JOURNAL OF MATERIALS SCIENCE **37** (2002) 385–388

Blends of ultrasonically devulcanized and virgin carbon black filled NR

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The ultrasonically devulcanized carbon black filled NR was mixed with virgin carbon black filled NR. The properties of the blends were studied and compared with those of the blends of fully cured ground NR and virgin NR. Curing characteristics of the blends indicated that an increase in the devulcanized NR content decreased the cure time and the scorch time. The tensile strength and elongation at break of the blends with ultrasonically devulcanized NR were much better than those of the blends with ground rubber. As the proportion of the virgin NR in the blends was increased, the mechanical properties progressively increased.

1. Introduction

The recycling of waste rubber has been of commercial and environmental interest for many years. Considerable work has been done on the reuse of recycled rubber in rubber compounding [1–5]. The reuse of recycled rubber is important both from the point of view of disposal of waste and the reduction in the product cost.

Waste rubbers can be either ground into particles or devulcanized. Ground waste rubber was used as a component of rubber products. However, there is a significant drop in the tensile strength [2, 5], even at low levels of ground rubber, because the bonding force between ground rubber and matrix is often low. Devulcanized rubber is suitable for use in some rubber compounds. Devulcanized rubber can enhance the bonding force of the blends. Also, the ultrasonically devulcanized rubber can be reprocessed in the same way as the virgin rubber [6–11].

In this study, the ultrasonically devulcanized NR vulcanizates were blended with virgin NR to investigate the curing behavior and the mechanical properties of the blends, and to compare with the blends of fully cured ground NR and virgin NR.

2. Experimental

2.1. Materials

In the present experiments, the natural rubber (NR, SMR CV 60) obtained from Akrochem Corp. was used. The curing recipe was 2 phr of sulfur, 1 phr of CBS (N-cyclohexylbenzothiazole-2-sulfenamide, Monsanto Inc.) as an accelerator, 5 phr of zinc oxide, 1 phr of stearic acid (Akrochem Corp.), and 35 phr of carbon black (HAF N330, Huber Engineered Carbons).

2.2. Preparation of vulcanizates

To improve the mixing quality and to prevent prevulcanization, a two-stage mixing process was applied. The rubber was premixed in a Banbury mixer (Farrel, Model 86EM9804) at 80°C for 1.5 minutes. After premixing, zinc oxide, stearic acid and CB were added to the mixer and the mixing was continued for 2.5 minutes. Then, a two-roll mill (Dependable Rubber Machinery Co.) was used at 50°C to prevent any scorch problem during this mixing step. 30 seconds was required to soften the compounds. After softening, sulfur and accelerator were added together. The total mixing time was 3 minutes.

The compression molding of slabs ($260 \times 260 \times 12\ mm^3$) were prepared at 160°C using an electrically heated compression molding press (Wabash). According to the cure curve, the cure time was determined based on the time required to achieve maximum torque.

After molding, the vulcanized samples were ground using the Nelmor grinding machine. The particle size distributions of the ground sample are given in Table I.

2.3. Ultrasonic devulcanization

The particles were devulcanized in an extruder with an ultrasonic die attachment [6, 7] developed by National Feedscrew and Machining, Inc. The temperature of the extruder barrel was set at 120°C. The gap between the die plate and the 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 an amplitude of 5 μm.

2.4. Preparation of blends

The blending of devulcanized NR (DNR) with virgin NR and ground NR (GNR) with virgin NR were carried out on a two-roll mill for 6 minutes with the same amount of curing ingredients as the recipe of virgin NR. Slabs ($127 \times 127 \times 2\ mm^3$) were prepared at 160°C by the compression molding press (Wabash) at pressure of 13.8 MPa. The cure time was based on the time required to achieve maximum torque.

TABLE I Particle size distribution of GNR

Particle size (microns)	Mesh	Distributions (%)
$x > 1700$	10	67.1
$1700 > x > 841$	20	25.8
$841 > x > 600$	28	3.0
$600 > x > 425$	35	1.6
$425 > x > 300$	48	0.9
$300 > x > 250$	60	0.4
$250 > x > 150$	100	0.9
$150 > x$		0.3

2.5. Characterization

A Monsanto oscillating disc rheometer was used to obtain the torque-time curves according to ASTM D2084.

Monsanto Tensiometer (Flexsys T2000) was used for the tensile property measurement according to ASTM D412 (type C). All the tests were performed at room temperature with a crosshead speed of 500 mm/min.

3. Results and discussions

The cure curves for blends of DNR and virgin NR are given in Fig. 1. The amount of curatives is added based on the total rubber content of the blends. It is seen from the figure that the curing characteristics of the blends depend on the proportion of DNR. An increase in the DNR content decreased the scorch time and the cure time. The curing of ultrasonically devulcanized NR starts immediately upon heating [8, 10, 11]. An increase of torque due to curing compensates for a decrease of viscosity due to heating. This reaction leads to the decreased scorch time of the ultrasonically devulcanized rubber. The latter is thought to be the characteristic of devulcanized rubber [12] and is due to the presence of crosslink precursors.

In order to compare the effect of ultrasonically devulcanized NR on blends, fully cured ground NR was blended with virgin NR. Fig. 2 presents the cure curves for blends of GNR and virgin NR. The blends were prepared by adding curatives with the amount based on virgin NR. It is seen from the figure that, as the concentration of GNR increases, maximum torque and scorch time decrease and minimum torque increases. This increase in the minimum torque is caused by an increase in viscosity of the blend. Gibala and Hamed [13] reported that ground rubber provided more rubber into which the curatives could migrate. The migration of sulfur from the virgin compound to the ground vulcanizate can reduce maximum torque. Also, diffusion of accelerator from ground rubber into virgin rubber would reduce scorch time. This migration of curatives leads to further crosslinking of the ground rubber, while decreasing the crosslinking of the matrix. Since the maximum torque of the blends containing ground rubber is largely controlled by the matrix, the maximum torque of the blends is reduced.

Fig. 3 shows the cure curves for blends of GNR and virgin NR prepared using the amount of curatives based on the total rubber content of the blend. As expected, due to excess of curatives and migration of curatives, the maximum and minimum torque and the cure rate are increased and the scorch time is decreased with increasing GNR content.

Figs 4 and 5 give respectively tensile strength and elongation at break of DNR/virgin NR and GNR/virgin NR blends. It is seen that the blends of DNR and virgin NR have much better tensile properties than blends of GNR and virgin NR. It is thought that ultrasonic devulcanization causes a better bonding of the devulcanized rubber to the virgin rubber in the blends than that in the case of GNR/virgin NR blends. As the proportion of the virgin NR in the blends with DNR was increased, the mechanical properties progressively increased at or above the rule of mixers. The inferior properties of devulcanized NR vulcanizates may be explained by the breakup of the main chains during

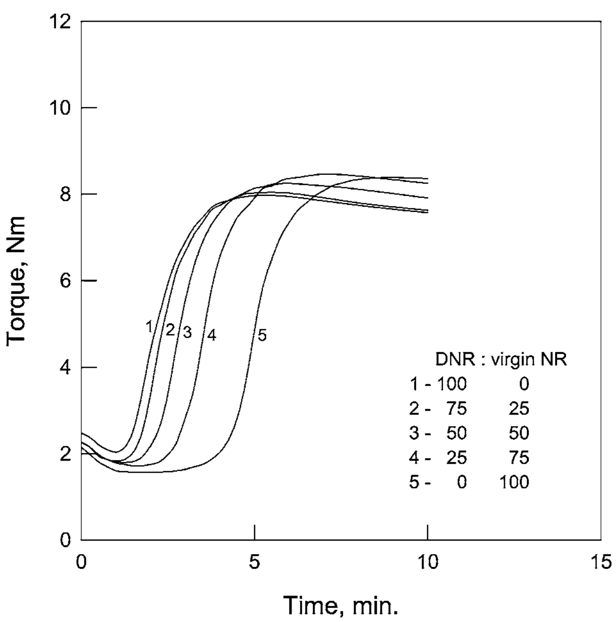

Figure 1 Cure curves for blends of DNR and virgin NR at 160°C. Amount of curatives were added based on the total rubber content.

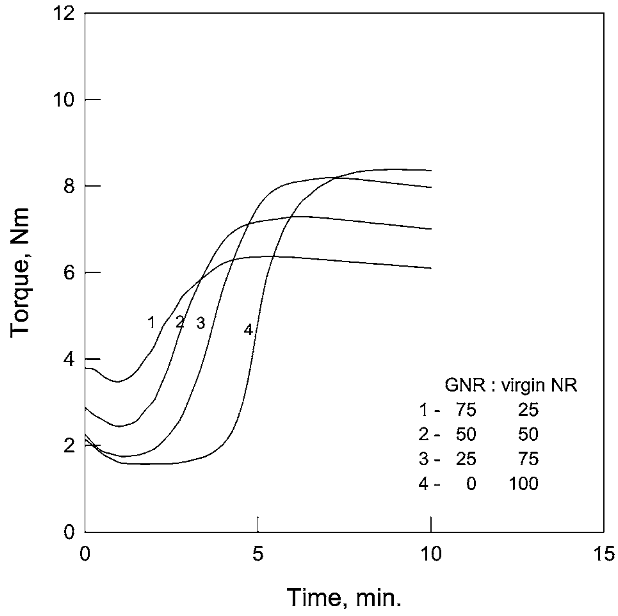

Figure 2 Cure curves for blends of GNR and virgin NR at 160°C. Amount of curatives were added based on the virgin rubber.

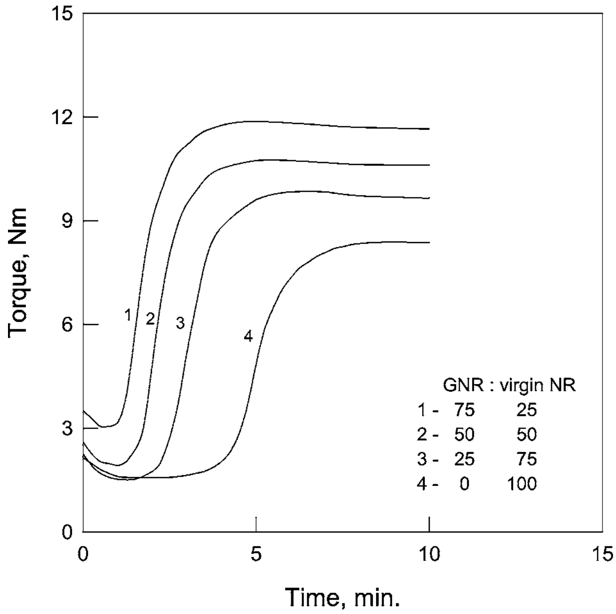

Figure 3 Cure curves for blends of GNR and virgin NR at 160°C. Amount of curatives were added based on the total rubber content.

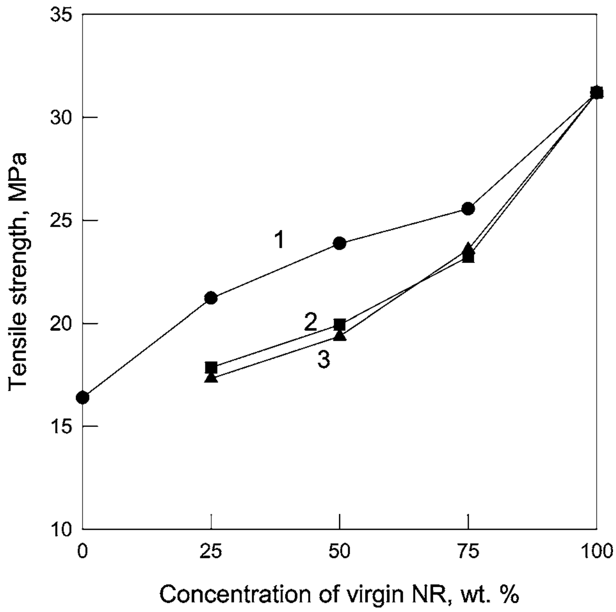

Figure 4 Tensile strength of DNR/virgin NR and GNR/virgin NR blends. (1) Blends of DNR and virgin NR; amount of curatives were added based on the total rubber content, (2) blends of GNR and virgin NR; amount of curatives were added based on the virgin rubber content and (3) blends of GNR and virgin NR; amount of curatives were added based on the total rubber content.

ultrasonic treatment [11]. In the blends of GNR and virgin NR, the tensile properties are not good because the bonding force between ground rubber and matrix rubber is low. The ground rubber in the blends acts as a stress-raising flaw in tensile testing [14]. In contrast, the results with blends of DNR and virgin NR indicate that their mechanical properties can be improved significantly by ultrasonic devulcanization.

The modulus at 100% strain of DNR/virgin NR and GNR/virgin NR blends is shown in Fig. 6. It is seen that the blends of DNR with virgin rubber show only a little drop in the modulus. At the same time, the modulus of the blends of GNR and virgin rubber, prepared by

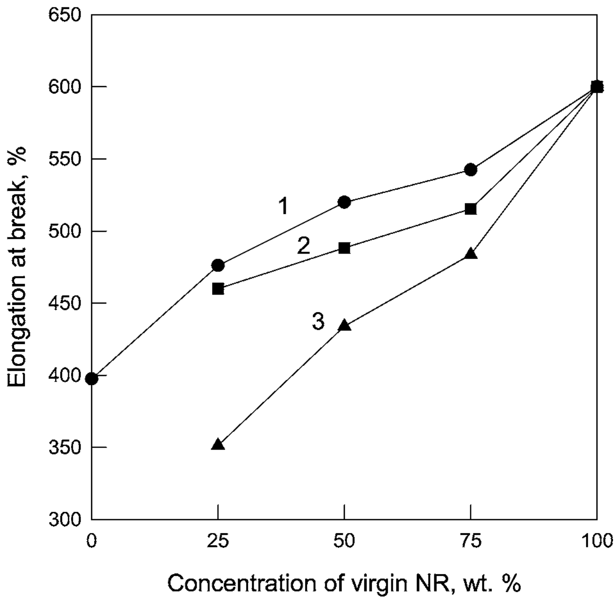

Figure 5 Elongation at break of DNR/virgin NR and GNR/virgin NR blends. Notations are same as in Fig. 4.

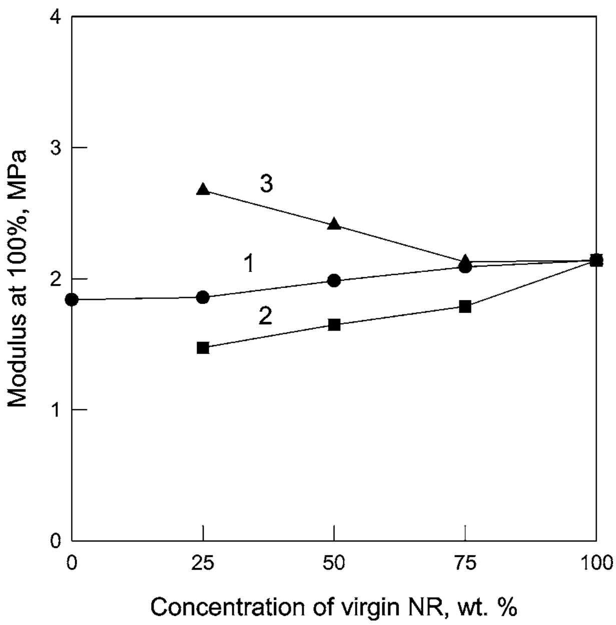

Figure 6 Modulus at 100% strain of DNR/virgin NR and GNR/virgin NR blends. Notations are same as in Fig. 4.

using the amount of curatives based on virgin rubber, is reduced. This is apparently due to the migration of curatives as explained earlier. The blends of GNR and virgin rubber with the amount of curatives based on total rubber content show higher modulus. However, as shown earlier they indicate lower tensile strength and elongation at break due to an excess of curatives.

4. Conclusions

In this study, the ultrasonically devulcanized NR vulcanizates were mixed with virgin NR and the cure behavior and tensile properties are compared with those of the blends of fully cured ground NR and virgin NR. Curing characteristics of the blends indicated that an increase in the DNR content decreased the scorch time and the cure time. In the blends of GNR and virgin

NR vulcanizates cured with the amount of curatives based on virgin rubber, as the concentration of GNR increases, maximum torque and scorch time are decreased. The mechanical properties of DNR/virgin NR blends were much better than those of GNR/virgin NR blends. The results indicate that the mechanical properties of these kinds of blends can be improved significantly by ultrasonic devulcanization. As the proportion of the virgin NR in the blends of DNR was increased, the mechanical properties progressively increased at or above the rule of mixers.

Acknowledgement

This work is supported by the grants from the National Science Foundation (DMI 9712043).

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Received 5 May 2000
and accepted 16 January 2001