JOURNAL OF MATERIALS SCIENCE **40** (2005) 2883–2889

Blends of ultrasonically devulcanized tire-curing bladder and butyl rubber

WENLAI FENG, A. I. ISAYEV*
Institute of Polymer Engineering, The University of Akron, Akron, OH 4325-0301, USA
E-mail: aisayev@uakron.edu

The devulcanization of the butyl rubber based tire-curing bladder was carried out with a grooved barrel ultrasonic extruder. The devulcanized rubber was blended at different ratios with the carbon black filled virgin butyl rubber and cured. The rheological and mechanical properties, as well as gel fraction and crosslink density of the revulcanized rubber and vulcanizates of blends have been measured. The blend of ground tire-curing bladder and carbon black filled butyl rubber has also been prepared for comparison purpose. Compared to the blend containing the ground rubber, compounding of the blends containing the devulcanized bladder were easier and their vulcanizates had smoother surface. In addition, the vulcanizates containing devulcanized tire-curing bladder and virgin rubber showed substantially improved mechanical properties than the vulcanizate of the devulcanized rubber alone. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Tire-curing bladder is commonly made of resin cured butyl rubber because of its excellent thermal stability and air impermeability. It is used as a heat transfer and shaping medium during the production of the pneumatic rubber vehicle tires. By application of high pressure and high temperature, green or uncured tire is molded and cured. Normally tire-curing bladder has a life time of 300–700 curing cycles. For recycling of butyl rubbers, thermo-mechanical process [1] and radiation methods [2, 3] have been reported. Also ground butyl or halobutyl is used as a filler in the cure recipe of different rubbers [1, 4].

Recently, the ultrasonic devulcanization of tire curing bladder was carried out [5]. These studies have shown that ultrasonic waves, at a certain level of pressure and temperature, can rapidly break up the three-dimensional rubber network leading to devulcanization. Strictly speaking, devulcanization is defined as a process of cleaving crosslinks only. However, ultrasonic devulcanization of rubber as defined in this paper is a process causing a preferential breakup of crosslinks along with some degradation of the main chains. As the most desirable consequence, the ultrasonically devulcanized rubber can be reprocessed and revulcanized in a manner similar to that employed with unvulcanized elastomers.

This paper describes the results of our recent experiments related to the utilization of ultrasonically devulcanized tire-curing bladder by means of blending it with carbon black filled butyl rubber at different ratio. In this study, the rheological and mechanical properties, morphology, and structure of rubber blends were investigated.

2. Experimental

2.1. Materials

The butyl rubber used in this study was EXXON® Butyl 268 which was kindly supplied by Exxon Chemical Co. (Baytown, TX). Unsaturation was 1.5–1.8 mol%. Mooney viscosity (ML1 + 8) at 125°C was 51. The curing ingredients were zinc oxide, stearic acid (Akrochem Corp., Akron, Ohio), and brominated octylphenol/formaldehyde resin SP-1055 (Schenectady International, Schenectady, NY). High abrasion furnace (HAF) carbon black, N330 (Huber Engineered Carbons, Altanta, GA) was used as the filler.

The used tire-curing bladders were obtained from a major tire making company. The exact recipe is unknown, but it is believed to be carbon black (CB) filled butyl rubber cured by the phenolic resin [6]. The bladder was ground using a Nelmor Q1012M1 grinding machine (N. Uxbridge, MA) having a screen with holes of 5 mm in diameter. The particle size distribution of the ground tire-curing bladder obtained by sieving method is shown in Table I.

2.2. Ultrasonic devulcanization and sample preparation

The particles of the ground tire-curing bladder were fed into a grooved barrel reactor [5]. The extruder was preheated to 120°C. The temperature was kept uniform for all barrel zones. The gap between the rotating shaft and

---

*Author to whom all correspondence should be addressed.

TABLE I Particle size distribution of the ground tire-curing bladder

Particle size (μm)	Mesh	Distribution (%)
>1700	12	55.2
1700–1000	18	39.0
1000–850	20	3.4
850–600	30	1.5
<600	–	0.9

the horn was 2 mm, and the amplitude of ultrasound was 10 μm. The feeder, providing "starved feed" to the extruder, controlled the flow rate of 1.26 g/s. In the extruder, the screw speed was 50 rpm, the ground rubber was compressed and conveyed by the screw to the devulcanization zone. The ultrasonic treatment of the rubber occurred in the gap. After reaching the steady state conditions indicated by the pressure transducer and ultrasonic power wattmeter, the ultrasonically treated samples were collected as described earlier [5].

The filled butyl rubber (50 phr carbon black) was prepared in a 1200 cc, water-cooled Farrel Banbury internal mixer (Model 86EM9804). The mixing time in the internal mixer was 8 min. The mixing was carried out at 50 rpm. The CB-filled rubber was further compounded with the devulcanized tire-curing bladder at different blend ratio, and then compounded with the curing ingredients on a two-roll mill. Also, 50/50 blend of the CB-filled rubber with the ground tire-curing bladder was prepared. This blend was difficult to mix than the blend of CB-filled rubber with devulcanized rubber. The curing recipe was 100 phr rubber, 12 phr of SP-1055, 5 phr of zinc oxide, and 1 phr of stearic acid relative to the total amount of rubbers in both blends.

The curing was carried out with a compression molding press (Wabash Metal Products Co., Model 12-12-2T, Wabash, Indiana) at 180°C and 17.2 MPa. The cure time was 40 min corresponding to T_{90} which was obtained with an Advanced Polymer Analyzer (APA 2000, Alpha Technologies, Akron, Ohio) [7]. The vulcanized sheets with dimensions of $127 \times 127 \times 2$ mm^3 were obtained and used for mechanical testing.

2.3. Characterization

The dynamic properties of the uncured and cured rubbers at 120°C were investigated with an APA 2000 within a frequency range of 0.1–200 rad/s and a strain amplitude of 4.2% (angular amplitude of 0.3°). The biconical rotor with an angle of 7° and a diameter of 63.5 mm was used.

The curing behavior was investigated with an APA 2000 at 180°C, a frequency of 10.47 rad/s and a strain amplitude of 42% (angular amplitude of 3°).

The gel fractions of cured rubbers were measured by the Soxhlet extraction method with cyclohexane as a solvent. The crosslink density of the gel of these rubbers was also measured by the swelling technique with cyclohexane as a solvent. The extraction time was 24 h. The crosslink density was calculated using the Flory-Rehner equation [8]. The interaction parameter $\chi = 0.43$ was used in the calculation [9]. Due to the presence of filler, the Flory-Rehner equation has been modified using the Kraus correction factor, C. The value of C was taken as 1.17 for HAF carbon black [10] that is a typical filler used in the tire-curing bladder compounds [6].

A Flexsys testing machine (Tensometer 2000, Swindon, UK) was used for the tensile test (ASTM D412) and tear test (ASTM D624, Die C). All tests were performed at room temperature and a crosshead speed of 500 mm/min. The hardness of the original and revulcanized samples were measured using a Shore A durometer, according to ASTM D2240.

In order to observe the morphology of the rubber particles in the ground rubber crumb and morphology of the devulcanized rubber, they were suspended in xylene (ca. 5 mg of rubber in 1 ml of xylene) and subjected to ultrasonic dispersion for approximately 1 h. After waiting for about 5 min, the suspension was separated in the form of pellet and supernatant. A drop of the supernatant was placed on an aluminum stub, dried and coated with thin layers of gold and examined under a Cambridge S-360 Scanning Electron Microscope (SEM).

3. Results and discussion

3.1. Morphology and size distribution

Fig. 1 shows the SEM photographs of ground (a) and devulcanized (b) tire-curing bladder at an amplitude of

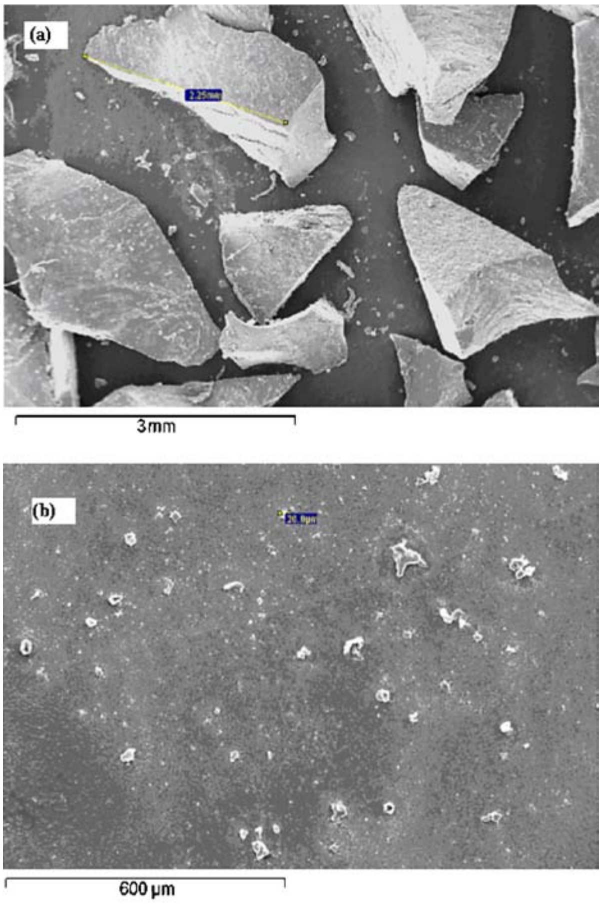

Figure 1 SEM photographs of ground (a) and devulcanized (b) tire-curing bladder.

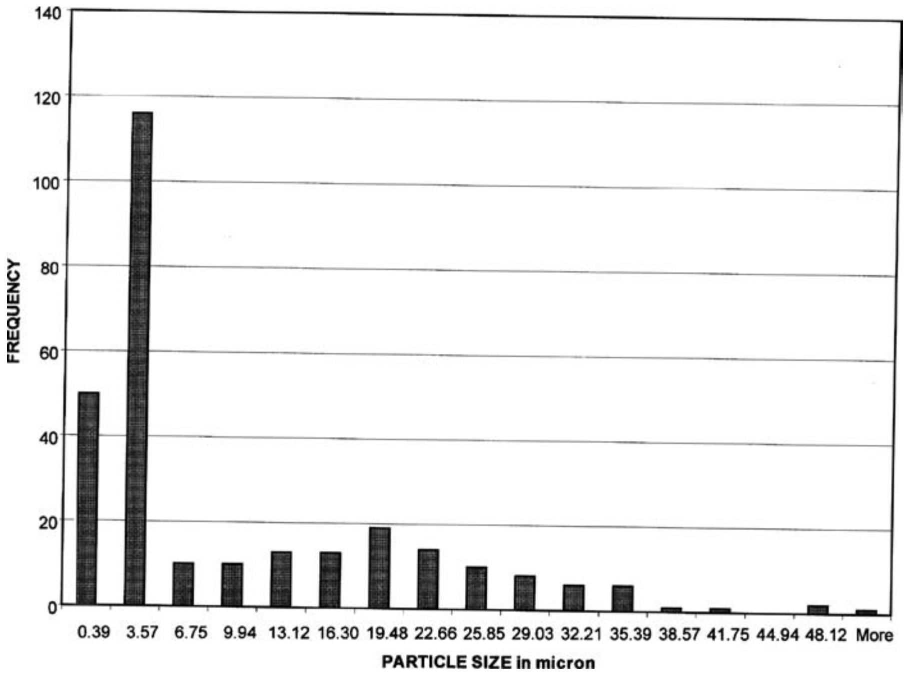

Figure 2 Particle size distribution of devulcanized tire-curing bladder.

10 μm and a flow rate of 1.26 g/s. From Fig. 1a, the ground tire-curing bladder particles were particles with sharp edge and a size of about 2 mm for majority of particles (also shown in Table I). After devulcanization, the three-dimensional structure of cured rubber was broken with formation of sol and gel of reduced crosslink density. This gel contained some particles with their sizes greatly reduced, as clearly shown in Fig. 1b. The gel particle size distribution of the tire-curing bladder devulcanized at 10 μm and a flow rate of 1.26 g/s is shown in Fig. 2. Clearly, all of the particles remaining in the gel had a particle size less than 50 μm, and most of those particles had a size smaller than 4 μm. Compared to the size of ground particles (2 mm), the gel particle size of devulcanized rubber was greatly reduced, which also gave the devulcanized rubber better homogeneity for milling and compounding and smoother surface of their vulcanizates.

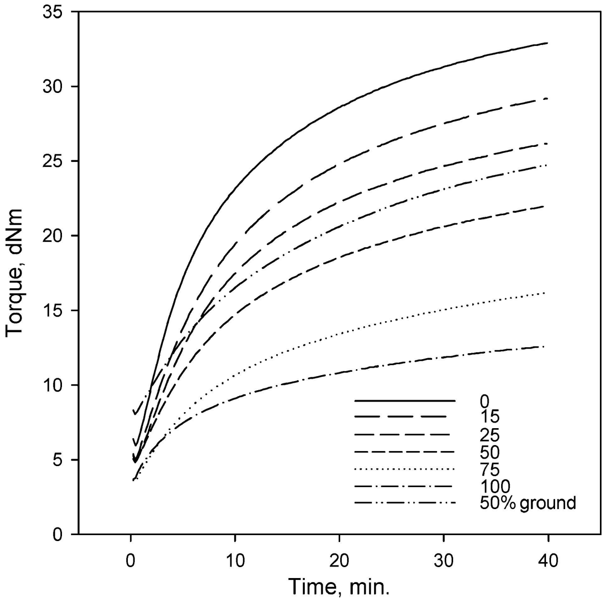

Figure 3 Cure curves of blends of CB-filled butyl rubber and devulcanized tire-curing bladder at various compositions at a cure temperature of 180°C. 50/50 blend with ground bladder is also shown.

3.2. Cure behavior

Fig. 3 shows the cure curves of the blends of the CB-filled virgin butyl rubber and devulcanized tire-curing bladder at various compositions at a cure temperature of 180°C. In addition, for comparison purpose, the cure curve of the blend of the ground rubber and CB filled butyl rubber at 50/50 ratio is also shown in Fig. 3. After 40 min, the curing was still marching and did not reach a maximum torque. This was because of the use of the resin curing system. As the concentration of the devulcanized rubber increased, the minimum and final torque showed lower values. Unlike that in the blend of the natural rubber with devulcanized natural rubber [11], the final torques of virgin rubber was about 3 times higher than that of the devulcanized tire-curing bladder. The blends with less amount of devulcanized rubber had a higher crosslink density and gel content as shown in Fig. 4, which caused a higher final torque in the cure curve in Fig. 3. Also, the blends containing more devulcanized rubber contained more low-molecular-weight sol and therefore showed lower minimum torque in the cure curve and lower viscosity as shown in Fig. 5a.

The cure curve of 50/50 blend of the CB filled butyl rubber and ground tire-curing bladder showed much higher torque during the whole curing time compared to the cure curve of the blend of the CB filled butyl rubber and devulcanized rubber at the same concentration. This is possibly because the ground particles in the blend act as a filler, which give much higher torque values during curing.

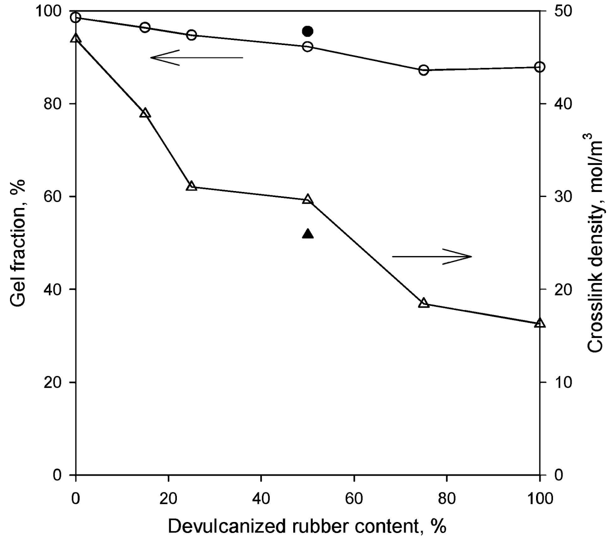

Figure 4 Gel fraction (circles) and crosslink density (triangles) of blends of CB-filled butyl rubber and devulcanized tire-curing bladder (open symbols). 50/50 blend with ground bladder is also shown (solid symbols).

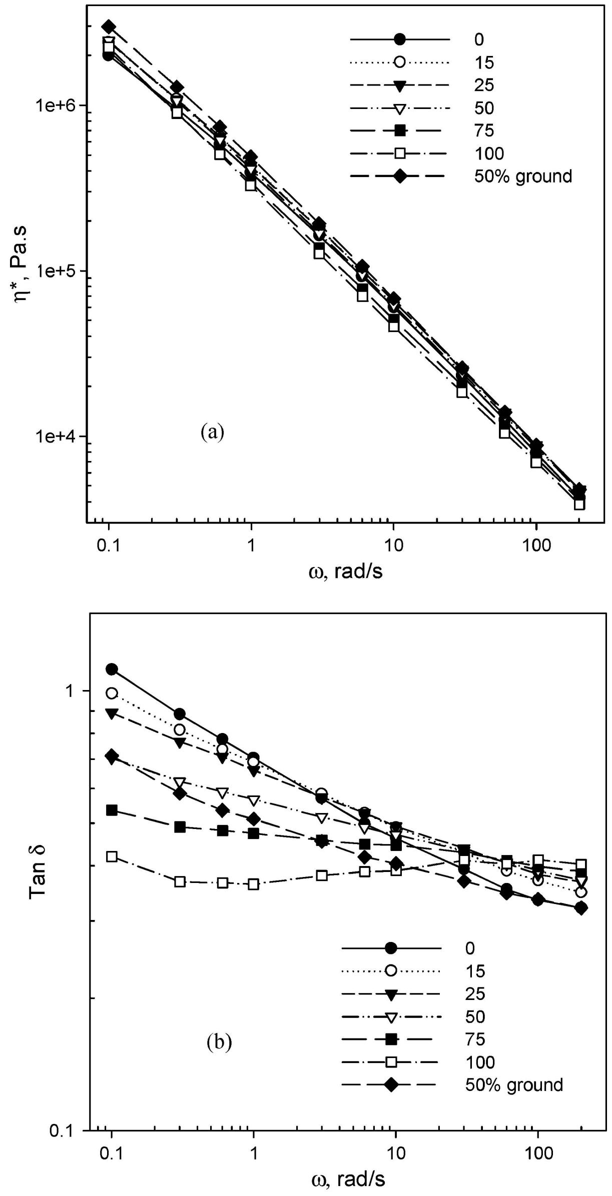

Figure 5 Complex dynamic viscosity (a) and loss tangent (b) as a function of frequency for blends of CB-filled butyl rubber and devulcanized tire-curing bladder. 50/50 blend with ground bladder is also shown.

3.3. Gel fraction and crosslink density

Fig. 4 represents the gel fraction and crosslink density of the cured blends of the CB filled butyl rubber and devulcanized tire-curing bladders at different blend ratio. Both the gel fraction and crosslink density of the gel decreased monotonically with devulcanized rubber content. The gel fraction and crosslink density of the devulcanized tire-curing bladder were 51% and 5.4 mol/m^3, respectively [5]. As shown in Fig. 4, after revulcanization the gel fraction and crosslink density of the revulcanized rubbers were much higher than that of the devulcanized rubber with their respective values being 87% and 15.6 mol/m^3. Clearly, most sol generated by devulcanization was cured during revulcanization, while a small part of sol, presumably of low molecular weight, in the devulcanized rubber still remained uncured.

In addition, for comparison purpose, the gel fraction and crosslink density of the cured blend of the ground rubber and CB filled butyl rubber at 50/50 ratio is also shown in Fig. 4. It is reasonable that the gel fraction was a little higher than that of 50/50 blend of the devulcanized sample, since there was more sol in the devulcanized sample compared to the ground rubber. However, the crosslink density of the blend containing the ground rubber was slightly lower than that of 50/50 blend of the devulcanized sample because of possible better interaction between the devulcanized and virgin rubbers.

3.4. Viscoelastic properties

Fig. 5 shows the complex viscosity (a) and tan δ (b) vs. frequency for the uncured blends of the CB filled butyl rubber and devulcanized tire-curing bladder. Results for 50/50 blend of the CB filled butyl rubber and ground tire-curing bladder are also given in Fig. 5. The complex viscosity of blends with higher content of the devulcanized rubber was lower. This was the result of the presence of high sol fraction in the devulcanized tire-curing bladder. Also, the complex viscosity of the blend of the CB filled butyl rubber and ground tire-curing bladder showed the highest value throughout the frequency range, because the ground particles acted as a filler in the blend.

It was also noted from Fig. 5b that the tan δ value of the blends of the CB filled butyl rubber and devulcanized tire-curing bladder were less dependent on the frequency upon the addition of the devulcanized rubber. This was because of the higher gel content in the blends. Moreover, tan δ of 50/50 blends of the CB filled butyl rubber and ground tire-curing bladder was lower than that of the corresponding blend of the CB filled butyl rubber and devulcanized rubber, which indicated that the latter was less elastic due to the presence of less gel.

Fig. 6a shows the storage modulus as a function of frequency of the blends of the CB filled butyl rubber and devulcanized tire-curing bladder. Similar data are also shown for 50/50 blend of the CB filled butyl rubber and ground tire-curing bladder. At the low frequency end, the CB filled butyl rubber showed the lowest storage

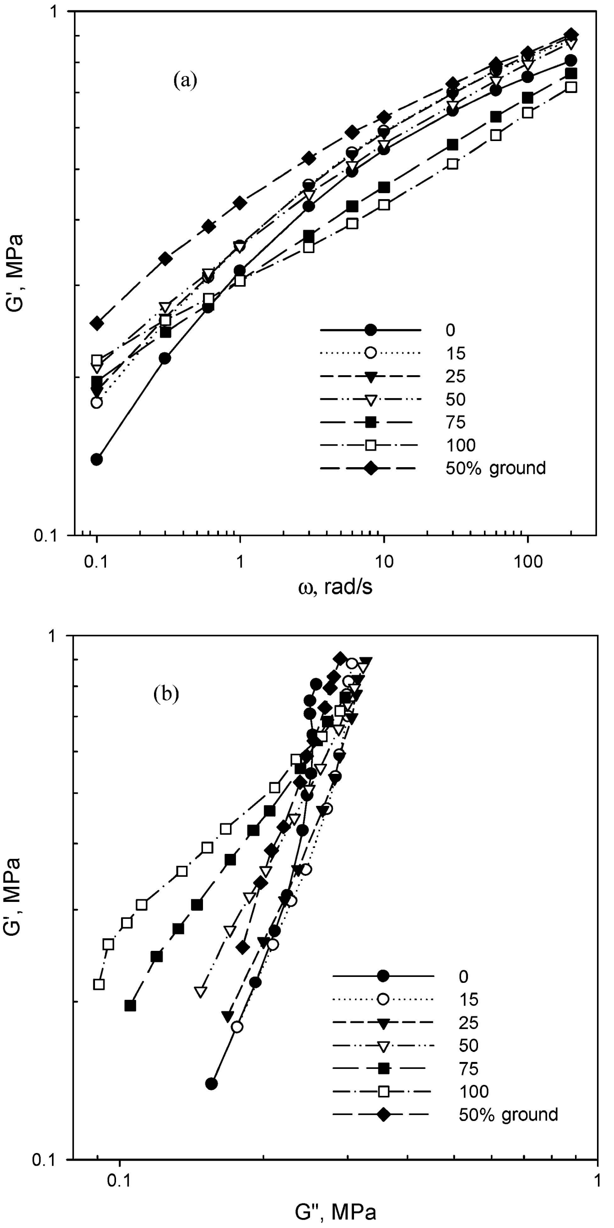

Figure 6 Storage modulus as a function of frequency (a) and loss modulus (b) for blends of CB-filled butyl rubber and devulcanized tire-curing bladder. 50/50 blend with ground bladder is also shown.

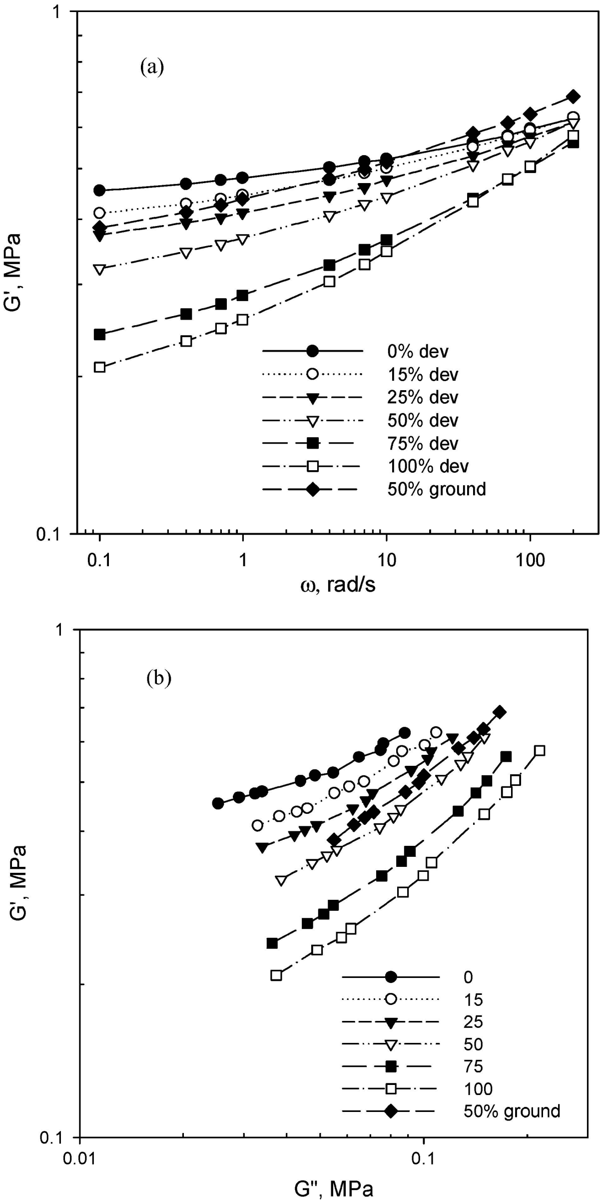

Figure 7 Storage modulus as a function of frequency (a) and loss modulus (b) for blend vulcanizates of CB-filled butyl rubber and devulcanized tire-curing bladder. 50/50 blend vulcanizate with ground bladder is also shown.

modulus. The blends with a higher content of devulcanized rubber (>15%) were less sensitive to the frequency due to the higher gel content. At the high frequency range, similar to the pure devulcanized rubber, the blends showed lower storage modulus at higher content of devulcanized rubber (>75%). It was also interesting to note that the blends with up to 50% devulcanized rubber content showed higher storage modulus than the CB filled butyl rubber indicating the existence of some kind of interaction between the butyl rubber and devulcanized rubber. The blend of the CB filled butyl rubber and ground tire-curing bladder exhibited a higher storage modulus than the blend of the CB filled butyl rubber and devulcanized tire-curing bladder with same concentration.

The storage modulus (G') vs. loss modulus (G'') for the blends of the CB filled butyl rubber and devulcanized tire-curing bladder is given in Fig. 6b. Clearly, the blends with higher content of devulcanized rubber showed a higher storage modulus at lower values of the loss modulus. This behavior indicated a higher elasticity of the blends with higher devulcanized rubber content in the lower range of the loss modulus.

Fig. 7 shows the storage modulus as a function of the frequency (a) and the loss modulus (b) for the cured blends of the CB filled butyl rubber and ground or devulcanized tire-curing bladder. The storage modulus of the blends decreased when more devulcanized rubber was added to the blends (Fig. 7a). The lower storage modulus was possibly because of the lower crosslink density of the vulcanizates containing a higher content of devulcanized rubber, as seen in Fig. 4. In addition, the G' vs. G'' plot of the blends vulcanizates of the CB filled butyl rubber and devulcanized tire-curing bladder depicted in Fig. 7b indicated that at the same loss modulus, the blends with higher (>50%) content of devulcanized rubber had a lower storage modulus

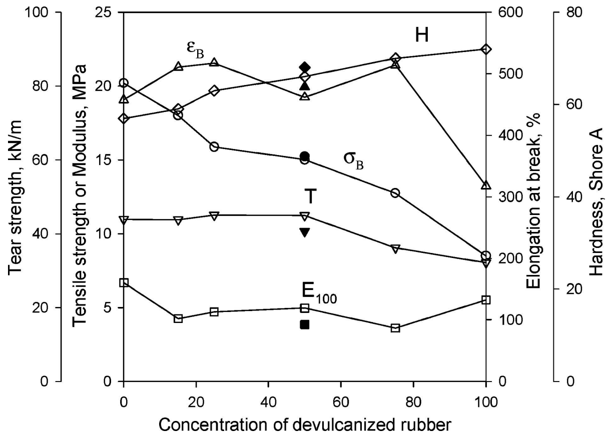

Figure 8 Mechanical properties of blend vulcanizates of CB-filled butyl rubber and devulcanized tire-curing bladder (open symbols) as a function of concentration. 50/50 blend vulcanizate with ground bladder is also shown (solid symbols).

than that of the vulcanizate of 50/50 blend containing the ground tire-curing bladder. This behavior indicated that the blends with a higher content of devulcanized rubber were less elastic. Also it was seen from Figs 6b and 7b that the devulcanized and revulcanized rubbers obtained at different blend ratio showed different G' vs G'' curves. The latter was a clear indication that different materials were obtained at each blend ratio.

3.5. Mechanical properties

The tensile strength, σ_B, modulus at 100% elongation, E_{100}, and elongation at break, ε_B, of the cured rubber blends, as a function of the concentration of devulcanized tire-curing bladder, are shown in Fig. 8. This Fig. also includes the tear strength, T, and hardness, H. One could observe that the tensile strength decreased, while hardness increased with an increase of the devulcanized rubber content. Like the blends of the other rubbers with devulcanized rubber [11–13], these dependences followed curves close or above the additivity rule. On the other hand the tear strength up to 50% content of the devulcanized rubber was not affected and decreased only at 75% content of the devulcanized rubber. The ε_B of the blend vulcanizates at different concentration of the devulcanized tire-curing bladder were higher than those of the devulcanized sample and CB filled butyl rubber. The modulus at 100% strain of the blend vulcanizates was independent of the devulcanized rubber content and was lower than those of the vulcanizates prepared from the devulcanized sample and CB filled butyl rubber. Based on the mechanical properties, one could conclude that the performance of the vulcanizates of the blends of the CB filled butyl rubber and devulcanized tire-curing bladders could be adjusted for different applications by varying the concentration of the devulcanized rubber.

The mechanical properties of vulcanizate of 50/50 blend of the CB filled butyl rubber and ground tire-curing bladder are also shown by solid symbols in Fig. 8. The tear strength and modulus at 100% strain were slightly lower than those of the blend of the CB filled butyl rubber and devulcanized rubber at the same concentration, while the values of hardness, tensile strength and elongation at break were similar.

4. Conclusion

The recycling of tire-curing bladder by ultrasonic devulcanization was carried out with a grooved barrel ultrasonic reactor. The devulcanized rubber prepared from the tire-curing bladder contained some sol and gel of a lower crosslink density. The gel contained some particles with their sizes greatly reduced compared to that of the ground tire-curing bladder.

The devulcanized tire-curing bladder was used for blending with the CB filled butyl rubber at different ratios. The rheological properties and curing behavior of the blends were measured. The rheological and mechanical properties, as well as gel fraction and crosslink density of the cured blends have been measured. A comparison of properties between the blend of the devulcanized and ground tire-curing bladder with carbon black filled butyl rubber has been carried out. The results showed that compared to the blend containing the ground rubber, the blends containing the devulcanized samples were easier to mix and their vulcanizates exhibited enhanced properties.

The gel fraction and crosslink density of the cured blends were reduced with addition of more devulcanized rubber in the blends. The dynamic viscoelastic properties indicated that the cured blends became less elastic with addition of more devulcanized rubber. The mechanical properties of the blend vulcanizates were found to depend on the devulcanized rubber content, while the elongation at break of the blend vulcanizates were higher than that of the vulcanizates of the CB-filled butyl rubber and the tear strength were intact up to 50% content of the devulcanized tire-curing bladder.

Acknowledgments

The financial support was provided by the grant DMI-0084740 from the National Science Foundation, Division of Engineering. The authors wish to thank Dr. P. Sadhukhan of the Bridgestone/Firestone Research LLC for useful discussion.

References

1. H. J. MANUEL, W. DIERKES and A. HENDRIKS, *Kautschuk Gummi Kunststoffe* **53** (2000) 730.
2. T. ZAHARESCU, C. CAZAC, S. JIPA andR. SETNESCU, *Nucl. Instr. Meth. Phys. Res. B* **185** (2001) 360.
3. J. YANG, in "Environmental Applications of Ionizing Radiation," edited by W. J. Cooper, R. D. Curry and K. E. O'Shea (Wiley, New York, 1998) p. 601.
4. N. L. SQUIRE, M. S. JAMES and W. J. O'BRISKIE, USP 6444743 (2002).
5. W. FENG and A. I. ISAYEV, Paper #26, Presented at the 166th ACS Rubber Division Meeting, Columbus, Ohio, October, 2004.
6. J. V. FUSCO and P. HOUS, in "The Vanderbilt Rubber Handbook," 13th ed., edited by R. F. Ohm (1990) p. 102.

7. J. S. DICK, C. HARMON and A. VARE, *Polym. Test.* **18** (1999) 327.
8. P. J. FLORY and J. JR. REHNER, *J. Chem. Phys.* **11** (1943) 512.
9. A. BARTON, in "CRC Handbook of Polymer-Solvent Interaction Parameters and Solubility Parameters" (CRC Press, Boston, 1990) Chapt. 9, p. 72.
10. G. KRAUS, *J. Appl. Polym. Sci.* **7** (1963) 861.
11. C. K. HONG and A. I. ISAYEV, *J. Mater. Sci.* **37**(2) (2002) 385.
12. S. GHOSE and A. I. ISAYEV, *J. Elast. Plast.* **36** (2004) 213.
13. J. YUN and A. I. ISAYEV, *J. Appl. Polym. Sci.* **92** (2004) 132.

Received 18 October
and accepted 17 December 2004