to enhance the dehydrogenation of rubber chains.[39]

Compared with the cure curve of virgin rubber, the devulcanized rubbers have a lower maximum torque and a higher minimum torque. In the case of minimum torque, a correlation with the dynamic complex viscosity of devulcanized rubber was found as shown in Figure 8. Here, the sample showing a higher minimum torque on the cure curves also shows a higher dynamic complex viscosity, which is attributed to the presence of gel in the devulcanized EPDM rubbers.

Dynamic viscoelastic properties

Because dynamic viscoelastic properties are important in evaluating the recyclability of rubber, dynamic vis-
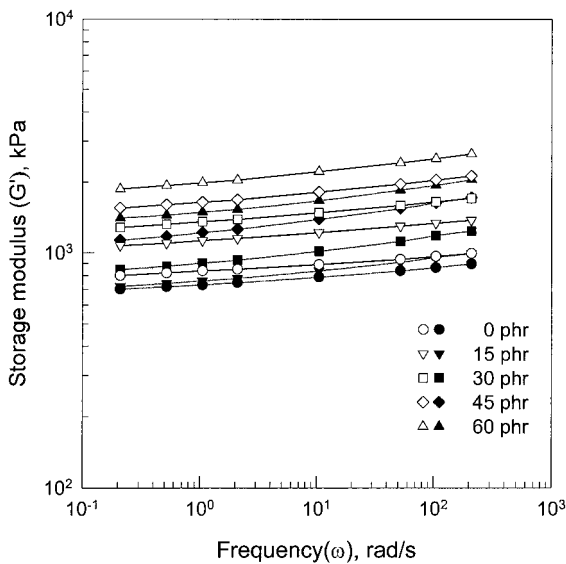
Figure 10 Storage modulus versus frequency for virgin vulcanizates (open symbols) and revulcanized EPDM rubbers (solid symbols) devulcanized at an amplitude of 10 μm and a flow rate of 0.63 g/s.

coelastic properties of devulcanized EPDM rubbers and their revulcanizates were measured using APA 2000. Figure 8 shows the dynamic complex viscosity versus frequency of uncured virgin and devulcanized EPDM compounds at 100°C and strain amplitude γ_0 = 0.07. The dynamic complex viscosity of devulcanized EPDM rubbers is higher than that of uncured virgin EPDM rubbers at a low frequency region. This is possibly the result of a high gel content in the devulcanized EPDM rubbers. The complex viscosity of uncured virgin and devulcanized EPDM rubber increases with an increase of CB loading attributed to the reinforcement of carbon black.

Figure 9 depicts the tan δ versus frequency and G' versus G'' for virgin gum compound and devulcanized EPDM. In particular, Figure 9(a) indicates that the tan δ of an uncured virgin EPDM compound decreased with frequency, whereas that of devulcanized EPDM was almost independent of frequency. As the CB content increases, the slopes of tan δ versus frequency for an uncured EPDM compound decreases. In general, if the effect of filler concentration on tan δ is considered at various temperatures, then at low temperatures tan δ is reduced by increasing the loading and the reverse is true at high temperatures with a crossover point.[40] In Figure 9(a), a similar crossover point may be observed for uncured virgin EPDM compounds, which indicates that the dependency of tan δ on frequency is decreased with carbon black loading. Moreover, tan δ is reduced significantly after devulcanization, which indicates that devulcanized EPDM rubbers are more elastic because of the presence of gel. In addition, there is no crossover point in the tan δ behavior of

devulcanized rubbers, which is attributed to the absence of the terminal zone in viscoelastic behavior of devulcanized rubbers containing a large amount of gel.

The loss modulus (G'') versus the storage modulus (G') for uncured virgin and devulcanized EPDM rubber is given in Figure 9(b). Clearly, at all frequencies, devulcanized EPDM rubbers exhibit a higher storage modulus than the original uncured EPDM rubbers at the same loss modulus; also, it indicates a higher elasticity of devulcanized rubbers. A conclusion can be made that devulcanized EPDM rubber exhibits a higher modulus than that of an uncured virgin compound because of the presence of gel in the devulcanized EPDM rubbers. Similar behavior was also observed in devulcanized unfilled EPDM rubber.[21]

Figures 10 and 11 depict the dynamic properties of revulcanized EPDM rubbers at 80°C and strain γ_0 = 0.042. In particular, Figure 10 shows storage modulus versus frequency for revulcanized EPDM rubbers and the virgin vulcanizates. The storage modulus of
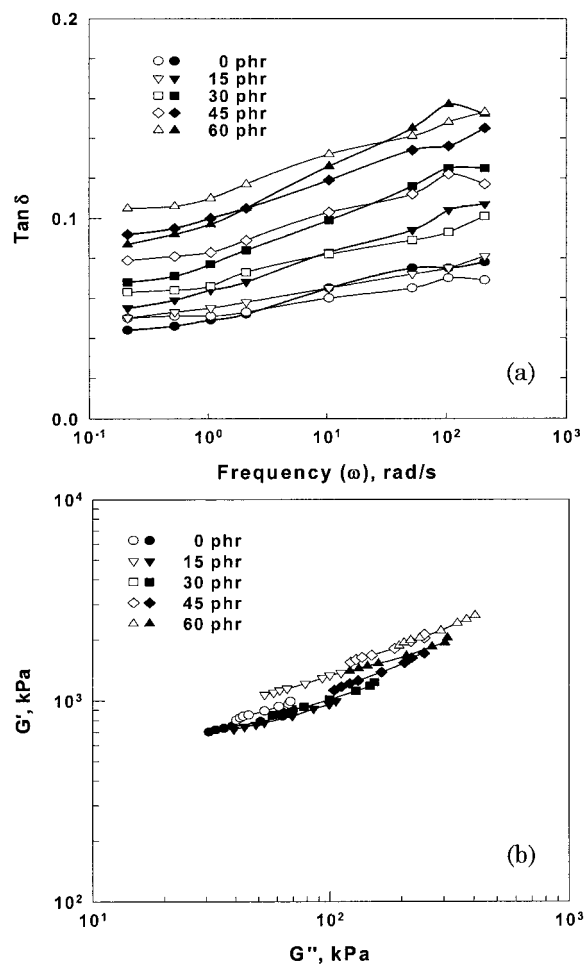

Figure 11 Plots of (a) tan δ versus frequency and (b) G' versus G'' for virgin vulcanizates (open symbols) and revulcanized EPDM rubbers (solid symbols) devulcanized at an amplitude of 10 μm and a flow rate of 0.63 g/s.
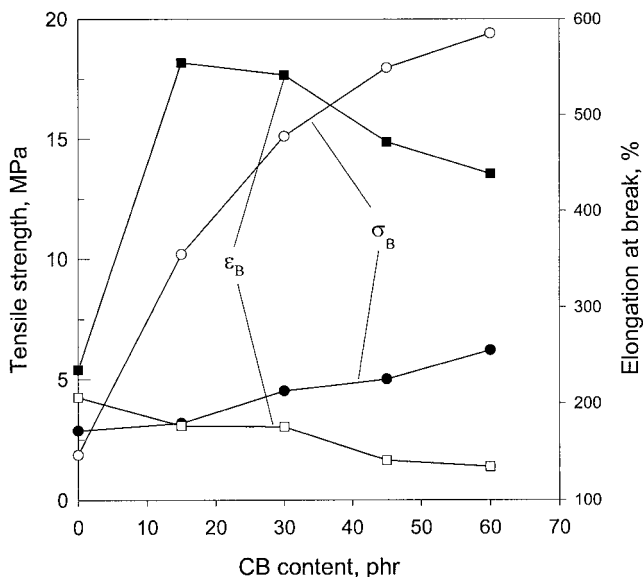
Figure 12 Tensile strength and elongation at break versus CB content of virgin vulcanizates (open symbols) and revulcanized EPDM rubbers (solid symbols) at a flow rate of 0.63 g/s and an amplitude of 10 μm.

tion of properties is observed after revulcanization. In fact, unfilled revulcanizates show higher tensile strength, modulus, and energy at break than those of virgin vulcanizates. This is in agreement with our previous study.[21] However, there is a significant deterioration in the tensile strength, elongation at break, and energy at break of revulcanized rubbers with an increase of filler contents.

It is well known that carbon black surfaces contain functional groups capable of reacting with polymer molecules because of the chemical and physical interaction during processing and vulcanization.[41] These chemical and physical interactions between rubber and carbon black can cause adsorption of the polymer molecules onto the filler surface. This adsorption leads to two phenomena that are well documented: the formation of bound rubber[42] and a rubber shell on the carbon black surface. Both are related to the restriction of the segmental movement of the polymer molecules.[43] Bound rubber is defined as the rubber portion in an uncured compound that cannot be extracted by a good solvent because of the adsorption of the rubber molecules onto the filler surface.

Therefore, the mobility of such rubber chains is considerably restricted at the surface of the filler particle. It is believed that, because of the reduced mobility, filled rubbers may exhibit an increasing probability of the breakup of the bound chains by the ultrasonic treatment leading to the partial deactivation of the filler. This effect is believed to be the main reason for the observed loss of performance characteristics of rubber after ultrasonic devulcanization in CB-filled SBR,[44] CB-filled NR,[45] and silica-filled silicone rubber.[20] Without the presence of CB in rubber, the performance properties of revulcanized rubbers are improved or do not deteriorate significantly because of the presence of a bimodal network and the absence of the effect of deactivation of filler.[19,21,46]

To increase the mechanical properties of recycled EPDM rubber obtained by ultrasonic devulcanization, 30 phr CB-filled devulcanized rubber was blended with virgin 30 phr CB-filled virgin EPDM compound at various concentrations. Figure 13 represents the

virgin vulcanizates is higher than that of revulcanizates at various CB loadings, which indicates that the revulcanizates are not able to achieve the modulus values of virgin vulcanizates and which also correlates with a lower maximum torque of revulcanizates in cure curves (Fig. 7). Figure 11(a) indicates that tan δ of revulcanized EPDM rubbers is slightly higher than that of virgin vulcanizates at a low filler loading. Also, the storage modulus of revulcanized EPDM rubber is lower than that of the original vulcanizate at the same loss modulus [Fig. 11(b)]. It is easily concluded that the elasticity of revulcanized EPDM rubbers is lower than that of virgin EPDM vulcanizates.

Mechanical properties

The tensile properties of revulcanized EPDM rubbers are compared to those of virgin vulcanizates in Figure 12 and Table II. For the unfilled rubber, no deterioration

TABLE II
Mechanical Properties of Revulcanizates of Devulcanized EPDM Obtained at Various Devulcanization Conditions

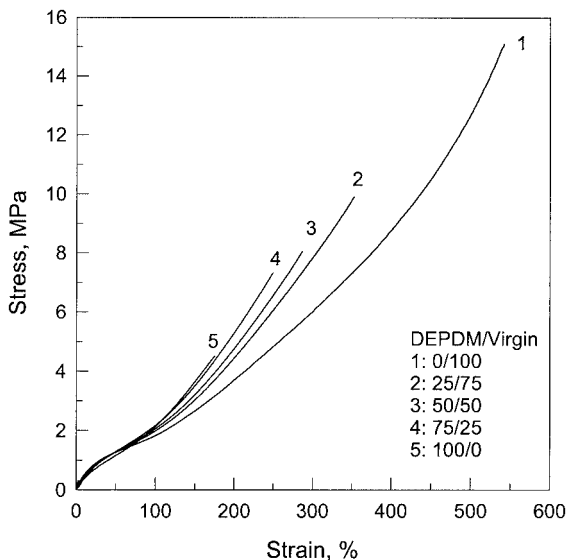| Sample	CB (phr)	Devulcanization condition			Mechanical property			
		Gap (mm)	Amplitude (μm)	Output (g/s)	$E_{100\%}$ (MPa)	σ_b (MPa)	ε_b (%)	Energy at break (J)
Virgin	0	—	—	—	1.1	1.8	234	1.8
Devulcanized	0	1.02	10	0.63	1.3	2.9	206	3.8
Devulcanized	0	2.03	10	1.26	1.3	2.0	183	2.0
Virgin	30	—	—	—	1.8	15.1	541	36
Devulcanized	30	1.02	10	0.63	2.1	4.5	176	3.8
Devulcanized	30	2.03	10	1.26	2.7	4.4	146	3.8

Figure 13 Stress–strain curves of 30 phr CB-filled devulcanized (DEPDM)/virgin EPDM rubber blend vulcanizates. Rubber was devulcanized at a flow rate of 0.63 g/s and an amplitude of 10 μm.
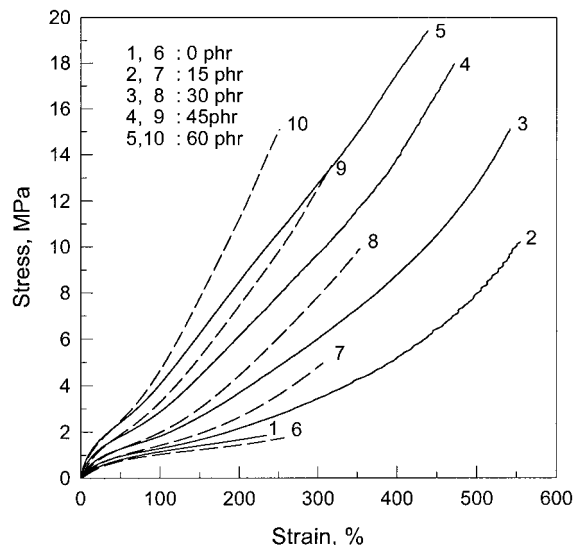

Figure 15 Stress–strain curves of virgin vulcanizates (solid lines, 1–5) and 25/75 devulcanized/virgin blend vulcanizates (dashed lines, 6–10). Rubber was devulcanized at a flow rate of 0.63 g/s and an amplitude of 10 μm.

stress–strain curves, and Figure 14 depicts the modulus, tensile strength, and elongation at break of the blend vulcanizates. It is seen that the modulus at 100% elongation increases with the content of devulcanized rubber following the values above the rule of mixtures. The tensile strength and elongation at break of blend vulcanizates decrease with the content of devulcanized rubber following the values at or slightly below the rule of mixtures.

In Figures 15 and 16, the mechanical properties of the blend vulcanizates consisting of 25% of devulca-

nized rubber and 75% virgin EPDM rubber are compared to those of virgin vulcanizes. In fact, by adding 25% of devulcanized EPDM rubber into virgin filled rubber, considerably higher mechanical properties than those of the revulcanizates of 100% devulcanized EPDM rubber are obtained at any content of filler, as indicated by comparing Figure 16 and Figure 12. As the filler content increases, a lower tensile strength and elongation at break of blend vulcanizates are observed compared with those of virgin vulcanizates. Evidently, the deactivated filler upon ultrasonic devulcanization exhibits a limited efficiency to enhance
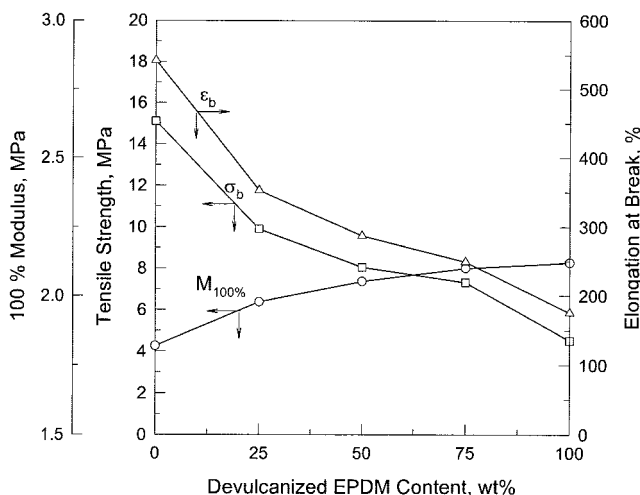

Figure 14 Tensile properties of 30 phr CB-filled devulcanized/virgin EPDM rubber blend vulcanizates versus concentration of devulcanized rubber. Rubber was devulcanized at a flow rate of 0.63 g/s and an amplitude of 10 μm.
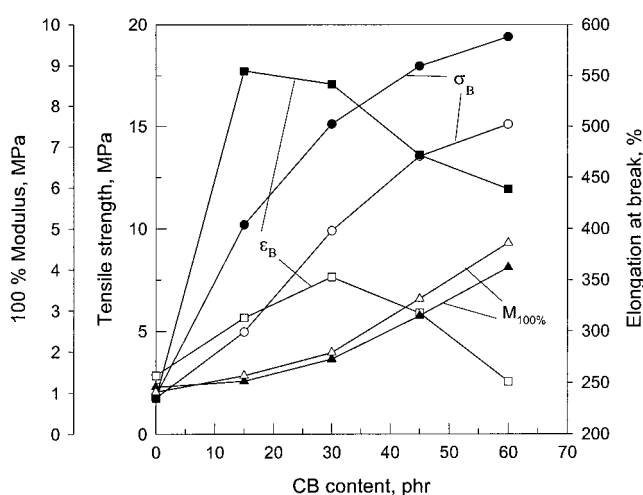

Figure 16 Tensile properties of virgin vulcanizates (solid symbols) and 25/75 devulcanized/virgin blend vulcanizates (open symbols). Rubber was devulcanized at a flow rate of 0.63 g/s and an amplitude of 10 μm.

mechanical properties of revulcanizates because it does not adhere well to the blend of virgin EPDM rubber and partially devulcanized rubber. The modulus at 100% elongation in the blends is higher than that in virgin rubbers because of the presence of gel in the devulcanized rubber.

CONCLUSIONS

The possibility of recycling of CB-filled EPDM rubber was shown using a new grooved-barrel ultrasonic reactor. By means of this reactor, it was possible to increase the output by two times in comparison with the coaxial reactor built earlier. The crosslink density and gel fraction measurements indicate that more devulcanization was achieved at higher amplitude for all compositions of filler. However, less devulcanization of CB-filled rubbers was obtained because a certain portion of ultrasonic energy was consumed to break the physical and chemical bonds between EPDM rubbers and carbon black, which possibly possesses a lower bond energy than that of chemical bonds in polymer chains and crosslinks. Dynamic viscoelastic properties indicate that devulcanized EPDM rubber is more elastic than an uncured virgin EPDM compound, whereas revulcanized EPDM rubbers are less elastic than the virgin vulcanizate. Mechanical properties of the revulcanizates deteriorated with an increase in CB concentration because the fillers became partially deactivated under ultrasonic treatment. Considerably better mechanical properties were obtained in blend vulcanizates containing various amounts of devulcanized rubber and virgin rubber.

References

1. Nicholas, P. P. Rubber Chem Technol 1982, 55, 1499.
2. Phadke, A. A.; Bhattacharya, A. K.; Chakraborty, S. K.; De, S. K. Rubber Chem Technol 1983, 56, 726.
3. Klingensmith, B. Rubber World 1991, 203 (March), 16.
4. Fesus, E. M.; Eggleton, R. W. Rubber World 1991, 203 (March), 23.
5. Harshaft, A. A. Environ Sci Technol 1972, 6, 412.
6. Fix, S. R. Elastomerics 1980, 112, 38.
7. Mouri, M.; Sato, N.; Okamoto, H.; Matsushita, M.; Fukumori, K. In: Proceedings of the 155th Meeting of the ACS Rubber Division, Chicago, IL, 1999; Paper No. 84.
8. Khait, K.; Torkelson, J. M. Polym-Plast Technol Eng 1999, 38, 445.
9. Bilgili, E.; Arastoopour, H.; Bernstein, B. Rubber Chem Technol 2000, 73, 340.
10. Warner, W. C. Rubber Chem Technol 1994, 67, 559.
11. Adhikari, B.; De, D.; Maiti, S. Prog Polym Sci 2000, 25, 909.
12. Isayev, A. I. In: Rubber Recycling; White, J. R.; De, S. K., Eds.; Rubber Technologist's Handbook; Rapra Technology: Shawbury, UK, 2001; p. 511.
13. Isayev, A. I.; Chen, J.; Tukachinsky, A. Rubber Chem Technol 1995, 68, 267 .
14. Tukachinsky, A.; Schworm, D.; Isayev, A. I. Rubber Chem Technol 1996, 69, 92.
15. Boron, T.; Klingensmith, B.; Forest, C.; Shringarpurey, S. In: Proceedings of the 156th Meeting of the ACS Rubber Division, Orlando, FL, 1999; Paper No. 136.
16. Yun, J.; Oh, J. S.; Isayev, A. I. Rubber Chem Technol 2001, 74, 317.
17. Levin, V. Y.; Kim, S. H.; Isayev, A. I.; Massey, J.; von Meerwall, E. Rubber Chem Technol 1996, 69, 104.
18. Tapale, M.; Isayev, A. I. J Appl Polym Sci 1998, 70, 2007.
19. Diao, B.; Isayev, A. I.; Levin, V. Y. Rubber Chem Technol 1999, 72, 152.
20. Shim, S. E.; Isayev, A. I. Rubber Chem Technol 2001, 74, 303.
21. Yun, J.; Isayev, A. I. Gummi Fasern Kunstst 2002, 10, 628,.
22. Suzuki, Y.; Owaki, M.; Mouri, M.; Sato, N.; Honda, H.; Nakashima, K. Toyota Tech Rev 1998, 48, 53.
23. Easterbrook, E. K.; Allen, R. D. In: Rubber Technology; Morton, M., Ed.; Van Nostrand Reinhold: New York, 1987; p. 260.
24. Strong, A. G. Elastomerics 1984, 116, 19.
25. Kidd, R. Elastomerics 1984, 116, 37.
26. Verbruggen, M. A. L.; van der Does, L.; Noordermeer, J. W. M. Rubber Chem Technol 1999, 72, 731.
27. Dick, J. S.; Harmon, C.; Vare, A. Polym Test 1999, 18, 327.
28. Flory, P. J.; Rehner, J., Jr. J Chem Phys 1943, 11, 512.
29. Kraus, G. J Appl Polym Sci 1963, 7, 861.
30. Baldwin, F. P.; Ver Strate, G. Rubber Chem Technol 1972, 45, 709.
31. Studebaker, M. L.; Nabors, L. Rubber Age 1957, 80, 837.
32. Edwards, D. C. J Mater Sci 1990, 25, 4175.
33. Leblanc, J. L. J Appl Polym Sci 1997, 66, 2257.
34. Yushanov, S. P.; Isayev, A. I.; Levin, V. Y. J Polym Sci Part B: Polym Phys 1996, 34, 2409.
35. Yushanov, S. P.; Isayev, A. I.; Kim, S. H. Rubber Chem Technol 1998, 71, 168.
36. Gordon, M. Proc R Soc London 1962, A268, 240.
37. Dobson, G. R.; Gordon, M. J Chem Phys 1965, 43, 705.
38. Yashin, V. V.; Isayev, A. I. Rubber Chem Technol 2000, 73, 325.
39. Studebaker, M.; Nabors, L. Rubber Age 1957, 80, 837.
40. Wang, M. J. Rubber Chem Technol 1998, 71, 520.
41. Rivil, D. Rubber Chem Technol 1971, 44, 307.
42. Stickney, P. B.; Falb, R. D. Rubber Chem Technol 1964, 37, 1299.
43. Wolf, S.; Wang, M. J. In: Carbon Black: Science and Technology; Donnet, J. B.; Bansal, R. C.; Wang, M. J., Eds.; Marcel Dekker: New York, 1993; Chapter 9.
44. Kim, S. H.; Isayev, A. I. In: Proceedings of the 156th Meeting of the ACS Rubber Division, Nashville, TN, 1998; Paper No. 55.
45. Hong, C. K.; Isayev, A. I. J Appl Polym Sci 2001, 79, 2340.
46. Isayev, A. I.; Kim, S. H.; Levin, V. Y. Rubber Chem Technol 1997, 70, 194.