

Blends of Ultrasonically Devulcanized and Virgin Carbon Black Filled Ethylene–Propylene–Diene Monomer Rubbers

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ABSTRACT: Ultrasonically devulcanized ethylene–propylene–diene monomer (dEPDM) rubber was blended with virgin ethylene–propylene–diene monomer (vEPDM) rubber. The properties of these blends were investigated and compared with those of blends of ground ethylene–propylene–diene monomer (gEPDM) and vEPDM. The dynamic properties and curing characteristics were studied. The dynamic properties of the uncured blends showed that the gEPDM/vEPDM compounds were more elastic than the dEPDM/vEPDM compounds at a low frequency range, whereas the opposite trend was observed at a high frequency range. In contrast, the dynamic properties of gEPDM/vEPDM vulcanizates were less elastic than those of

dEPDM/vEPDM vulcanizates at a low frequency range. The curing characteristics of the blends indicated that an increase in the dEPDM content in the dEPDM/vEPDM blends reduced the scorch time and the maximum torque and increased the minimum torque. A similar but more pronounced tendency was also found for the gEPDM/vEPDM blends. The tensile properties of the dEPDM/vEPDM vulcanizates were much better than those of the gEPDM/vEPDM vulcanizates, indicating the significant benefit of ultrasonic devulcanization. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 132–138, 2004

Key words: blends; recycling; ultrasound

INTRODUCTION

The recycling of waste rubbers has become a serious challenge for our society in its pursuit of a clean environment. This is an important issue for both waste disposal and cost reduction. The recycling of waste rubbers has been studied in many ways, including catalysis,¹ mechanical,^{2–4} thermomechanical,⁵ and microwave methods.⁶ Waste rubbers can be either ground into particles or devulcanized. Ground waste rubbers are reused as fillers in plastics^{7,8} and rubber compounds.⁹ Also, devulcanized tire rubber is used to prepare rubber/plastic blends.^{8,10} However, inferior mechanical properties are obtained because of the weak adhesion between ground or devulcanized rubber and plastic. Compatibilization is needed to increase the mechanical properties of blends. A number of functionalized polymers have been used as compatibilizers to improve the adhesion between the polymer matrix and ground rubber tire.¹¹ A natural rubber (NR) was reported to be a compatibilizer in a polypropylene (PP)/ground rubber tire (GRT) blend,⁷ and maleic anhydride grafted PP was used in a devulcanized GRT/PP blend.⁸ Devulcanized rubbers are suit-

able for incorporation into rubber compounds. In particular, blends of devulcanized NR and virgin NR have shown better properties than mixtures of ground and virgin NR.¹² Ultrasonically devulcanized rubber can be reprocessed in the same way as virgin rubber; examples include GRT,^{13–15} styrene butadiene rubber (SBR),¹⁶ NR,¹⁷ silicone rubber,^{18,19} and unfilled ethylene–propylene–diene monomer (EPDM).²⁰

In this study, ultrasonically devulcanized ethylene–propylene–diene monomer (dEPDM) was blended with virgin ethylene–propylene–diene monomer (vEPDM), and blend vulcanizates were obtained. The dynamic properties, curing behavior, and tensile properties of the blends were investigated and compared with those of blend vulcanizates of ground ethylene–propylene–diene monomer (gEPDM) and vEPDM.

EXPERIMENTAL

Materials

EPDM (Keltan 2506) was obtained from DSM Copolymer. The comonomer ethylidene norbornene (ENB) content was approximately 4.5 wt %, and the ethylene content was 56 wt %. The Mooney viscosity was 28 [ML(1+4) at 125°C]. The compounding ingredients used were zinc oxide, stearic acid, sulfur, tetramethylthiuram disulfide (TMTD), 2-mercaptobenzothiazole (MBT; Akrochem Corp., Akron, OH), and carbon black (HAF N330, Huber Engineered Carbons, Atlanta, GA).

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

Particle size (μm)	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

Preparation of the vulcanizates

The carbon black filled compounds (phr) were prepared with a Banbury mixer (model 86EM9804, Farrel, Ansonia, CT). To improve the mixing quality and prevent prevulcanization, we applied a two-stage mixing process. First, EPDM was premixed with zinc oxide, stearic acid, and carbon black in a Banbury mixer at 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 scorching problems during this mixing step. One minute was required to soften the compounds. After the softening, the sulfur and accelerator were added together. The total mixing time was 5 min.

The compression molding of slabs (260 mm \times 260 mm \times 12 mm) was performed with an electrically heated compression-molding press (Wabash, Wabash, IN) at 160°C and at 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 the molding, the vulcanized samples were ground with a grinding machine (Nelmor, N. Uxbridge, MA) with a screen with holes 5 mm in diameter. The particle size distributions of 30 phr carbon black filled EPDM are given in Table I. The cure recipe for the virgin vulca-

nizates was 5 phr zinc oxide, 1 phr stearic acid, 1.5 phr sulfur, 1 phr TMTD, and 0.5 phr MBT. This recipe was based on ASTM D 3568.

Ultrasonic devulcanization

The ground rubber was devulcanized in a grooved-barrel reactor (Fig. 1) with two ultrasonic water-cooled horns (with 38.1 mm \times 38.1 mm rectangular cross sections) inserted into the barrel through two ports. In the grooved-barrel reactor, two helical channels were made on the barrel surface (grooved barrel). In this reactor, the rubber was forced to flow through the helical channel in the gap created between the rotating shaft and the tips of the horns.

The temperature of the extruder barrel was set at 120°C. The temperature was kept uniform for all barrel zones. The gap between the horn and the rotating shaft was 1.02 mm. The flow rate was 0.63 g/s. Devulcanization was carried out at a frequency of 20 kHz and at an amplitude of 10 μm .

Preparation of the blends

The blending of dEPDM with vEPDM and of gEPDM with vEPDM was carried out on a two-roll mill for 6 min. The same amounts of the curing ingredients used for the recipe of vEPDM were added to the blends. For dEPDM/vEPDM, the amounts of the curatives were based on the total amount of rubber. For gEPDM/vEPDM, the amounts of the curatives were based on the amount of vEPDM.

The vulcanization was carried out with a compression-molding press at 160°C and at a pressure of 13.8 MPa. The curing was based on the time required to achieve 90% of the maximum torque on the cure curve. Vulcanized sheets (127 mm \times 127 mm \times 2 mm) were obtained and used for mechanical testing.

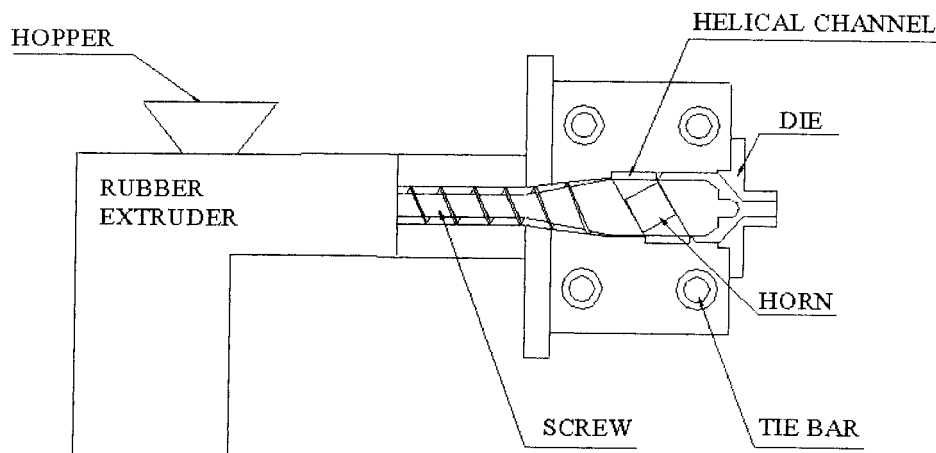


Figure 1 Schematic drawing of the grooved-barrel ultrasonic reactor.

Characterization

An Advanced Polymer Analyzer (APA) 2000 (Alpha Technology, Akron, OH) was used to obtain the torque–time curve at 160°C.²¹ Also, the dynamic behavior of the uncured blends and cured blends was investigated at 100 and 80°C, respectively, with the APA. The gel fractions of the virgin vulcanizates and devulcanized EPDM were measured by the Soxhlet extraction method with benzene as a solvent. Also, the crosslink density of the gel of these rubbers was measured by the swelling technique with benzene as the solvent. The crosslink density was determined with the Flory–Rehner equation²² with the Kraus correction.²³ The gel fraction and crosslink density of the virgin vulcanizate of 30 phr carbon black filled EPDM rubber were 0.93 and 183 mol/m³, respectively. After devulcanization at an ultrasonic amplitude of 10 μm, a gap size of 1.01 mm, and a flow rate of 0.63 g/s, the gel fraction and crosslink density of the gel were reduced to 0.70 and 60 mol/m³, respectively.

Stress–strain measurements were acquired at room temperature according to ASTM D 412 (type C) at a crosshead speed of 500 mm/min with an Instron 5567 tensile tester (Canton, MA).

RESULTS AND DISCUSSION

Dynamic properties of the uncured blends

From a viscoelastic property point of view, an ideal material that is able to meet the requirements of a high-performance tire should have a low loss tangent ($\tan \delta$) at a temperature of 50–80°C; this indicates good rolling resistance and saves energy.²⁴ Because dynamic viscoelastic properties are also important in the evaluation of the suitability of recycled rubber for dynamic applications, the properties of dEPDM/vEPDM blends and gEPDM/vEPDM blends were measured with the APA 2000.

Figure 2(a) shows the complex viscosity of the uncured blends versus the frequency at 100°C and at a strain amplitude (γ_0) of 0.07. The complex viscosity of the gEPDM/vEPDM blends is higher than that of the dEPDM/vEPDM blends at the same composition over the entire frequency range. This is the result of the higher gel fraction and crosslink density of gEPDM in comparison with those of dEPDM. In the dEPDM/vEPDM blends, the crossover point can be observed around 10 rad/s. This indicates a stronger dependency of the viscosity on the frequency with an increase in the dEPDM loading. Evidently, a sol-containing low-molecular-weight polymer in a devulcanized sample affects the dependency on the frequency. However, no crossover point has been observed in the gEPDM/vEPDM blends because gEPDM is fully cured.

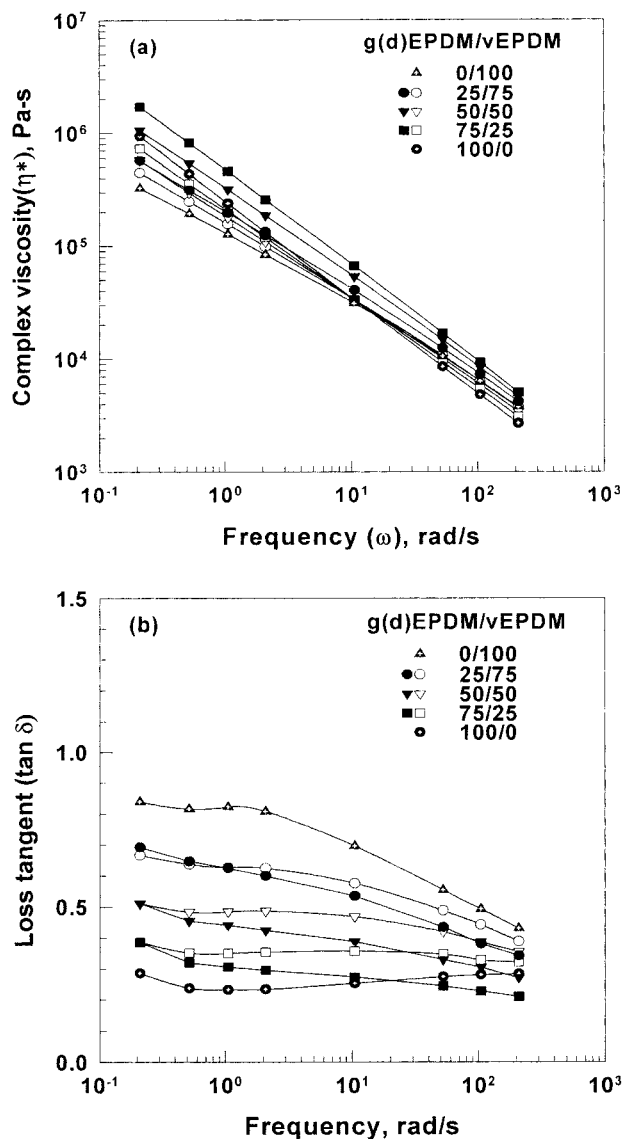


Figure 2 (a) Complex viscosity and (b) $\tan \delta$ versus the frequency for dEPDM/vEPDM (open symbols) and gEPDM/vEPDM (solid symbols) compounds at 100°C and $\gamma_0 = 0.07$.

Figure 2(b) depicts $\tan \delta$ versus the frequency of dEPDM/vEPDM gum blends and gEPDM/vEPDM gum blends. By definition,²⁴ $\tan \delta$ is determined as a ratio of the loss modulus to the storage modulus. Therefore, $\tan \delta$ is a ratio of the energy converted into heat (or the work absorbed by the compound) to the recovered energy, for a given work input. $\tan \delta$ of 100% vEPDM decreases with frequency, whereas that of 100% dEPDM is almost independent of frequency. In addition, with an increase in the dEPDM content, the dependence of $\tan \delta$ on the frequency for blends of dEPDM and vEPDM gradually decreases, whereas with an increase in the gEPDM content, the strong dependence of $\tan \delta$ on the frequency for blends of gEPDM and vEPDM remains. Furthermore, it is

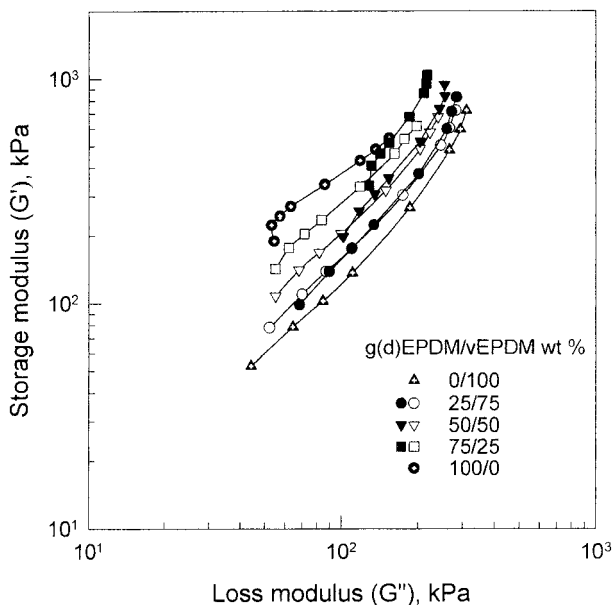


Figure 3 Storage modulus (G') versus the loss modulus (G'') for dEPDM/vEPDM (open symbols) and gEPDM/vEPDM (solid symbols) compounds at 100°C and $\gamma_0 = 0.07$.

known that for perfectly viscous fluids, $\tan \delta$ is infinity, whereas for perfect elastic solids, $\tan \delta$ is 0. Therefore, 100% devulcanized rubber has much higher elasticity than 100% virgin gum. Also, blends of gEPDM and vEPDM show a higher elasticity than blends of dEPDM and vEPDM in a high frequency range.

Figure 3 shows the storage modulus as a function of the loss modulus for various blends. At the same level of the loss modulus, the elasticity of both dEPDM/vEPDM and gEPDM/vEPDM increases with increasing devulcanized rubber and ground rubber contents. Also, the data for 25/75 and 50/50 dEPDM/vEPDM and gEPDM/vEPDM blends lie approximately on the same line. However, the 75/25 gEPDM/vEPDM blend shows a higher elasticity than the 75/25 dEPDM/vEPDM blend in a high frequency range.

Cure behavior

Figure 4 shows the cure curves for dEPDM/vEPDM and gEPDM/vEPDM blends at 160°C. For the dEPDM/vEPDM blends, the amounts of the curatives are added according to the total rubber contents, whereas for the gEPDM/vEPDM blends, they are added according to the virgin rubber content because of the presence of fully cured ground rubber in the blends. The curing characteristics of dEPDM/vEPDM blends depend on the dEPDM content. An increase in the dEPDM content reduces the scorch time and the maximum torque and increases the minimum torque. The cure curves of dEPDM show a higher minimum torque than that of vEPDM, evidently because of the

presence of a gel in the devulcanized rubbers. At the same time, it shows a lower maximum torque than vEPDM because of the reduced number of sites available for curing in dEPDM.

For the gEPDM/vEPDM blends, the cure curves show a reduction of the scorch time and the maximum torque and a significant increase in the minimum torque with an increase in gEPDM. The curing characteristics of the gEPDM/vEPDM blends are consistent with the results of Gibala and Hamed,²⁵ who observed reductions in the scorch time and maximum rheometry torque when ground vulcanizates were added to an SBR compound. According to their proposal, the migration of sulfur from the ground vulcanizate to the matrix causes torque reduction, and the migration of acceleration fragments from the ground vulcanizate to the matrix causes a reduction of the scorch time. This migration of curatives leads to further crosslinking of the ground rubber and reduces the crosslinking of the matrix. Because the maximum torque of the blends containing ground rubber is largely controlled by the matrix, the maximum torque of the blends is reduced.

Dynamic properties of the cured blends

Figure 5(a) shows the storage modulus as a function of the frequency for vulcanizates of the dEPDM/vEPDM and gEPDM/vEPDM blends. The storage modulus of the dEPDM/vEPDM and gEPDM/vEPDM blends depends on the composition of the blend. An increase in the content of gEPDM and dEPDM rubber reduces the storage modulus of the blends. Also, the storage mod-

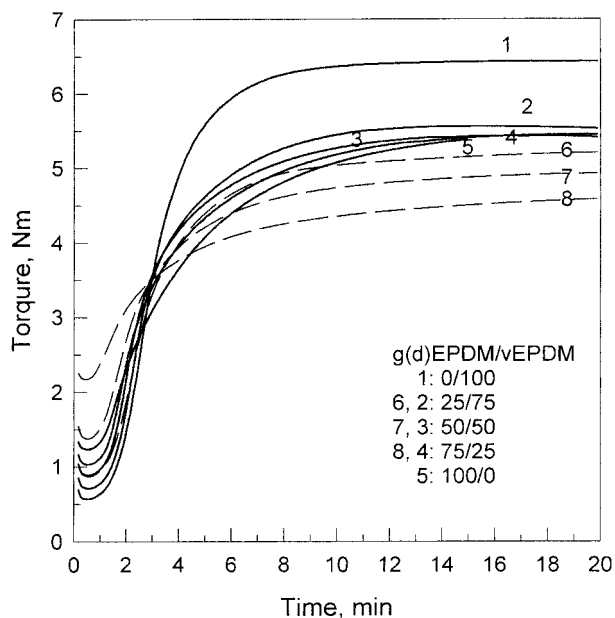


Figure 4 Cure curves for (—) dEPDM/vEPDM and (---) gEPDM/vEPDM blends at 160°C.

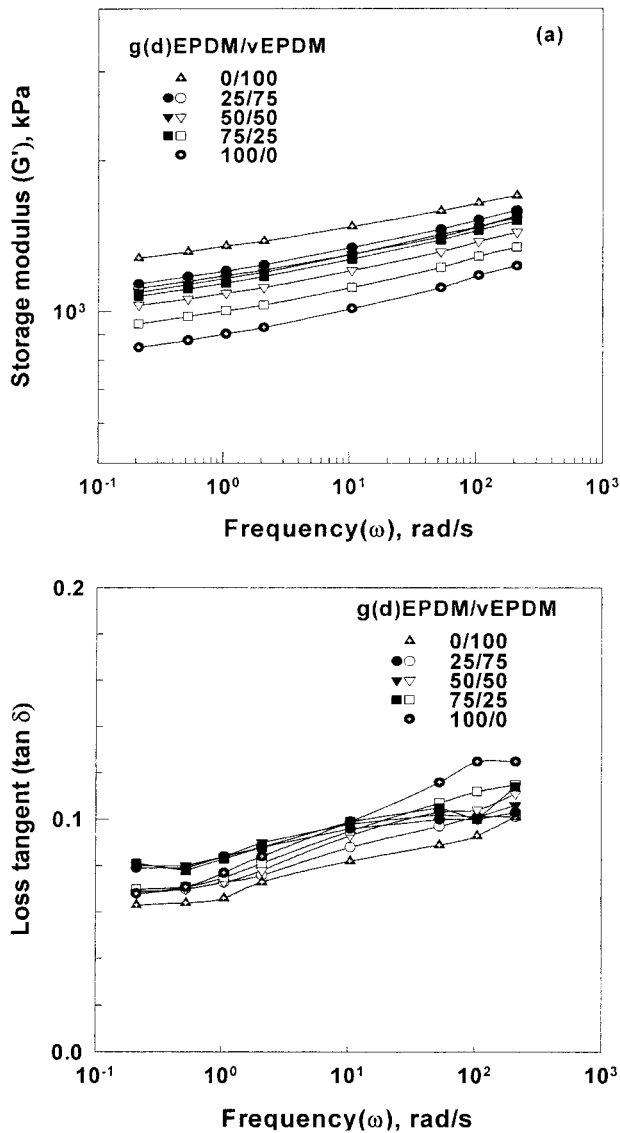


Figure 5 (a) Storage modulus (G') and (b) $\tan \delta$ versus the frequency for vulcanizates of dEPDM/vEPDM (open symbols) and gEPDM/vEPDM (solid symbols) compounds at 80°C and $\gamma_0 = 0.042$.

ulus of the gEPDM/vEPDM blends is higher than that of the dEPDM/vEPDM blends.

Figure 5(b) shows $\tan \delta$ as a function of the frequency for the vulcanizates of the dEPDM/vEPDM and gEPDM/vEPDM blends. The $\tan \delta$ value of 100% vEPDM is lowest, and this means that 100% vEPDM is the most elastic material. The value of $\tan \delta$ increases with the contents of gEPDM and dEPDM. The higher values of $\tan \delta$ of the gEPDM/vEPDM blends indicates that these blends are less elastic than the dEPDM/vEPDM blends in a low frequency region.

Figure 6 shows the storage modulus as a function of the loss modulus for both dEPDM/vEPDM and gEPDM/vEPDM vulcanizates. At the same level of the loss modulus, the storage moduli of both blends

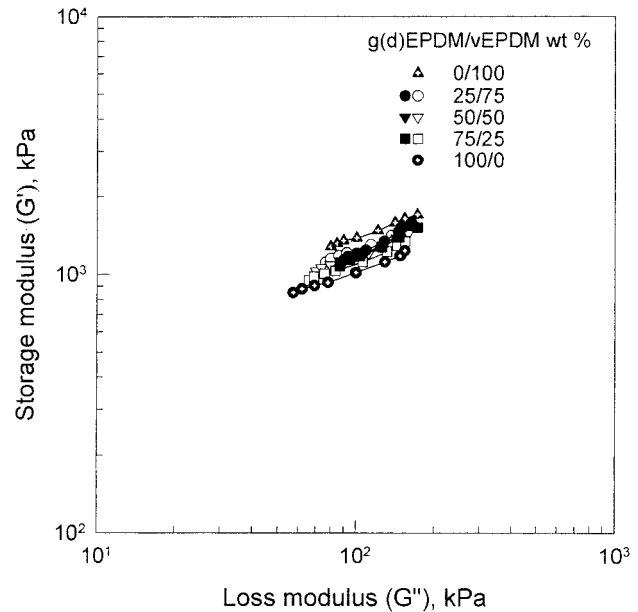


Figure 6 Storage modulus (G') versus the loss modulus (G'') for vulcanizates of dEPDM/vEPDM (open symbols) and gEPDM/vEPDM (solid symbols) compounds at 80°C and $\gamma_0 = 0.042$.

are between the moduli of 100% dEPDM and 100% vEPDM, and they are almost the same for both blend systems.

Mechanical properties

Figures 7 and 8 show the tensile strength and elongation at break, respectively, of vulcanizates of dEPDM/

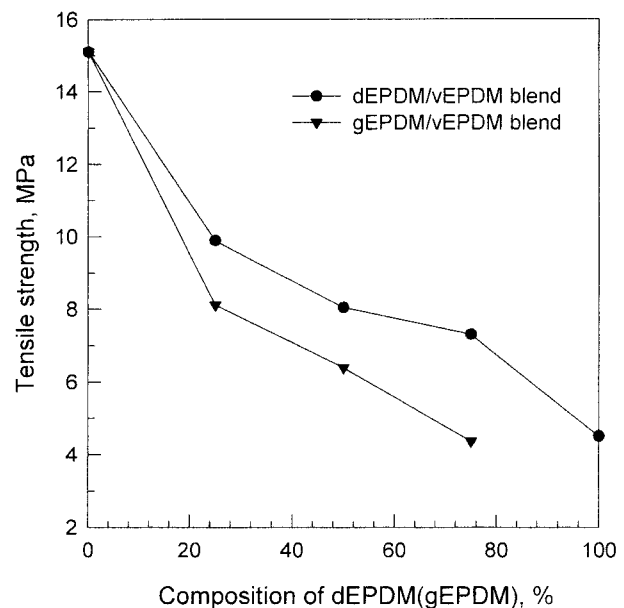


Figure 7 Tensile strength of vulcanizates of dEPDM/vEPDM and gEPDM/vEPDM.

vEPDM and gEPDM/vEPDM blends versus the concentration. The tensile properties of the dEPDM/vEPDM blends are much better than those of the gEPDM/vEPDM blends. dEPDM possibly exhibits better adhesion to vEPDM in the blends than gEPDM does. Similar effects were reported earlier for vulcanizates of blends of ultrasonically devulcanized and ground NR with virgin NR.¹² As the composition of vEPDM in the blends increases, the tensile properties progressively increase. The inferior properties of ultrasonically devulcanized carbon-filled EPDM rubber may be explained by the deactivation of carbon black during the ultrasonic treatment.²⁶ In the gEPDM/vEPDM blends, the tensile properties are inferior because of the low adhesion between gEPDM and vEPDM. The ground rubber inclusions in tensile samples cause multiple cracking and act as stress-raising flaws.²⁷ In conclusion, these results indicate that the tensile properties of blends of recycled and virgin rubber can be improved significantly by ultrasonic devulcanization.

The modulus at 100% elongation of the dEPDM/vEPDM and gEPDM/vEPDM blends is shown in Figure 9. The modulus of the dEPDM/vEPDM and gEPDM/vEPDM blends increases with an increase in the composition of dEPDM and gEPDM. However, the modulus at 100% elongation of gEPDM/vEPDM is lower than that of dEPDM/vEPDM, and this is consistent with the maximum torques of cure curves (Fig. 4).

CONCLUSIONS

In this study, dEPDM has been blended with vEPDM, and the dynamic properties, cure behavior, and tensile

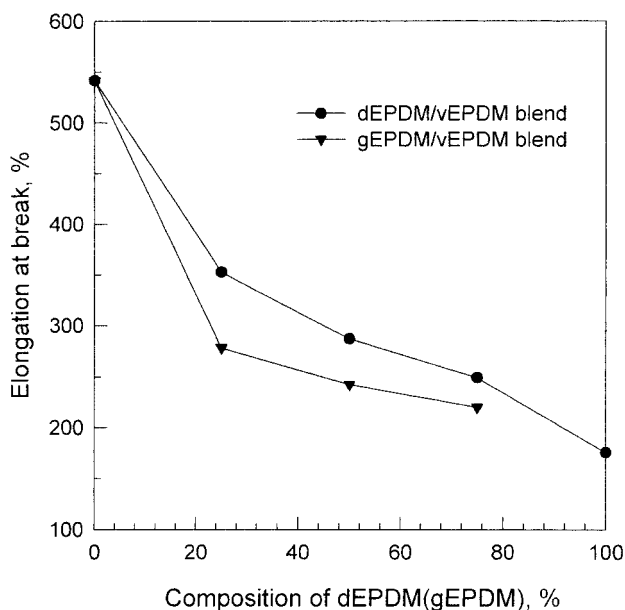


Figure 8 Elongation at break of vulcanizates of dEPDM/vEPDM and gEPDM/vEPDM.

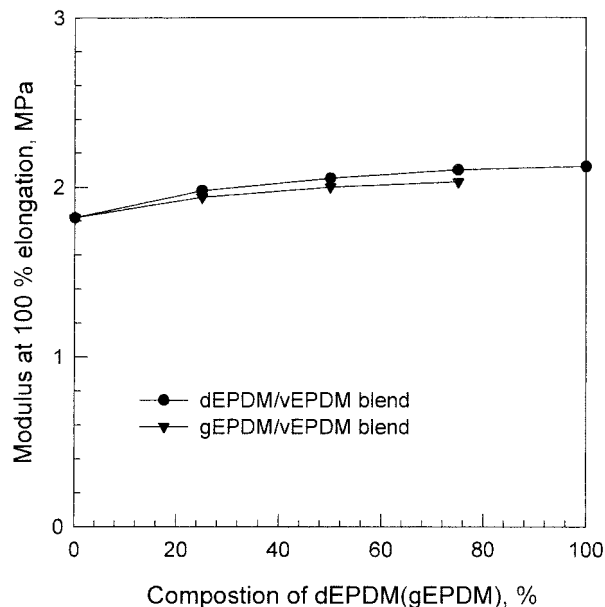


Figure 9 Modulus at 100% elongation of vulcanizates of dEPDM/vEPDM and gEPDM/vEPDM.

properties have been compared with those of blends of fully cured gEPDM and vEPDM. The dynamic properties for uncured blends show that gEPDM/vEPDM blends are more elastic than dEPDM/vEPDM blends at a high frequency region. Also, the dynamic properties of cured blends show that gEPDM/vEPDM blends are less elastic than dEPDM/vEPDM blends in a low frequency region. However, these blends have almost the same storage modulus at the same level of the loss modulus.

The cure curves of the blends indicate that an increase in the dEPDM content reduces the scorch time and the maximum torque and increases the minimum torque. In the gEPDM/vEPDM blends, an increase in the gEPDM composition leads to a significant increase in the minimum torque and a decrease in the maximum torque and scorch time. The tensile properties of the dEPDM/vEPDM blends are much better than those of the gEPDM/vEPDM blends. As the content of vEPDM in the blends increases, the tensile properties progressively increase.

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