

# Properties of ultrasonically devulcanized and revulcanized used tire rubber and their blends with carbon black-filled virgin natural rubber

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Waste tire rubber provides a great potential to reduce usage of the virgin natural and synthetic rubber. It is driven by the more stringent environmental regulations and increasing price of raw rubbers.

**TECHNICAL NOTEBOOK**  
Edited by John Dick

However, rubber recycling is a difficult task due to the presence a crosslink network, which needs to be undone to create a flowable elastomeric material. Over many years, many approaches were developed to deal with recycling of used tire rubber. The earliest approach utilizes a grinding process reducing bulk rubber into particles of small sizes with insignificant rupture of the cross-link bonds.

In addition, many reclamation methods have been developed, including mechanical<sup>1-4</sup>, chemical<sup>5-7</sup>, mechanochemical<sup>8-10</sup>, microwave<sup>11-14</sup>, biological<sup>15-19</sup>, and continuous ultrasonic<sup>20</sup> and supercritical carbon dioxide<sup>21</sup> methods. Several articles provided reviews on various mechanical, chemical, physical and biological processes developed to break the

## Executive summary

Continuous ultrasonic devulcanization of 40 mesh ground tire rubber (GTR) powder at a frequency of 40 kHz and ultrasonic amplitudes at 0  $\mu$ m (without ultrasonic treatment) and 8  $\mu$ m was carried out using an ultrasonically assisted twin-screw extruder.

Blends of GTR and devulcanized GTR with virgin natural rubber (NR) containing 60 phr of carbon black (CB) were prepared at GTR concentrations of 10, 20, 35 and 50 wt percent. The gel fraction, crosslink density, vulcanization and rheological behavior of these blends and NR/CB were investigated.

In general, gel fraction and crosslink density of vulcanized blends decreased in comparison with those of NR/CB, while their dynamic properties showed little differences until 50 wt percent. During vulcanization of blends, minimum torque was continuously increased and maximum torque was decreased only at 50 wt percent in comparison with those of NR/CB. The stress-strain behavior and abrasion loss of vulcanized blends and NR/CB were also measured.

Modulus at 100-percent elongation, tensile strength and elongation at break of blends was above 3.4 MPa, 20 MPa and 350 percent, respectively, while NR/CB vulcanizate exhibited modulus at 100-percent elongation, tensile strength and elongation at break of 3.3 MPa, 28 MPa and 470 v, respectively.

Abrasion loss of vulcanized blends containing CB was generally good, but higher than that of NR/CB vulcanizate. Comparison of abrasion loss of current blends with our earlier study of GTR/NR blends without an addition of CB indicated that the current blends showed significant improvements in level of abrasion loss. The obtained results indicated a suitability of the utilization of ultrasonically devulcanized GTR for incorporation into new tire and rubber product formulations.

three-dimensional crosslink network.<sup>6,22-24</sup> Also, an extensive comparative study of different devulcanization technologies, including supercritical fluid, ultrasonic and biological methods at their optimal conditions, was carried out.<sup>25</sup>

Various devulcanized samples were analyzed and compounded with virgin NR at 10 phr to provide a direct comparison of these optimized techniques. The rheological and mechanical proper-

ties of these vulcanizates along with virgin NR were investigated and compared to find out the rubber providing the highest compatibility for compounding and revulcanization.

It was stated that the continuous ultrasonic method, which does not use any chemicals, is the most useful technique to control the investigated properties of the vulcanizates with a possibility of achieving good performance characteristics of vulcanizates. In the process of ultrasonic devulcanization, ultrasonic horn can induce in rubber high frequency compression and extension waves, generating bubbles in the vicinity

of voids and impurities in the rubber.<sup>22</sup> The process provides high acoustic energy, which leads to the rupture of crosslinks along with some carbon-carbon bonds. After ultrasonic devulcanization, GTR can be reprocessed alone, as a typical rubber, or possibly incorporated into new tires or other rubber products through compounding with virgin rubber and subsequent vulcanization. Such a blending is a common way to improve usage of devulcanized rubbers.

Among these blends, the blend containing ultrasonically devulcanized GTR showed the highest tensile strength (34 MPa), but

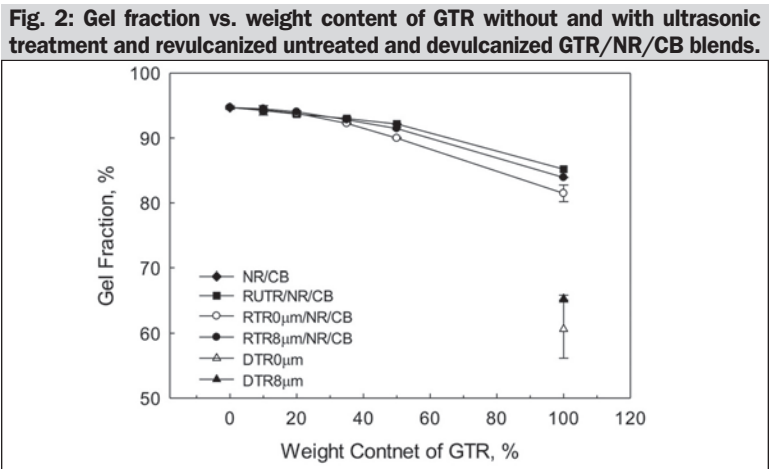
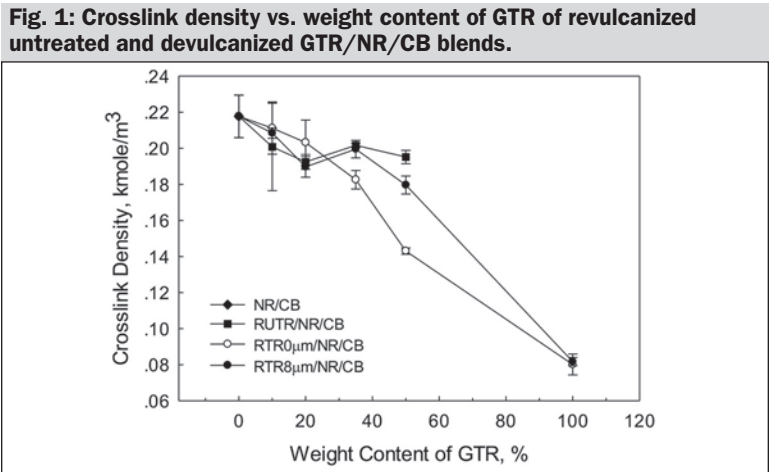
still being below that of virgin NR vulcanizate (37 MPa).<sup>25</sup> Many other studies on blending of devulcanized rubber with virgin NR were carried out.<sup>8,26-29</sup> In particular, study<sup>8</sup> dealt with the devulcanized GTR (dGTR) obtained using a pan-milled type mechanochemical reactor with its subsequent blending with virgin NR.

A comparison was made between the GTR/NR and dGTR/NR blends. It was shown that at the GTR content of 10 percent the tensile strength of the dGTR/NR blend was 23.2 MPa compared with 13.7 MPa of the GTR/NR blend. Investigation<sup>26</sup> described results of devulcanization of NR from used truck tires by thermochemical method using diphenyl disulfide as a devulcanization agent. The devulcanized rubber was compounded with virgin NR. It was stated that the prepared blends with content of up to 40 percent of devulcanized rubber provided blends with acceptable mechanical properties when curing system and compounding recipes for the blends were optimized.

Moreover, mechanochemical reclaiming of GTR was carried out by using tetra methyl thiuram disulfide in the presence of spindle oil at ambient temperature.<sup>27</sup> The measurement of cure characteristics and dynamic mechanical properties of the virgin NR/reclaim GTR blend indicated a

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Table 1: Compounding recipe of GTR/NR and GTR/NR/CB blends.						
Weight Content of GTR	0%	10%	20%	35%	50%	100%
Rubber (phr)	100	100	100	100	100	100
Sulfur (phr)	2.0	1.9	1.8	1.65	1.5	1.0
CBTS (phr)	1.0	1.0	1.0	1.0	1.0	1.0
ZnO (phr)	5.0	4.63	4.25	3.69	3.13	1.25
Stearic Acid (phr)	1.0	0.93	0.85	0.74	0.63	0.25



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decrease of the optimum cure time without affecting the scorch time. Also, an increase in the storage modulus was observed with the addition of reclaimed GTR into virgin NR.

In the study<sup>28</sup>, devulcanized GTR powder, obtained using a counter-rotating twin-screw extruder, was compounded with virgin NR. It was found that an increase of NR content increased tensile strength and elongation at break of blends. Recent review<sup>29</sup> summarized results obtained by using supercritical carbon dioxide (scCO<sub>2</sub>) in combination with common organic agents used in devulcanization of tire rubber. It was shown that vulcanized compounds of the devulcanized rubber with virgin NR exhibited curing and mechanical properties closely matching those of virgin NR.

A study also was conducted on blending of microwave devulcanized GTR obtained in batch process with virgin NR compound containing 60 phr of CB.<sup>30</sup> It was shown that blending improved tear strength of blend

vulcanizates but not the tensile strength and elongation at break.

Recently, the GTR powder of 40 mesh and GTR ultrasonically devulcanized in the twin-screw extruder was compounded with the virgin NR in various proportions.<sup>31</sup> Rheological behavior of these compounds and their vulcanizates, mechanical performance and abrasion loss of vulcanizates was measured and compared.

At all blending ratios, revulcanized blends of virgin NR with tire rubber devulcanized at an ultrasonic amplitude of 8  $\mu$ m exhibited better mechanical properties and lower abrasion loss than revulcanized blends of NR with untreated tire rubber.

In view of earlier findings on blends of virgin unfilled NR with GTR powder and ultrasonically devulcanized GTR powder<sup>31</sup>, to make their full utilization and improve their properties, the present study is devoted to blending of virgin NR/CB compound containing 60 phr of CB with the original GTR and ultrasonically devulcanized GTR powder in various proportion.

Rheological behavior of these blends and their vulcanizates is measured and compared with earlier findings for blends with unfilled NR.<sup>31</sup> In addition, the



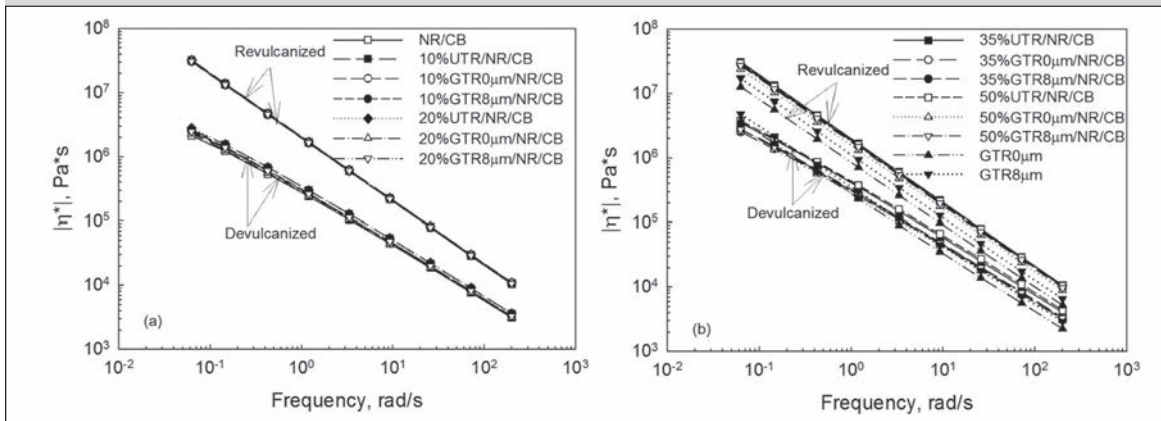
Isayev

## The author

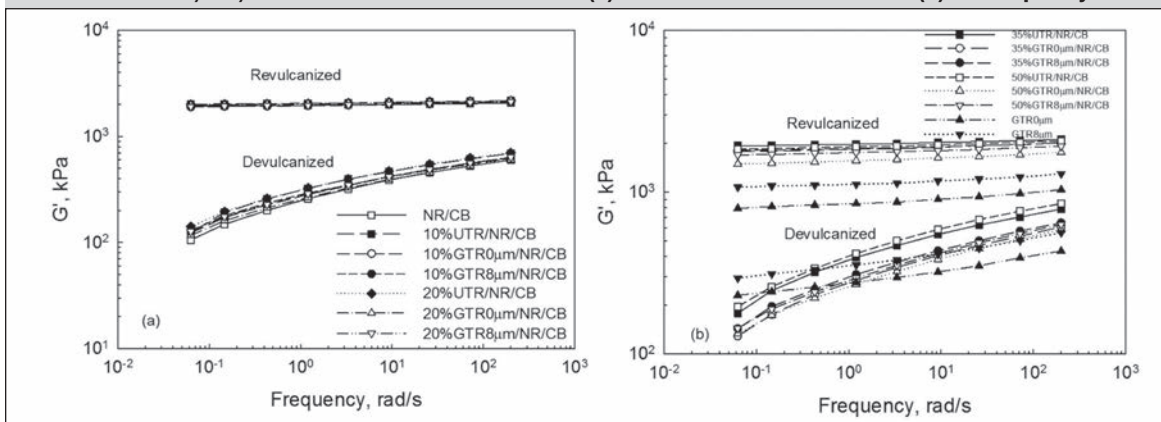
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stress-strain behavior and abrasion loss of various blend vulcanizates are studied and compared. This study is an important step toward the possibility of incorporation of ultrasonically devulcanized GTR into manufacturing process of new tires and other rubber products.

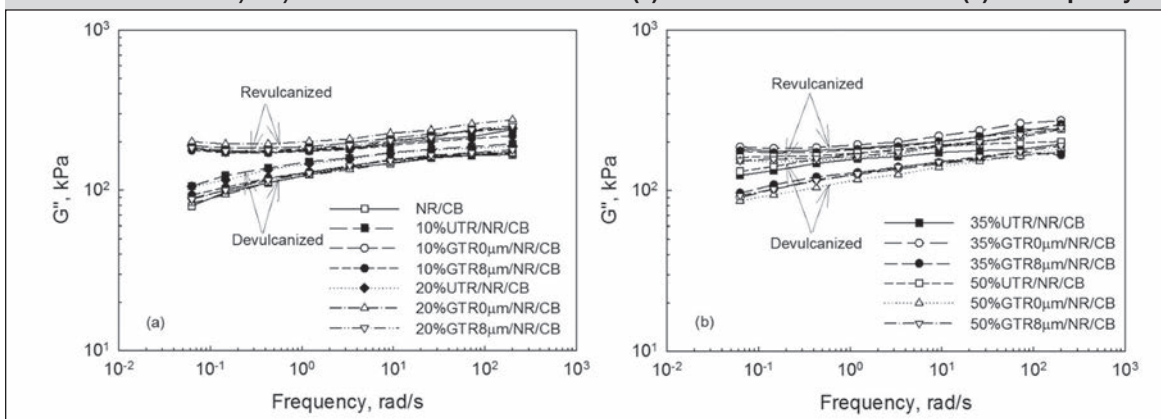
**Fig. 3: Complex viscosity of untreated and devulcanized GTR/NR/CB blends and revulcanized untreated and devulcanized GTR/NR/CB blends at 10% and 20% GTR (a) and at 35% and at 50% GTR (b) vs. frequency.**



**Fig. 4: Storage modulus of untreated and devulcanized GTR/NR/CB blends and revulcanized untreated and devulcanized GTR/NR/CB blends at 10% and 20% GTR (a) and at 35% and at 50% GTR (b) vs. frequency.**



**Fig. 5: Loss modulus (a) and (b) of untreated and devulcanized GTR/NR/CB blends and revulcanized untreated and devulcanized GTR/NR/CB blends at 10% and 20% GTR (a) and at 35% and at 50% GTR (b) vs. frequency.**



Isayev received his Ph.D. in polymer science and engineering at the Topchiev Institute of Petrochemical Synthesis of the USSR Academy of Sciences, Moscow. Other degrees include master's in applied mathematics at the Institute of Electronic Machine Building, and a master's in chemical engineering at the Azerbaijan Institute of Oil and Chemistry, Baku, USSR.

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His research interests focus in polymer and composite processing, process modeling, rheo-optics, rheology and constitutive equations of polymers, oil products and disperse systems; the injection, co-injection, trans-

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Isayev has co-authored four editions of one monograph on rheology, edited or co-edited eight books, published 279 papers in refereed journals, 37 chapters in books, eight papers in encyclopedias and 181 papers in conference proceedings. He holds 30 patents, has advised 49 doctorate, 42 master's students and 31 post-docs and visiting scientists.

## Experimental

### Materials

Micronized GTR powder of 40 mesh obtained from used truck tires under the trade name 40TR, manufactured by Lehig Technologies Inc. (Tucker, Ga.) was used. Since GTR was produced from used tires, its exact composition is unknown. Apparently, GTR mainly consists of natural rubber (NR) with some styrene-butadiene rubber (SBR) and butadiene rubber (BR). Other ingredients are CB, inorganic additives, and process oil. The natural rubber (SMR CV60) was supplied by Akrochem Corp. (Akron). Carbon black N330 was from Sid Richardson (Fort Worth, Texas). The vulcanization system includes sulfur, accelerator (N-cyclohexyl-2-benzothiazole sulfonamide, CBTS), zinc oxide (ZnO) and stearic acid. These ingredients were courtesy of Akrochem.

### Ultrasonically aided devulcanization reactor

The continuous ultrasonic devulcanization of GTR was carried out by a co-rotating twin-screw extruder (Prism USALAB 16, Thermo Electron Co., United Kingdom) having a diameter (d) of 16 mm and L/d ratio of 25. This extruder was modified to install an ultrasonic horn into the barrel. The schematic of the ultrasonic twin-screw extruder was shown earlier.<sup>31</sup> The 40 mesh GTR particles were fed into the heated barrel by the feeder (K2V-T20, K-Tron Soder, USA). The function of twin screws is to convey and mix rubbers.

Devulcanization occurred in the ultrasonic treatment zone where the ultrasonic waves at a frequency of 40 kHz was imposed into rubbers through the horn. The horn is a 28 mm × 28 mm square cross section, which was mounted in the barrel and connected to a booster. The gap between screws and the horn tip was 2.5 mm. The volume of ultrasonic treatment zone was 1.9 cm<sup>3</sup>. The diameter of the die of the extruder was 4 mm with its length of 11 mm.

A pressure transducer (PT460E-5M-6, Dynisco Instruments, Sharon, MA) was installed in the die. The barrel temperature of each section was monitored by thermo-

couples inserted in the barrel. The ultrasonic horn was cooled by water set at 45°C using a thermostat (GP-100, NESLAB Instruments Inc., Newington, N.H.).

### Extrusion process

Devulcanization of GTR of 40 meshes was carried out using the ultrasonic twin-screw extruder, which was mentioned earlier in the paper. The ultrasonic devulcanization method was previously studied and optimized.<sup>32</sup> It was found that the best condition for devulcanization was at an ultrasonic amplitude of 8  $\mu$ m. Thus, the ultrasonic amplitude of 8  $\mu$ m was used.

For comparative purposes, an experiment also was conducted without imposition of ultrasound (0  $\mu$ m). The GTR powder was put into a feeder (K-Tron Co., Glassboro, NJ), which connected to the extruder. The flow rate of rubbers was set at 6 g/min. The barrel temperatures of each section from entrance of extruder to the die were set at 170°C, 170°C, 170°C, 170°C and 170°C. The rotation speed of the screws was 250 rpm. During ultrasonic treatment, the die pressure, power consumption, torque and barrel temperatures were recorded.

### Blending, compounding and molding

After extrusion, original GTR and devulcanized GTR (dGTR) at 0  $\mu$ m and 8  $\mu$ m were blended with virgin NR at the ratios of 0/100, 10/90, 20/80, 35/65, 50/50 and 100/0 using a Brabender mixer manufactured by C.W. Brabender Instruments, Inc. (85 mL, Model Plasti-corder, S. Hackensack, N.J.). The rotor speed was 55 rpm, the setup temperature was 60°C and the filling factor was 70 percent. The content of CB in the TR40 was found to be 29.9 percent.<sup>33</sup>

To keep GTR/NR ratios and CB content in NR equals to that of GTR, the blending ratios of GTR/NR/CB were 0/100/43, 10/90/38, 20/80/34, 35/65/28, 50/50/21. NR was first mixed for 1 minute, then GTR was added for 2 minutes, and, finally, CB was added. The total mixing time was 8 min.

After compounding, blends were mixed with curatives on a two-roll mill (Reliable Rubber & Plastic Machinery Co., North Bergen, NJ). The temperature of



the rolls was set at 40°C and the rotation speed was set at 15 rpm. The blend passed the two-roll mill 40 times in total. The curing recipe is 1 phr sulfur, 1 phr CBTS, 1.25 ZnO and 0.25 phr stearic acid for dGTR. The curing recipe is 2 phr sulfur, 1 phr CBTS, 5 phr ZnO and 1 phr stearic acid for NR.

For blends of GTR/NR, the curing recipes were adjusted based on their weight ratio. For compounds of GTR/NR/CB, recipes based on GTR/NR ratios were used. Curing recipes for compounds are shown in **Table 1**.

After compounding polymer blends with curatives, the curing curves were obtained using the Advanced Polymer Analyzer (APA 2000, Alpha Technologies, Akron) at 160°C. The frequency was 1.67 Hz, and the strain amplitude was 4.2 percent.

According to curing curves, curing time was set at T95. Then polymer blends were molded by a compression-molding press (Carver, Wabash, Ind.) at a temperature of 160°C. The revulcanized RUTR/NR/CB and RTR0 $\mu$ m/NR/CB and RTR8 $\mu$ m/NR/CB sheets with dimensions of 152 mm  $\times$  152 mm  $\times$  1.5 mm were obtained.

#### Characterization method

Advanced Polymer Analyzer (APA 2000) was used to measure the dynamic properties of untreated and ultrasonically treated devulcanized GTR/NR blends at a temperature of 90°C, and a strain amplitude of 4.2 percent within a frequency range from 0.00318 Hz to 31.8 Hz. To determine dynamic properties of the revulcanizates, the untreated and devulcanized GTR/NR blends and GTR/NR/CB blends with curatives were vulcanized at 160°C in APA 2000, and then tested by APA 2000 at a temperature of 90°C and a strain amplitude of 4.2 percent within a frequency range from 0.00318 Hz to 31.8 Hz.

Swelling tests were used to measure the crosslink density and gel fraction by the Soxhlet extraction apparatus. The weight of each sample was 0.5-1.0 g. The sol part was extracted from rubbers by benzene. The sample was swollen for 24 hours. Then it was taken out and weighed, followed by placing it in a vacuum oven for another 24 hours to dry at 60°C. The crosslink density was calculated using Flory-Rehner equation<sup>34</sup>:

$$e = -\ln(1 - V_r + V_r + \chi V_r^2) / V_1(V_r - 1.5V_r) \quad (1)$$

where  $V_e$  is the crosslink density,  $V_r$  is the volume fraction of rubber in the swollen sample, and  $\chi$  is the polymer-solvent interaction parameter. The  $\chi$  is 0.42, 0.4 and 0.4 for NR/benzene, BR/benzene and SBR/benzene, respectively.<sup>35</sup>

Because GTR mainly contains NR, BR and SBR, the  $\chi$  of ground tire rubber 0.4 is used. The  $\chi$  of the compounds of GTR and NR is assumed to be 0.41. The molar volume of benzene  $V_1$  is  $8.834 \times 10^{-5} \text{ m}^3/\text{mol}$ .

The Kraus correction<sup>36</sup> was used to correct crosslink density for the presence of CB filler:

$$V_r V_o = 1 - \phi [3C_1 - V_r V_o + V_r V_o - 1] \quad (2)$$

where  $V_r$  is the volume fraction of rubber for the unfilled swollen sample, and  $V_r$  is the

volume fraction of rubber for the filled swollen sample.  $\phi$  is the volume fraction of filler for the filled sample after drying.  $C$  is a constant that depends on the type of CB. High abrasion furnace CB in GTR is assumed. So the value of  $C$  is 1.17. The solid content of rubbers required in the Kraus correction is 35.1 percent.<sup>33</sup>

The gel fraction,  $\xi$ , of various vulcanizates was determined using the following equation:

$$\xi = \text{weight of rubber after drying} / \text{weight of solid-weight of rubber before swelling-weight of solid} \quad (3)$$

The gel fraction of tire rubber of 40 mesh was measured to be 85.2 percent.<sup>37,38</sup>

The cured sheets were cut into dumbbell shape specimens by Die C according to ASTM D412. Mechanical properties of samples were tested using an Instron tensile tester (Model 5567, Instron, Canton, MA) at an elongation rate of 500 mm/min.

UTR/NR, DTR/NR, UTR/NR/CB and DTR/NR/CB with curatives were cured and compression molded in cylindrical molds with a height of 12 mm and a diameter of 16 mm. Abrasion loss was measured using a Deutsches Institut für Normung Abrader (Zwick Abrasion Tester 6102) according to DIN 53516 at a load of 10 N and a pathway of 40 m.

## Results and discussion

### Crosslink density and gel fraction

**Fig. 1** shows the crosslink density of revulcanized untreated and devulcanized GTR/NR/CB blends as a function of weight content of GTR. The crosslink density values of GTR/NR/CB blends slightly increased compared with GTR/NR blends.<sup>31</sup> This is due to the presence of CB filler in NR providing rubber-filler interaction restricting the mobility of rubber chains in the vicinity of CB particles. The latter is limiting the swelling of these molecules, resulting in a higher apparent crosslink density.

Generally, crosslink density of GTR/NR/CB blends is seen to decrease with an increase of the weight content of GTR. This behavior is similar to crosslink density behavior of GTR/NR blend studied earlier.<sup>31</sup> When the weight content of GTR was less than 20 percent, the crosslink density of RTR0 $\mu$ m/NR/CB was higher than that of RUTR/NR/CB and RTR8 $\mu$ m/NR/CB leading to the better mechanical properties, as shown later.

**Fig. 2** shows the gel fraction of GTR without and with ultrasonic treatment (DTR) and revulcanized untreated and devulcanized GTR/NR/CB blends as a function of weight content of GTR. Gel fraction of GTR/NR/CB blends is seen to decrease with GTR content. These dependencies with respect to their values and tendency are similar to those of GTR/NR blends not containing CB, studied earlier.<sup>31</sup>

### Rheology

**Figs. 3, 4, 5 and 6**, respectively, show the complex viscosity, storage modulus, loss modulus and loss tangent of untreated and devulcanized GTR/NR/CB blends and revulcanized untreated and devulcanized GTR/NR/CB blends as a function

of frequency at 10 percent and 20 percent GTR (a), and 35 percent and 50 percent GTR (b).

Overall, the complex viscosity, storage modulus and loss modulus of GTR/NR/CB blends significantly increased compared with those of GTR/NR blends, studied earlier.<sup>31</sup> This is due to the increased resistance to flow due to the presence of CB in NR.

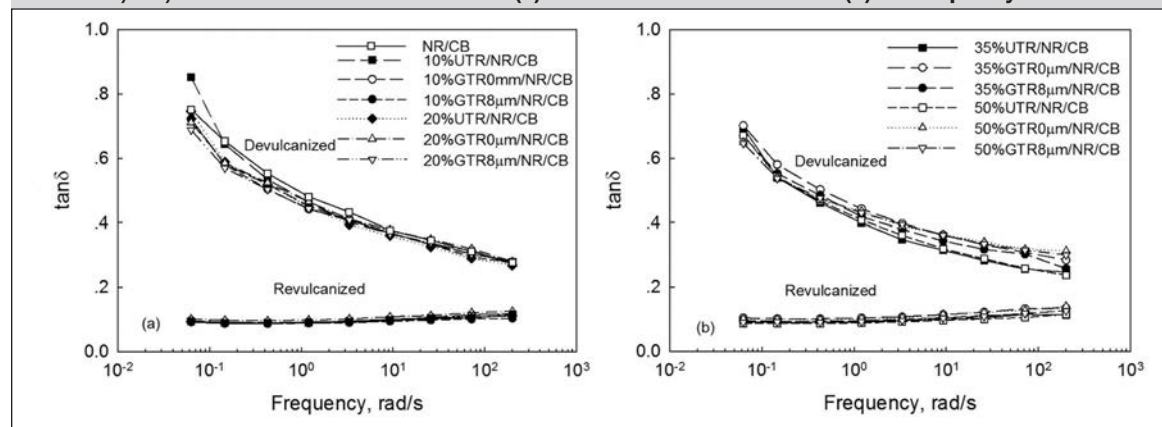
Accordingly, the values of loss tangent of untreated and devulcanized GTR/NR/CB blends decreased compared with untreated and devulcanized GTR/NR blends. However, the loss tangent of RTR/NR/CB blends increased compared with RTR/NR blends.<sup>31</sup> This is attributed to the fact that the rubber-filler and filler-filler interactions increased in the

case of RTR/NR/CB blends.

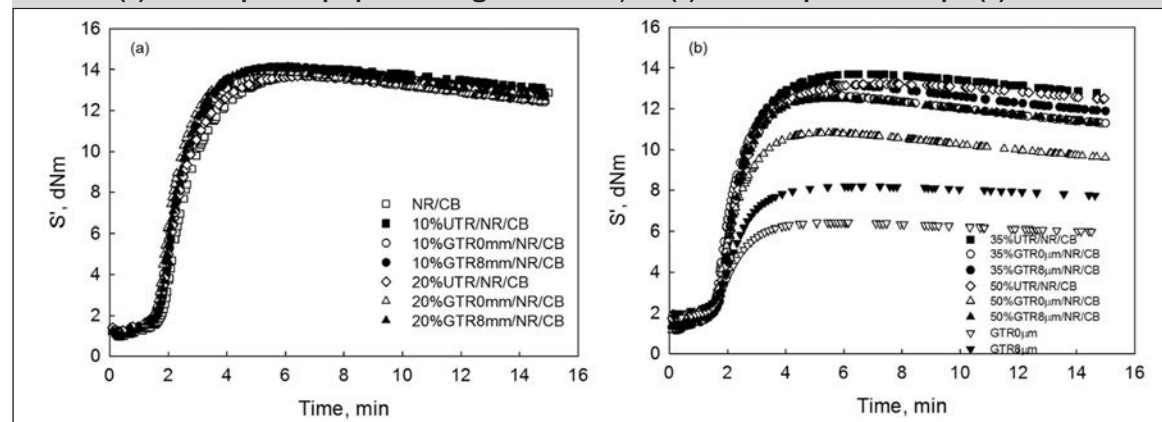
It should be noted that values of the loss modulus of untreated and devulcanized GTR/NR blends became lower after revulcanization, as shown in reference 31, while the loss modulus of untreated and devulcanized GTR/NR/CB blends after revulcanization became higher, as seen from **Fig. 5**.

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**Fig. 6: Loss tangent of untreated and devulcanized GTR/NR/CB blends and revulcanized untreated and devulcanized GTR/NR/CB blends at 10% and 20% GTR (a) and at 35% and at 50% GTR (b) vs. frequency.**



**Fig. 7: Curing curves of untreated and devulcanized GTR/NR/CB blends at 10% and 20% GTR (a) and at 35% and 50% GTR (b). For comparison purposes curing curves of NR/CB (a) and GTR0 $\mu$ m and GTR8 $\mu$ m (b) are also shown.**



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This is due to the increase of friction forces between rubber and filler. At the same time the difference of dynamic properties at different blending ratios became smaller due to the prevailing reinforcement effect of added CB filler.

## Curing behavior

**Fig. 7** shows torque of untreated and devulcanized GTR/NR/CB blends at 10 percent and 20 percent GTR (a), and at 35 percent and at 50 percent GTR (b) as a function of curing time. **Fig. 8** shows minimum torque (a), maximum torque (b) and difference between maximum and minimum torque (c) of untreated and devulcanized GTR/NR/CB blends as a function of weight content of GTR. Comparison of curing torque curves of GTR/NR/CB blends, depicted in **Fig. 7**, with those reported earlier on GTR/NR blends<sup>31</sup>, shows that the curing torque of CB-filled blends increased significantly compared with blends without CB. This is caused by the increase of viscosity and modulus after adding CB filler to the blends.

This is consistent with rheology data discussed above. It is also noted that adding CB filler to GTR/NR blends caused a large decrease in the induction time in comparison with induction time reported earlier for GTR/NR blends.<sup>31</sup> The latter is due to the fact that CB filler acts as a catalyst in vulcanization.<sup>39</sup>

Furthermore, as seen from **Fig. 8**, UTR/NR/CB blends still had the highest minimum and maximum torque compared with GTR0 $\mu$ m/NR/CB and GTR8 $\mu$ m/NR/CB blends. The minimum and maximum torque of GTR8 $\mu$ m/NR/CB blends are also higher than those of GTR0 $\mu$ m/NR/CB blends.

With the increase of weight content of GTR, the minimum torque of GTR/NR/CB blends also increased, but the maximum torque and difference between maximum and minimum torque decreased. The latter is due to the fact that the maximum torque and difference between maximum and minimum torque of NR/CB sample were much higher than those of GTR0 $\mu$ m and GTR8 $\mu$ m samples. The torque of blends at different blending ratios is between values of NR/CB, GTR0 $\mu$ m and GTR8 $\mu$ m samples.

## Stress-strain behavior

The stress-strain curves of NR/CB vulcanizate and devulcanized untreated and devulcanized GTR/NR/CB blends at different blending ratios are shown in **Fig. 9**.

**Fig. 10** shows the modulus at 100 percent elongation (a), tensile strength (b), and elongation at break (c) of revulcanized untreated and devulcanized GTR/NR/CB blends as a function of weight content of GTR.

The modulus at 100 percent elongation varied from 2.82 MPa to 3.71 MPa, the tensile strength varied from 6.49 MPa to 28.68 MPa, and the elongation at break varied from 171.1 percent to 469.1 percent. Stress-strain curves of CB-filled blends are very close to each other compared with blends without CB reported earlier<sup>31</sup>, due to the fact that the CB provided a substantial reinforcement.

It is also found that the modulus at 100 percent elongation and the tensile strength significantly increased after adding CB filler, but the elongation at break decreased, as evident from comparison of the present data with results obtained on blends GTR/NR blends without addition CB filler reported earlier.<sup>31</sup>

The enhancement of modulus is explained by the presence rubber-CB bonds increasing the number of crosslinks per unit vol-

ume<sup>40</sup>, which is associated with the increase of crosslink density values. Rubber-filler interactions limit the motion of rubber molecular chains. Friction forces increased between the surface of rubber and CB leading to the improvement of tensile strength.

In addition, rubber can be considered a soft matrix material compared to the rigid filler particles, and thus CB does not participate in the deformation.<sup>41</sup> Therefore, higher strain is experienced by rubber causing the reduction of the elongation at break. NR/CB sample had higher M100 than that of RTR0 $\mu$ m and RTR8 $\mu$ m samples, so decreasing trend of M100 with increasing weight content of GTR is generally observed.

The tensile strength still decreases with the increasing GTR content, but RUTR/NR/CB blends clearly showed the higher values of the tensile strength. This is possibly due to the fact that the portion of untreated tire rubber cannot absorb curative leading to more curatives transfer into the natural rubber enhancing the tensile strength. Besides, values of the tensile strength of RTR8 $\mu$ m/NR/CB blends are higher than those of RTR0 $\mu$ m/NR/CB blends.

The elongation at break also reduced with increasing concentra-

tion of GTR. Among various blends, RTR0 $\mu$ m/NR/CB blends show the best elongation at break, while RUTR/NR/CB and RTR8 $\mu$ m/NR/CB blends exhibit very close values of the elongation at break.

## Abrasion loss

Abrasion loss of revulcanized untreated and devulcanized GTR/NR/CB blends as a function of weight content of GTR is shown in **Fig. 11**. Comparison of the present data on abrasion loss of GTR/NR/CB blends with those obtained on GTR/NR blends, studied earlier<sup>31</sup>, indicates that the GTR/NR/CB-filled blends had lower abrasion loss. This can be explained by the reinforcement effect of CB.

This is also correlated with the values of crosslink density. NR/CB vulcanizates show the lowest abrasion loss. It is much lower than those of RTR0 $\mu$ m/NR/CB and RTR8 $\mu$ m/NR/CB vulcanizates. It is also seen that the abrasion loss shows an increase with weight content of GTR. RTR0 $\mu$ m/NR/CB blends exhibiting the highest abrasion loss at each blending ratio, while RUTR/NR/CB blends exhibit the lowest abrasion loss.

## Conclusion

Crosslink density, complex dynamic viscosity, storage modulus

and loss modulus of GTR/NR/CB blends is increased compared to GTR/NR blends reported earlier.<sup>31</sup> At the same time, gel fraction of GTR/NR/CB and GTR/NR blends is similar.

Comparison of curing torque curves of GTR/NR/CB blends with those reported for GTR/NR blends<sup>31</sup> shows that the curing torque of CB-filled blends increased significantly compared with blends without CB. The addition of CB increased the modulus at 100-percent elongation and tensile strength significantly but decreased the elongation at break. Generally, abrasion loss of vulcanizates of GTR/NR/CB blends decreased in comparison with those of GTR/NR blends reported earlier.<sup>31</sup>

The obtained results show a possibility of utilization of ultrasonically devulcanized tire rubber powder for possible incorporation into new tire rubber formulation

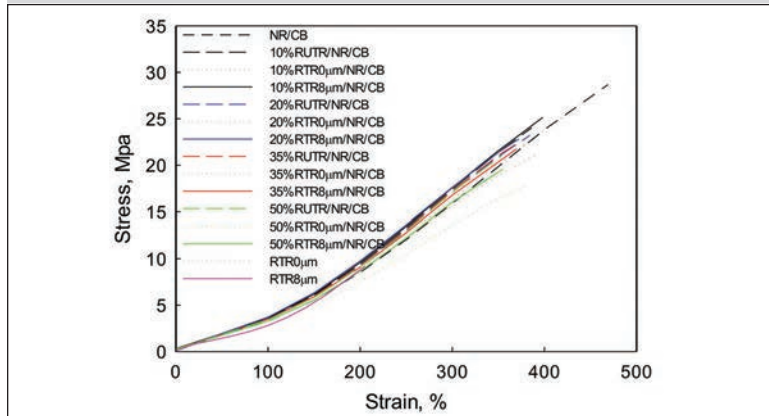
## Acknowledgments

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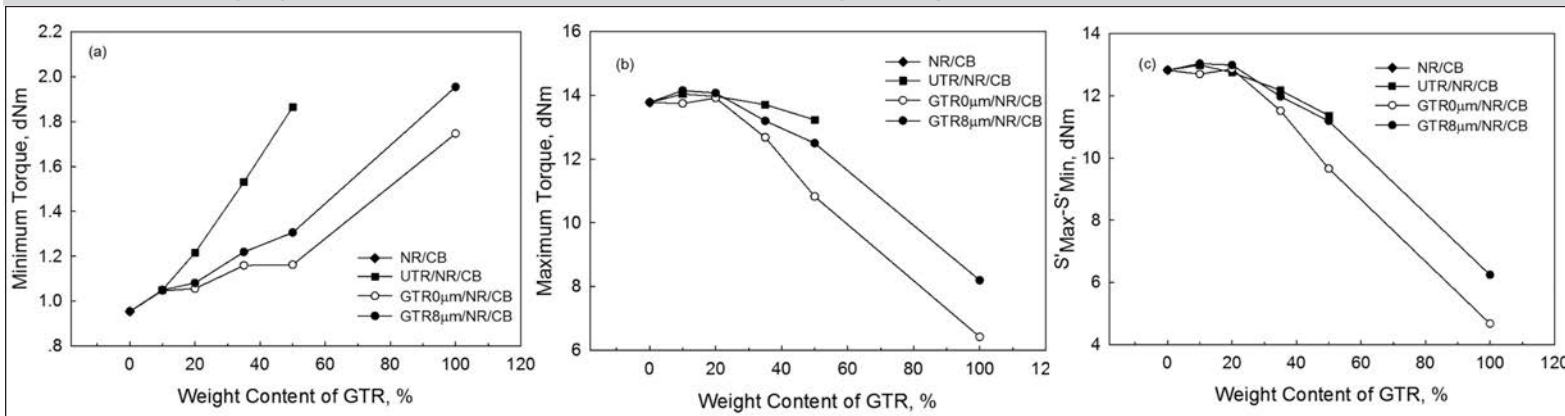
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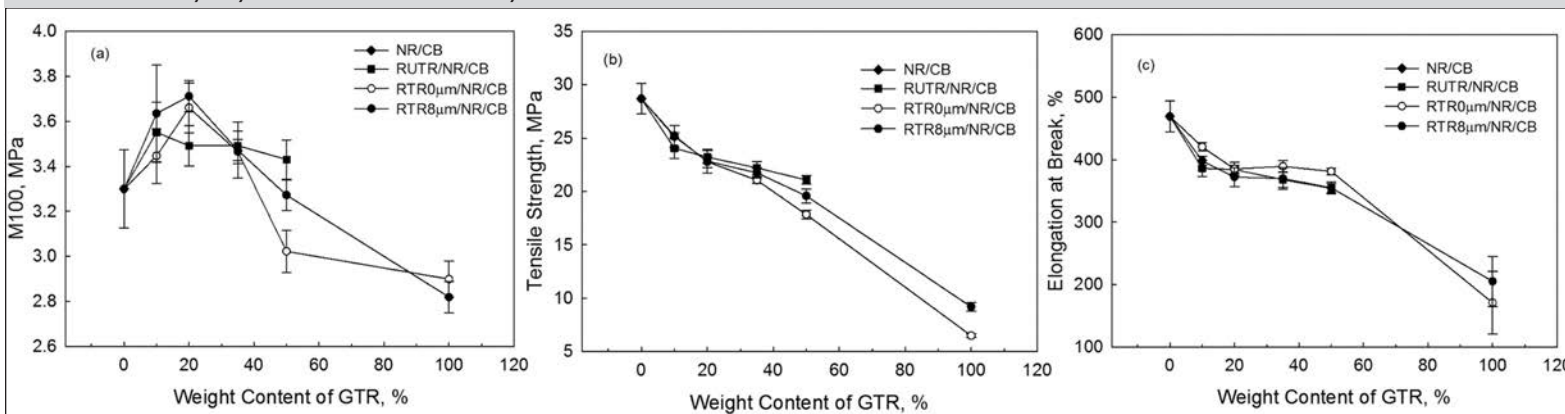
**Fig. 9: The stress-strain curves of revulcanized untreated and devulcanized GTR/NR/CB blends at different blending ratios and NR/CB, GTR0 $\mu$ m and GTR8 $\mu$ m vulcanizates.**



**Fig. 8: Minimum torque (a), maximum torque (b) and difference between the maximum and minimum torque (c) vs. weight content of GTR of untreated and devulcanized GTR/NR/CB blends. Value at zero content of GTR refers to NR/CB compound.**



**Fig. 10: Modulus at 100% elongation (a), tensile strength (b) and elongation at break (c) vs. weight content of GTR of revulcanized untreated and devulcanized GTR/NR/CB blends. Values for NR/CB vulcanizates are also shown.**





# Joe Walker: Dwindling supply of U.S.-made rubber chemicals a national security risk

By Erin Pustay Beaven

Rubber News Staff

COLUMBUS, Ohio—Joe Walker isn't holding back. Particularly when it comes to the rubber industry.

Because rubber, he said, holds the world together.

The parts and goods that the rubber industry manufactures may not always be apparent to consumers, but those parts are critical to their everyday lives.

"When you buy an automobile, the only thing you see that's rubber are the tires," Walker, president of Elastomer Technologies, said during his presentation at the ACS Rubber Division's Spring Technical Meeting. "You don't see the other 2,000 rubber parts that go into making that engine function. And it is the same with most of the parts that our industry produces. We create non-obvious, silent, invisible technology."

Invisible? Maybe. But critical? Most certainly.

That's why Walker continues to sound the alarm about looming shortages of key rubber chemicals, essential ingredients to the compounds for the parts that keep the world moving, healthy, fed and entertained.



Rubber News photo by Erin Pustay Beaven

**Industry veteran Joe Walker continues to sound the alarm on a looming shortage of essential chemicals for rubber products.**

"Think about what it would be like if you couldn't move goods from coast-to-coast," he said. "That would be truck tires, aircraft tires, seals, O-rings, gas-kets."

"Think about not being able to have a procedure done because there is no IV tubing or there are no catheters."

Those, he contends, are the things at risk if nothing is done to boost manufacturing of those chemicals in the U.S., where demand for them is growing at a

rate of more than 16 percent per year.

And the chemical supplies most concerning to Walker are cure chemicals and antidegradants.

"These chemicals improve quality, they are really an indispensable part," Walker said. "You cannot have the rubber article without them."

"In the rubber industry, although the amount of these additives are small in the overall formulation ... you may only have one part of this or two parts of that. But they play a decisive role because without that one or three (parts), you are not able to cure rubber."

At present, U.S. demand for the chemicals is around 345,000 tons. And U.S.-based supply of those chemicals is about 25 percent shy of its demand for the rubber chemicals at 288,000 tons. And given the growth rate of that demand, Walker said the problem will only compound.

"This lack of domestic manufacturing capability places the entire U.S. rubber industry at risk and consequently, our nation is at risk," Walker said.

The supply of the imported chemicals the industry relies on is also at great risk, Walker contends, particularly when you consider geopolitical concerns.

Walker said the solution to the looming chemicals shortage is a build-up of U.S. manufacturing for those chemicals, which allows the U.S. to become less reliant on off-shore production—particularly production in China.

But the rubber industry also needs to be its own advocate. Companies must work with customers to stabilize and shorten their supply chains.

"Involve your customers and engage them in risk mitigation activities," Walker said. "Let them know ... raise awareness. Build compounds and compositions using as much dual-sourced and U.S.-based products as you can."

He also encouraged everyone to write their representatives to make them aware of the importance of rubber goods. Because rubber products are essential to daily life in the U.S., Walker said any significant disruptions to the production of rubber products raise national security risks—think: exam gloves during the pandemic.

"Contact your people in Congress, make sure they understand the seriousness of the supply issue and make sure they understand the risk of doing nothing," Walker said. "Help them recognize that it's a national security problem."

## Tire

Continued from page 18

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**Fig. 11: Abrasion loss vs. weight content of GTR of revulcanized untreated and devulcanized GTR/NR/CB blends.**

