

# Thermoplastic Elastomeric Composition based on Maleic Anhydride–Grafted Ground Rubber Tire

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**ABSTRACT:** Ground rubber tire (GRT) powder was maleated in an internal mixer using maleic anhydride and dicumyl peroxide at 160°C. Maleated GRT was characterized by using X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, wet-tability, and differential scanning calorimetry. The physical properties of the dynamically vulcanized 60 : 40, rubber : plastic composition based on acrylated high-density polyethylene as the plastic phase and ethylene propylene diene rubber containing maleated GRT as the rubber phase were found to be greater than the corresponding composition containing nonmaleated GRT. The blend was found to be reprocessible, like thermoplastic elastomers. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 370–378, 2002; DOI 10.1002/app.10348

**Key words:** ground rubber tire; maleated ground rubber tire; acrylated HDPE; EPDM rubber; thermoplastic elastomer; recycling

## INTRODUCTION

The recycling of waste tire rubber is a global problem for environmental and economic reasons. Ground rubber tires, commonly called GRT, cannot be used in large quantity in a rubber compound because of poor mechanical properties and processability.<sup>1</sup> A scope for large-volume use of GRT lies in thermoplastics, with an aim of producing impact-resistant plastics and thermoplastic elastomers.<sup>2–3</sup> The properties of GRT-filled thermoplastics depend on the nature of the GRT, the plastic matrix, GRT loading, and the extent of adhesion between GRT and the plastics.<sup>4–5</sup> Baker and coworkers<sup>2,4,6,7</sup> reported the use of several compatibilizers and surface treatment of GRT for improved adhesion between GRT and thermoplastic matrices, Rodriguez<sup>8</sup> used a silane-coupling agent for enhancement of mechanical prop-

erties of GRT/plastic composites. Pramanik et al.<sup>9</sup> prepared melt-mixed GRT/plastic composites having good impact properties. Luo and Isayev<sup>10</sup> used maleic anhydride-grafted polypropylene (PP) as a compatibilizer for impact-resistant PP composites containing ultrasonically devulcanized GRT. Thermoplastic elastomeric compositions containing reclaimed rubber were also reported by Nevatia<sup>11</sup> and Al-Malaika et al.<sup>12</sup> Phadke and De found that virgin rubber acts as an adhesion promoter in a GRT/plastic composite and that incorporation of natural rubber (NR) increases the toughness of a GRT–PP composite.<sup>13</sup> An earlier communication<sup>14</sup> reports the preparation of a thermoplastic elastomeric composition based on a GRT/ethylene propylene diene rubber (EPDM)/acrylated high density polyethylene (A-HDPE) blend in the ratio of 68 : 30 : 40 parts by weight, 68 parts of GRT containing 30 parts of rubber hydrocarbon making a total rubber : plastic ratio of 60 : 40. It is believed that surface modification of GRT imparts better physical properties of the GRT/plastic composites through improved adhesion between the compo-

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**Table I Description of the Materials Used**

Material	Characteristics
Cryogenically ground rubber tire (GRT), obtained from Recovery Technology Inc., Ontario, Canada.	Particle size: 160–205 $\mu\text{m}$ , Composition: <sup>23</sup> rubber, 44%; carbon black, 27%; ash, 17%; acetone extractable volatiles, 12%
EPDM rubber (Royalene 525) obtained from Uniroyal Chemical Co, Naugatuck, CT	Ethylene content, 58%, $\text{ML}_{1+4}$ at 125°C, 65; density, 0.89
Ethylene-co-acrylic acid (A-HDPE) (Polybond 1009) obtained from Uniroyal Chemical Co.	Acrylic acid content, 6 mol%; $M_w$ , 9700; density, 0.95; MFI, 6 g/10 min at 190°C
Dicumyl Peroxide (DCP), obtained from Aldrich Chemical Company Inc. Milwaukee, WI.	98% pure.
Maleic Anhydride, obtained from Loba Chemie Pvt. Ltd., Mumbai, India	99% pure; melting point, 50–53°C.

nents. Waddell et al.<sup>15</sup> reviewed different surface modification techniques of polymers. Adam et al.<sup>16–17</sup> and Fuhrmann et al.<sup>18</sup> reported on the modification of waste rubber by grafting of monomers onto it. Grafting of maleic anhydride (MA) is a well-established and commercially exploited technique for modification of polymers.<sup>19–22</sup> This work deals with the maleation of GRT and the characterization of maleated GRT by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and surface wettability studies. Next, maleated GRT is used as a replacement for GRT in the thermoplastic elastomeric composition based on EPDM/GRT/A-HDPE.

## EXPERIMENTAL

### Materials

Details of materials used are shown in Table I.

### Maleation of GRT

Acetone extractables in GRT were first removed by acetone extraction,<sup>23</sup> using a Soxhlet apparatus. On the basis of the results of earlier studies on maleation of EPDM and polyethylene<sup>19–20</sup> and of the results of preliminary experiments on the maleation of GRT using different concentrations of MA and dicumyl peroxide (DCP), the loadings of MA and DCP were optimized. Five parts of maleic anhydride per 100 parts of rubber hydrocarbon content in GRT, and 0.2 parts of rubber (phr) of DCP were mixed in Brabender Plastimeter PLE 330 (Brabender, Duisburg, Germany) at 160°C and a screw speed of 60 rpm. After 5 min of mixing, the material was dumped out. The

same maleation technique also was applied to nonextracted GRT. GRT and its maleated derivative are abbreviated as GRT and m-GRT, respectively.

### Preparation of Rubber Sheet from GRT Powder

Compression molding of GRT powders was carried out at 120°C for 2 min at 6 MPa pressure in a hydraulic press between two teflon sheets to get a smooth sheet of GRT. After molding was over, the platens were cooled under pressure by water circulation through the platens of the press.

### X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) results were obtained using a VG scientific ESCA Lab MKII spectrometer (East Grinstead, England), employing an excitation radiation of 1250 eV (Mg K $\alpha$ ). 10  $\times$  10-mm samples cut from molded GRT and maleated GRT sheets were mounted with double-sided adhesive tape onto the probe tip. The working pressure in the spectrometer was 2  $\times$  10<sup>-9</sup> torr. All spectra were referenced to the C<sub>1s</sub> peak for carbon, which was assigned a value of 284.5 eV, and were recorded at an electron take-off angle of 90° with respect to the polymer surface. XPS peaks in the spectra were deconvoluted using a standard Gaussian multiple peak analyzer program. Atomic concentrations of the elements were calculated from their peak areas and standard photoionization cross sections.<sup>24</sup>

### Diffuse Reflectance Infrared Fourier Transform Spectral Analysis

Fourier transform infrared (FTIR) spectra of the modified and unmodified GRT particles were

taken in the range of 3900–400  $\text{cm}^{-1}$  using a Nicolet Nexus infrared spectrophotometer (Madison, WI) operating in diffuse reflectance infrared Fourier transform spectral (DRIFT) mode. 64 scans were taken at a resolution of 1  $\text{cm}^{-1}$ .

### Differential Scanning Calorimetric Study

Differential scanning Calorimetric (DSC) studies of the GRT samples (ca. 10 mg) were done in a DuPont Differential Scanning Calorimeter-910 (Delaware) at a heating rate of 20°C/min in nitrogen atmosphere in the temperature range of –120° to 100°C. A shift in baseline was assigned to the glass–rubber transition.

### Wettability

The wettability of the GRT powders was measured as the ability to wick a solvent through the porous column of the powders. The powders were tapped and filled in a scaled cylindrical glass tube (5 mm inner diameter and 45 mm long) with one end sealed with nylon nonwoven fabric. The tube was vertically placed, and the fabric sealed end was contacted with a solvent in a beaker. As the surface of the nylon fabric touched the solvent surface, the solvent penetrated up into the column of the powders by capillary action. The weight of the penetrating solvent increased with increasing time of contact up to a certain time. The weight and height of the penetrating solvent were measured using an electronic balance and scale on the tube surface as a function of contact time.

The contact angle of the solvent on the surface of the GRT powder and the surface energy of the GRT powders were calculated from the Washburn equation<sup>25</sup> using the same method reported earlier.<sup>26,27</sup>

### Blend Preparation and Molding

EPDM and GRT in 30 : 68 parts by weight were mixed in a Brabender Plasticorder PLE 330 for 5 min at room temperature (30°C) using a camtype rotor at 60 rpm. 68 parts of GRT contains 30 parts of rubber hydrocarbon; therefore, EPDM/GRT blend in a 30/68 composition consists of 60 parts of rubber hydrocarbon total. The mix was then milled in a Laboratory two-roll mill (6" × 13", Schwabenthan, Berlin, Germany) at a 2-mm nip setting and then sheeted out. Next, 40 parts of A-HDPE were taken in the Brabender at 160°C at a rotor speed of 30 rpm. After 2 min, the EPDM/GRT mix (prepared earlier) was added and mixed

at 60 rpm for 2.5 min. DCP (0.6 parts) was then added and allowed to mix for additional 1.5 min. The blends were sheeted out at a 2-mm nip gap on a two-roll mill shortly after they were taken out from the Brabender. The sheeted 60/40 rubber/plastic blends were remixed in the Brabender at 160°C for 2 min at a rotor speed of 60 rpm and finally sheeted out on the mill. A similar method was followed in preparing composites of maleated GRT/EPDM/A-HDPE.

The sheeted-out stocks were compression molded in an electrically heated hydraulic press at 170°C for 2 min at 6 MPa pressure and then cooled under pressure by water circulation through the platens.

### Measurement of Physical Properties

Dumbbell-shaped tensile specimens and un-nicked 90°-angle-tear test pieces were punched out from the molded sheets. Tensile strength, modulus, elongation at break, and tensile set at 100% elongation were measured on these tensile specimens according to ASTM D412-98a specification in a Zwick Universal Testing Machine (UTM, Ulm, Germany) model 1445 at a strain rate of 500 mm/min at 25°C. Tear strength of the blend specimens were measured according to ASTM D 624-98 in a Zwick UTM 1445. Tensile toughness or work of rupture was measured from the area under the stress–strain curve. Hardness of 10-mm-thick specimens was measured using Shore-A Durometer (New York). An average of three results is reported.

### Reprocessability

Reprocessability of the blends was done by the remixing and remolding of the specimens aged for 2 months at room temperature followed by measurement of the physical properties. The process was repeated twice.

## RESULTS AND DISCUSSION

### Characterization of Maleated GRT

#### *X-ray Photoelectron Spectroscopy (XPS)*

$\text{C}_{1s}$  and  $\text{O}_{1s}$  excitation peak areas, the corresponding binding energies of the deconvoluted peaks, and the relative element (%) in GRT and m-GRT are reported in Table II. Deconvoluted satellite peaks of  $\text{C}_{1s}$  and  $\text{O}_{1s}$  are shown in Figure 1(a–b). It was observed that the unmodified GRT sample

**Table II X-ray Photoelectron Spectroscopy results of Ground Rubber Tire (GRT) and m-GRT**

Sample	$C_{1s}$ satellite peak areas <sup>a</sup>			$O_{1s}$ satellite peak areas <sup>a</sup>		Relative Element %	
	$C_{1s}$ First Peak	$C_{1s}$ Second Peak	$C_{1s}$ Third Peak	$O_{1s}$ First Peak	$O_{1s}$ Second Peak	C	O
GRT	2334 (284.3 eV)	23 (287.3 eV)	000	654 (531.7 eV)	000	91.1	8.9
m-GRT	2159 (284.3 eV)	320 (285.8 eV)	53 (287.9 eV)	843 (531.8 eV)	35 (533.2 eV)	89.1	10.9

<sup>a</sup>Peak areas are in arbitrary units. Values in parentheses are the binding energies of the peak

shows a core  $C_{1s}$  peak (284.3 eV) (Fig. 1[a]) and a very small satellite peak at 287.3 eV. This suggests that most of the carbon atoms are of same type. The small peak caused by the shift of the  $C_{1s}$  excitation at higher energy arises from the presence of oxygen-containing groups ( $>C=O$ ,  $-COO-$ ) on the carbon black surface and/or on polymer chains generated by oxidation during processing/curing.<sup>27</sup> Maleation of GRT generates three types of carbon atoms (Fig.1[a]). The major component at 284.3 eV (lowest binding energy) is a result of the carbon atoms of the unchanged environment. The binding energies of the other two  $C_{1s}$  excitations are found to be 285.8 and 287.9 eV. The first shift to 285.8eV ( $\sim 1.5$  eV) is caused by the presence of the C–O group. The second shift to 287.9 eV ( $\sim 3.6$  eV) is caused by the combined effect of originally present oxygen-containing groups and anhydride ( $-CO-O-OC-$ ) or carboxylic acid moiety representing carbons of C=O bonds. The intensity of the peak at 285.8 eV is significantly higher than that of the peak at 287.9 eV (Fig. 1[a]). This indicates that the anhydride or acid group may form a salt by interacting with the metallic oxide (ZnO)<sup>23</sup> present in the GRT. The  $O_{1s}$  region of the unmodified GRT does not show any second component, indicating that all oxygen atoms are of the same type. Maleation of GRT creates a satellite  $O_{1s}$  peak at a higher energy (533.2 eV) (Fig. 1). The lower-energy (531.8 eV) peak is caused by the ketonic oxygen ( $>C=O$ ). The high-energy excitation at 533.2 eV is attributed to the anhydride oxygen  $-OC-O-CO-$  bound to adjacent carbon atoms by single bonds and the C–O bonds involved in the salt formation postulated earlier. Table II shows that after maleation, relative oxygen percentage is increased with a decrease in relative carbon percentage.

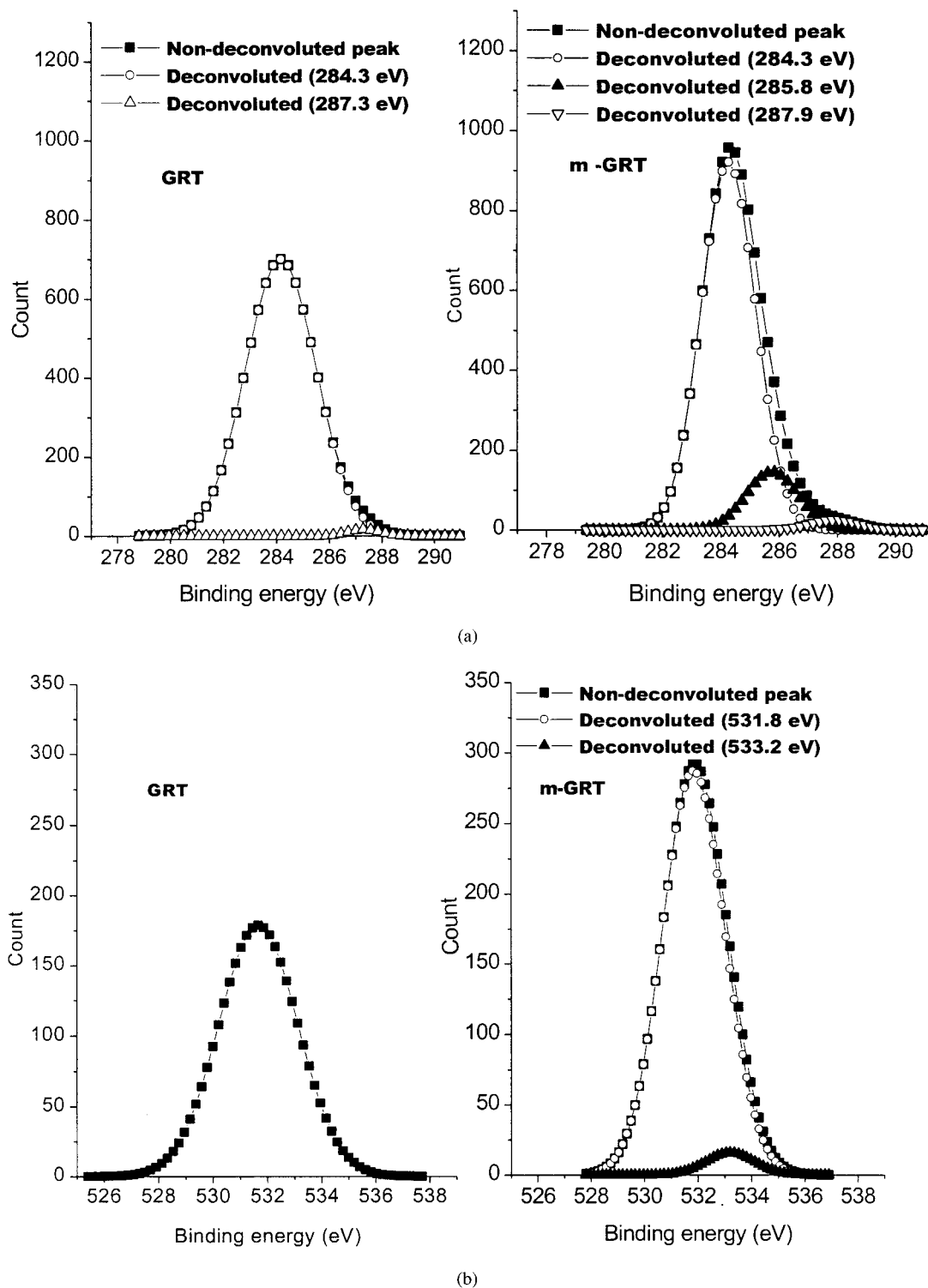
#### Diffuse Reflection Infrared Spectroscopy

DRIFT spectra of m-GRT and GRT are shown in Figure 2. GRT exhibits a broad peak with a max-

imum at  $1645\text{ cm}^{-1}$ , having shoulders at  $1735$  and  $1551\text{ cm}^{-1}$ . This suggests the presence of different kinds of functionality like  $>C=O$  ( $1735\text{ cm}^{-1}$ , in low concentration; as formed by oxidation of rubber and/or present on the carbon black surface),  $-COO^-$  ( $1551\text{ cm}^{-1}$ , from traces of Zn stearate present in the GRT), and  $>C=C<$  ( $1645\text{ cm}^{-1}$ ), all masked together. However, maleation of GRT does not affect the peak at  $1645\text{ cm}^{-1}$  significantly but increases the peak intensity at  $1550\text{ cm}^{-1}$ . The m-GRT does not exhibit any peak around  $1780\text{ cm}^{-1}$  corresponding to the carbonyl group of maleic anhydride. This suggests that maleic anhydride moiety in the modified GRT reacts with metallic oxide (ZnO) present in the GRT to form a salt, and hence, the distinct peak at  $1550\text{ cm}^{-1}$  is observed. The peak at  $1550\text{ cm}^{-1}$  may be attributed to the carboxylate asymmetric stretching vibration.<sup>28–29</sup> The peak intensity of the peak at  $1402\text{ cm}^{-1}$  corresponding to the C–H deformation of  $>C=CH-$  decreases after the grafting of maleic anhydride moiety onto the hydrocarbon backbone. As observed in GRT, m-GRT also exhibits shoulder at  $1735\text{ cm}^{-1}$  because of the presence of ketonic moiety ( $>C=O$ ).

#### Wettability

The wicking behavior of maleated and nonmaleated GRT is shown in Figure 3. It is observed that water penetration through the column containing m-GRT is higher than that of the column packed with GRT. This indicates enhancement of hydrophilicity by the maleation of GRT. In an earlier sections, the generation of polar groups by maleation has been discussed. Penetration of formamide in the m-GRT column is also higher than that in the column of GRT. The contact angle values calculated by using the Washburn equation are found to decrease by grafting maleic anhydride onto GRT;  $\theta_{\text{water}}$  for m-GRT is  $87^\circ$ , whereas that for GRT is  $90^\circ$ ;  $\theta_{\text{formamide}}$  for m-GRT is  $68^\circ$ , but the same for GRT is  $71^\circ$ . Hence, the surface energy of GRT is changed by maleation. The polar component of the surface en-

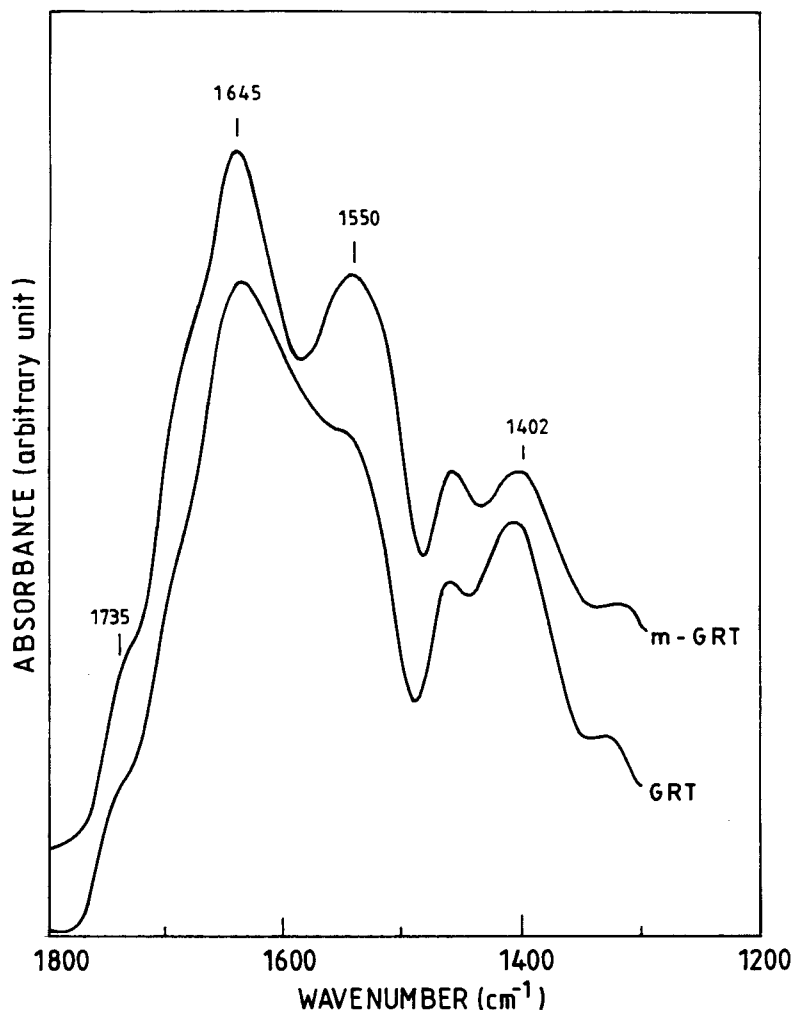


**Figure 1** (a)  $C_{1s}$  excitation peak of ground rubber tire (GRT) and m-GRT. (b)  $O_{1s}$  excitation peak of GRT and m-GRT.

ergy is found to increase from 3.89 mN/m for GRT to 4.79 mN/m for m-GRT. Total surface energy of m-GRT increases from 26.75 mN/m (for GRT) to 28.42 mN/m.

#### Differential Scanning Calorimetry

A DSC thermogram of both GRT and m-GRT are shown in Figure 4. Figure 4 shows that GRT



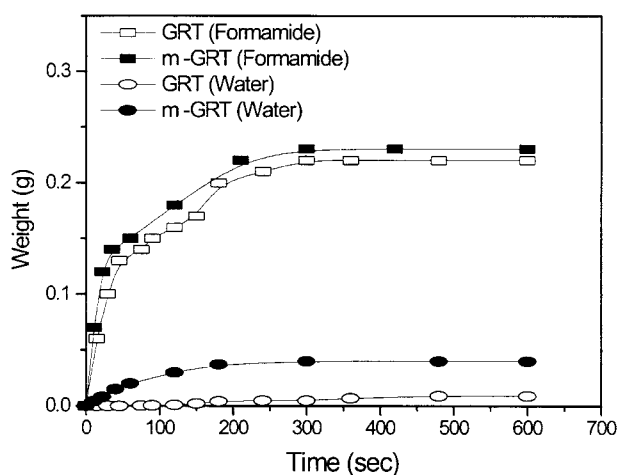
**Figure 2** Fourier transform infrared spectroscopy spectra of ground rubber tire (GRT) and m-GRT.

exhibits a broad baseline shift in the temperature range of  $-100^{\circ}$  to  $-25^{\circ}\text{C}$ , indicating a mixture of rubbers in the composition of GRT. However, m-GRT exhibits a high temperature-baseline shift in the temperature range of  $25^{\circ}$ – $80^{\circ}\text{C}$  along with the broad shift in the low-temperature range. The high-temperature transition is believed to be caused by the dissociation of the ionic clusters arising out of the salt of maleated GRT.<sup>30</sup>

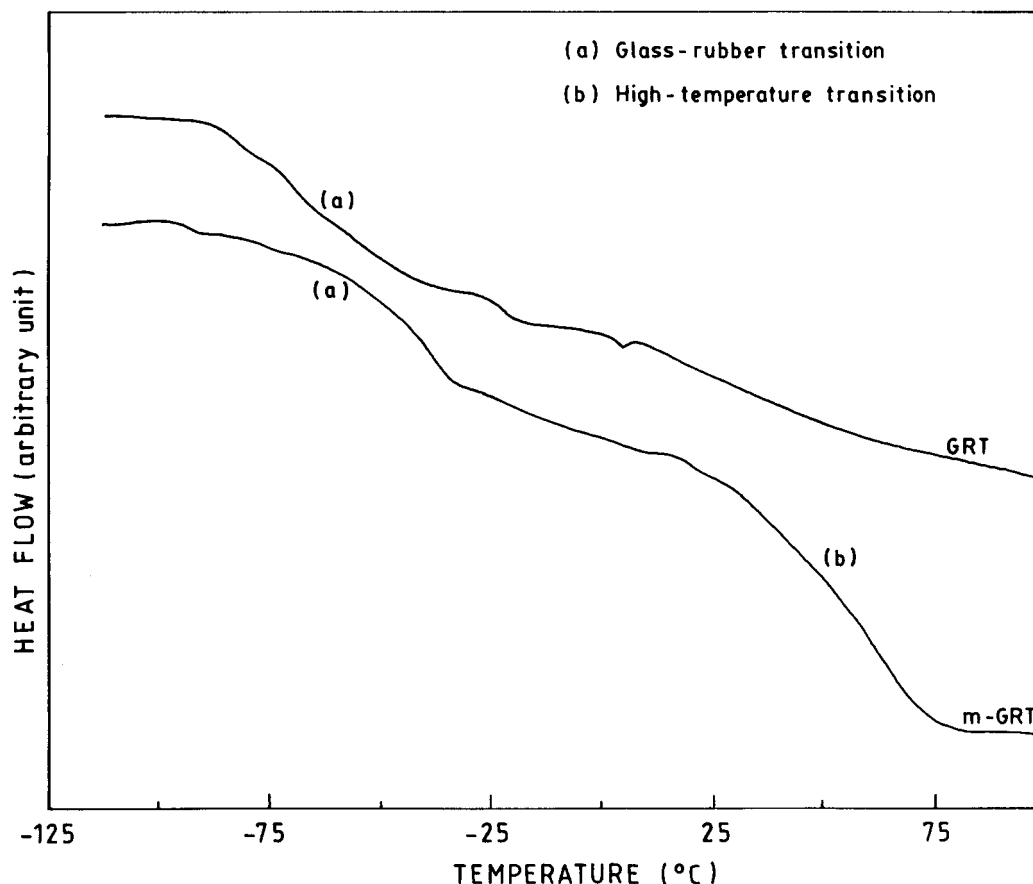
#### Properties of EPDM/GRT/A-HDPE and EPDM/m-GRT/A-HDPE Blends

##### Physical Properties

Physical properties of the 60 : 40 (rubber : plastic) thermoplastic elastomeric (TPE) composition based on EPDM (rubber) and A-HDPE (plastic), where 50% of EPDM is replaced by rubber hydrocarbon from GRT or m-GRT, are shown in Table



**Figure 3** Dynamic wicking behaviors of ground rubber tire (GRT) and m-GRT in different solvents (water and formamide).



**Figure 4** Differential scanning calorimetry thermogram of ground rubber tire (GRT) and m-GRT.

III. This ratio was chosen on the basis of the results of an earlier work.<sup>14</sup> The stress-strain curves for the composites are shown in Figure 5. It is found that by maleation of extracted GRT, the properties of the blend are improved. For example, tensile strength, Young's modulus, 100% modulus, work of rupture (tensile toughness), and tear strength are increased from 8.2 to 10.3 MPa

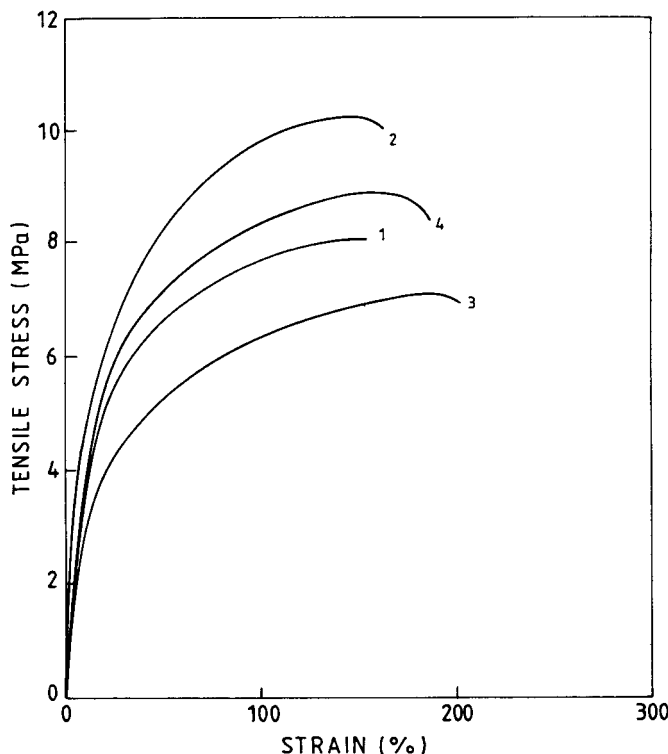
(25.6%), 36.6 to 41.2 MPa (12.5%), 7.8 to 9.9 MPa (26.9%), 4.5 to 5.9 kJ/m<sup>2</sup> (31.1%), and 56.6 to 62.5 kN/m (10.4%), respectively. Values in the brackets show percentage increase in the properties of the TPE composition on maleation. Shore A hardness of the blend also increases slightly from 82 to 85 unit. Tension set (percentage) at 100% elongation is found to be constant at 24%–26% for both

**Table III** Physical Properties of the 60/40 Rubber/Plastic Blends Containing Ground Rubber Tire (GRT) and m-GRT<sup>a</sup>

GRT Type in the Blend Composition <sup>b</sup>	Tensile Strength (MPa)	Ultimate Elongation (%)	Young's Modulus (MPa)	100% Modulus (MPa)	Work of Rupture (kJ/m <sup>2</sup> )	Tear Strength (kN/m)	Tension Set at 100% Elongation (%)	Hardness (Shore A)
GRT	8.2 (7.1)	152 (203)	36.6 (22.3)	7.8 (6.2)	4.5 (5.3)	56.6 (60.8)	24 (26)	82 (80)
m-GRT	10.3 (9.0)	158 (190)	41.2 (37.2)	9.9 (8.5)	5.9 (6.2)	62.5 (62.0)	24 (26)	85 (82)

<sup>a</sup>Values in parentheses indicate the properties of the corresponding blends based on GRT and m-GRT, where GRT was not acetone extracted to remove plasticizers and oils.

<sup>b</sup>EPDM/GRT/A-HDPE 30/68/40, parts by weight.



**Figure 5** Stress-strain curves of the blends containing acetone-extracted ground rubber tire (GRT), maleated derivative of acetone-extracted GRT, GRT (nonextracted), and maleated derivative of GRT (nonextracted).

maleated and nonmaleated composites, indicating the thermoplastic elastomeric nature of the compositions. It is probable that the salt formed by the interaction of m-GRT with ZnO provides a stronger interaction than the unmodified GRT in the thermoplastic elastomeric matrix based on the A-HDPE/EPDM blend.<sup>29</sup> Maleation of nonextracted GRT was also attempted, and similar 60 : 40 (rubber : plastic) compositions were prepared. The physical properties of these blends are also given in Table III. It was observed that the composition containing acetone-extracted GRT shows higher tensile strength, Young's modulus, and 100% modulus but lower ultimate elongation and tear strength than the corresponding nonextracted counterpart because of the removal of the oils and stearic acid acting as a plasticizer in the blend. However, nonextracted GRT can undergo successful maleation, and the composite containing its maleated form exhibits higher properties than its nonmaleated counterpart (e.g., tensile strength, Young's modulus, and work of rupture are raised from 7.1 to 9.0 MPa [26.8%], 22.3 to 37.2 MPa [66.8%], and 5.3 to 6.2 kJ/m<sup>2</sup> [16.9%], respectively). It is also observed from Table III that ultimate elongation and tensile set properties are hardly affected by maleation of GRT.

### Reprocessability

Reprocessability of the blend containing maleated GRT has been studied by remixing and remolding the specimens, aged for 2 months at room temperature. Physical properties of the reprocessed blends are shown in Table IV. It is observed that the properties decrease marginally with an increase in the number of processing cycles. But the decrease in properties is less than 5% of the original properties. Thus, results of the reprocessability studies indicate that the compositions are thermoplastic elastomeric in nature.

### CONCLUSIONS

GRT can be maleated in a Brabender Plasticorder. XPS and FTIR results show that the maleic anhydride moiety in the grafted GRT exists mainly in the ionic form because of salt formed by the interaction between the unreacted ZnO remaining in GRT and the acid anhydride of the modified GRT. DSC results indicate the formation of ionic cluster, which dissociates in the high-temperature range (~60°C). By maleation, the hydrophilicity of GRT is enhanced and the surface energy of GRT is



**Table IV Physical Properties of Reprocessed Blends Containing Maleated-Ground Rubber Tire (m-GRT)<sup>a</sup>**

Processing Cycle	Tensile Strength (MPa)	Ultimate Elongation (%)	Young's Modulus (MPa)	100% Modulus (MPa)	Tear Strength (kN/m)
1	10.3 (9.0)	158 (190)	41.2 (37.2)	9.9 (8.5)	61.5 (63.0)
2	10.0 (8.7)	151 (178)	41.5 (35.0)	9.8 (8.3)	60.0 (61.9)
3	9.8 (8.9)	140 (163)	40.8 (35.5)	9.4 (8.3)	58.5 (59.5)

<sup>a</sup>Values in parentheses indicate the properties of the corresponding blend based on m-GRT, where GRT was not acetone extracted to remove plasticizers and oils.

increased. Maleated GRT in the thermoplastic elastomeric composition based on 60 : 40 EPDM : A-HDPE, where 50% of the rubber phase is replaced by the rubber hydrocarbon content of GRT, imparts greater physical properties than the non-maleated counterpart. Removal of acetone extractables from GRT lowers ultimate elongation and tear strength but enhances the tensile strength and modulus of the thermoplastic elastomeric composition. Maleic anhydride derivative of the nonextracted GRT exhibits higher ultimate elongation and tensile toughness but lower tensile strength and modulus in the blend composition compared with the TPE composition containing the maleic anhydride derivative of extracted GRT.

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## REFERENCES

- Klingensmith, B. *Rubber World* 1991, 203(6), 16.
- Oliphant, K.; Baker, W. E. *Polym Eng Sci* 1993, 33, 166.
- Mennig, G.; Michael, H.; Rzymiski, W. M.; Scholz, H. *Int Polym Sci Technol* 1997, 24, T/100.
- Rajalingam, P.; Sharpe, J.; Baker, W. E. *Rubber Chem Technol* 1993, 66, 664.
- Deanin, R. D.; Hashemiolya, S. M. *Polym Mater Sci Eng* 1987, 8, 212.
- Pramanik, P. K.; Baker, W. E. *Plast Rubber Compos Process Appl* 1995, 24, 229.
- Rajalingam, P.; and Baker, W. E. *Rubber Chem Technol* 1992, 65, 908.
- Rodriguez, E. L. *Polym Eng Sci* 1988, 28, 1455.
- Pramanik, P. K.; Dickson, B. Presented at ANTEC '95, Society of Plastics Engineers, Boston, MA, May 7–11, 1995.
- Luo, T.; Isayev, A. I. *J Elast Plast* 1998, 30, 133.
- Nevatia, P. B. Tech. Thesis, Indian Institute of Technology, Kharagpur, 1995.
- Al-Malaika, S.; Amir, E. J. *Polym Deg Stab* 1989, 26, 31.
- Phadke, A. A.; De, S. K. *Polym Eng Sci* 1986, 26, 1079.
- Naskar, A. K.; Bhowmick, A. K.; De S. K. *Polym Eng Sci* 2001, 41, 1087.
- Waddell, W. H.; Evans, L. R.; Gillick, J. G.; Shuttleworth, D. *Rubber Chem Technol* 1992, 65, 687.
- Adam, G.; Sebenik, A.; Osredkar U.; Veksli, Z.; Ranogajec, F. *Rubber Chem Technol* 1990, 63, 660.
- Adam, G.; Sebenik, A.; Osredkar U.; Ranogajec, F.; Veksli, Z. *Rubber Chem Technol* 1991, 64, 133.
- Fuhrmann I.; Karger-Kocsis, J. *Plast Rubber Compos Process Appl* 1999, 28, 500.
- Chowdhury, N. R.; Bhowmick, A. K. *J Appl Polym Sci* 1989, 38, 1091.
- Sen, A. K.; Mukherjee, B.; Bhattacharyya, A. S.; De, P. P.; Bhowmick, A. K. *Die Angewandte Chemie* 1991, 191, 5.
- Coran, A. Y. *Rubber Chem Technol* 1988, 61, 281.
- Roy, A. K.; Jha, A.; Bhowmick, A. K. *J Elast Plast* 1997, 29, 201.
- Naskar, A. K.; Pramanik, P. K.; Mukhopadhyay, R.; De, S. K.; Bhowmick, A. K. *Rubber Chem Technol* 2000, 73, 902.
- Chan, C. M. In *Polymer Surface Modification and Characterisation*; Hanser: Munich, 1994; p. 119.
- Washburn, E.W. *Phys Rev* 1921, 17, 273.
- Yang, Y.; Zograf, G.; Miller, E. E. *J Colloid Interface Sci* 1988, 122, 35.
- Naskar, A. K.; De, S. K.; Bhowmick, A. K. *Rubber Chem Technol* 2001, 74, Sept.–Oct.
- Socrates, G. In *Infrared Characteristic Group Frequencies*; Wiley-Interscience: New York, 1980; p.65.
- Dutta, S.; De, S. K. *J Appl Polym Sci* 1996, 61, 177.
- Mondal, U. K.; Tripathy, D. K.; De, S. K. *Polym Eng Sci* 1996, 36, 283.