

# Partial Replacement of NR by GTR in Thermoplastic Elastomer Based on LLDPE/NR Through Using Reactive Blending: Its Effects on Morphology, Rheological, and Mechanical Properties

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**ABSTRACT:** Attempts have been made to use different amount of ground tire rubber (GTR) powder as a partial substitute for natural rubber (NR) in thermoplastic elastomer based on linear low-density polyethylene (LLDPE, 60 wt%) and NR (40wt%). Maleic anhydride (MA) and dicumyl peroxide (DCP) were used, during melt mixing of the compound, to modify GTR and vulcanize the rubber phases of the blends. Morphology of the blends was studied by scanning electron microscopy and rheological behavior investigated through rheomechanical spectroscopy. Mechanical properties of the blends were also measured, and the effect of GTR concentration on properties was evaluated. Obtained results showed that modification of GTR with MA and using DCP in the blends containing GTR improves the bonding between GTR and matrix. This

leads to a distinctive rheological behavior and enhances tensile strength and elongation at break compared to its corresponding simple blend. It can be said that using of MA and DCP during melt mixing of thermoplastic elastomers based on LLDPE/NR containing GTR, concludes to a better dispersion of GTR and formation of morphology similar to that of a dynamic vulcanized thermoplastic elastomer, which improves interfacial bonding between phases and causes a dramatically increase in mechanical properties. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2416–2422, 2010

**Key words:** blending; waste; compatibilization; vulcanization; mechanical properties

## INTRODUCTION

Thermoplastic elastomers are a new class of materials in which the properties of vulcanized rubber are embodied with the ease of processing of thermoplastics. These materials are replacing many of the conventional rubbers as well as leading thermoplastics. Thermoplastic vulcanizates (TPVs) are a particular family of thermoplastic elastomers (TPEs), which are produced through crosslinking of rubber phase during melt mixing of nonmiscible blends of rubbers and thermoplastic materials. TPVs exhibit enhanced elasticity, oil resistance, and low compression set in comparison to simple blends of rubbers and thermoplastic materials.<sup>1–3</sup> For both economical and ecological reasons, fully or partly replacement of rubber phase of TPEs by waste rubber powder is very important.<sup>4,5</sup>

With development of rubber industry, a lot of waste rubber is produced in the world every year. So, recycling of the waste rubber in special tires

which are the main source of waste rubbers is a great challenge in recent years. Developed countries have been paying great attention to the comprehensive utilization of the discarded tires.<sup>6–8</sup>

The major effort in tire rubber recycling is to reuse it as a finely ground crumb. Rubber part of the used tires can be grounded to small particles, known as ground tire rubber (GTR).<sup>5,9</sup> It may be used as a filler or modifying agent in polymeric compounds as well as in thermoplastic elastomers. GTR, due to its crosslinked structure, is not miscible with the polymer matrix in a compound. Therefore; the interfacial adhesion between the GTR particles and the matrix is poor.<sup>10</sup> Different methods can be used to enhance compatibility between GTR and polymeric phases of a compound. Modification of GTR through using sulfuric acid as an etching material, silane as coupling agent, and trichloroisocyanuric acid (TCI) for chlorination of GTR have been reported by Colom et al.<sup>11</sup> Lopez-Cuesta and coworkers used solution of potassium permanganate and  $\gamma$ -irradiation to oxidize GTR. They mixed the modified GTR with high-density polyethylene (HDPE) and concluded that oxidation cannot compensate for the lack of chemical reactivity of GTR powders.<sup>12</sup> Karger-Kocsis and coworkers used GTR in thermoplastic elastomers

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TABLE I  
Composition of the Blends

Blend component (wt %)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
LLDPE	100	60	60	60	60	60	60	60	60	60	60
NR	–	40	35	30	20	–	40	35	30	20	–
GTR	–	–	5	10	20	40	–	5	10	20	40
MA	–	–	–	–	–	–	3	3	3	3	3
DCP	–	–	–	–	–	–	0.5	0.5	0.5	0.5	0.5

based on LDPE in combination with styrene butadiene rubber (SBR), NR, or ethylene propylene diene monomer (EPDM) as the rubber phase.<sup>13</sup> Using of maleic anhydride (MA), methyl methacrylate and butyl acrylate,<sup>9</sup> ethylene vinyl acetate (EVA),<sup>14,15</sup> acrylamide (AAM),<sup>16</sup> and ethylene-propylene-diene terpolymer, dicumyl peroxide (DCP), and dimethyl silicone oil<sup>17</sup> in thermoplastic elastomers contain GTR have also been reported.

In this study different amounts of GTR were used as a partial substitute of natural rubber (NR) in thermoplastic elastomer based on linear low-density polyethylene (LLDPE)/NR (60/40 wt %) and the possibility of replacing of NR with GTR to obtain a blend with acceptable mechanical performance was evaluated. MA and DCP were used as a modifier and curing agent, respectively. The effects of GTR content, GTR modification, and dynamic vulcanization of rubber phases during reactive melt blending upon mechanical properties, morphology, and rheological behavior of the blends were studied.

## EXPERIMENTAL

### Materials

LLDPE was obtained from Iranian Petrochemical Industry. The used LLDPE was a general purpose extrusion grade one (melt flow rate at 190°C and 2.16 kg load 0.9 g/10 min, density 0.913 g/cm<sup>3</sup>). GTR powder was provided by Isatiss Co. (a subsidiary of Yazd Tire Co., Iran). Its maximum particle was 400 μm and the presence of double bonds on the surface of GTR was evidenced by infrared analysis. Ribbed smoked sheet in the name of RSS1 from Thailand was used as NR. MA (LUKEM, china) as a compatibilizer, DCP 99% as an initiator and cross-linking agent, and analytical grade of toluene as the solvent were used in this work. All materials were used as received.

### Preparation of the blends and specimens

The composition of the blends has been listed in Table I. A Brabender internal mixer (W50, Germany) was used to prepare blends. For the blends which contained LLDPE, NR, and GTR, to achieve better distribution of the ground rubber powder in rubber

phase, mixing of the components was carried out at two stages. At the first stage, a masterbatch of NR/GTR was prepared by mixing of NR, GTR with 25% of the used MA in an internal mixer. The mixer was used at temperature of 60°C and rotor speed of 60 rpm and 85% of the mixer volume filled with the compound during melt mixing. At the second stage, the masterbatch was mixed with other ingredients to prepare TPE.

TPEs were prepared in an internal mixer at 150°C and a rotor speed of 60 rpm. In all cases, polyethylene was first fed in to the mixer and allowed to melt, followed by addition of MA. Then GTR and NR or the prepared masterbatch, depending on the composition of the blend, was added. For the blends which contained DCP, it was added after mixing of the other components of the compound.

To prepare specimens for measuring physical and mechanical properties of the blends, compression molding process was employed by using a hydraulic press at temperature 160°C and pressure of 70 bar and blends were formed into the sheets in a standard mold.

### GTR analysis

FTIR (Bomem, Canada) was used to investigate presence of double bonds on the surface of GTR.

### Mechanical properties

Tensile properties of the molded specimens were measured according to ASTM D 412, using a computer-controlled testing machine (Santam, Iran) at a crosshead speed of 500 mm/min. The hardness of the samples was also measured on the surface of the tensile test specimens with a Shore A hardness tester according to ASTM D 2240.

To determine each property of any formulation at least three specimens were tested and the average values were reported.

### Morphological study

Morphological studies of the blends were carried out using a scanning electron microscope (Model XL300, Philips Co.). The molded specimens of the

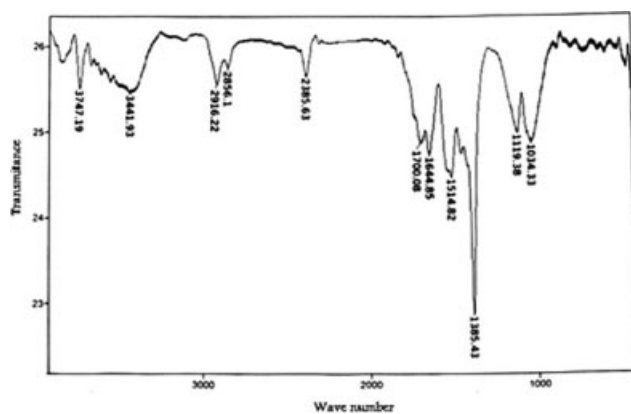


Figure 1 FTIR spectrum of the used GTR.

blends were broken in liquid nitrogen to avoid any damage or phase deformation. To facilitate the scanning electron microscopy (SEM) investigation, the uncured NR phase of the samples was extracted by using toluene. The samples were then dried in a vacuum oven at 45°C for 24 h. The dried surfaces were gold coated and then examined by SEM.

### Rheological behavior

Rheomechanical spectrometer (RMS) model UDS 200 (Paar Physica, Austria) was used to study the shear viscosity and rheological properties of the various blend samples. For these purposes the required amount of the sample was put into the rheometer without initial thermal deformation to prevent change in the sample morphology, and the experiment was carried out at a temperature of 150°C by using of a 25-mm-diameter parallel plate with 1-mm gap and the strain set at 0.1.

## RESULTS AND DISCUSSION

### Analysis of GTR

The FTIR spectrum for the used GTR is shown in Figure 1. In this figure, the peak at 1645  $\text{cm}^{-1}$  indicated presence of double bond in chemical structure of GTR, so it is expected that the used GTR can react with MA and DCP during their reactive melt blending with LLDPE/NR.

### Mechanical properties

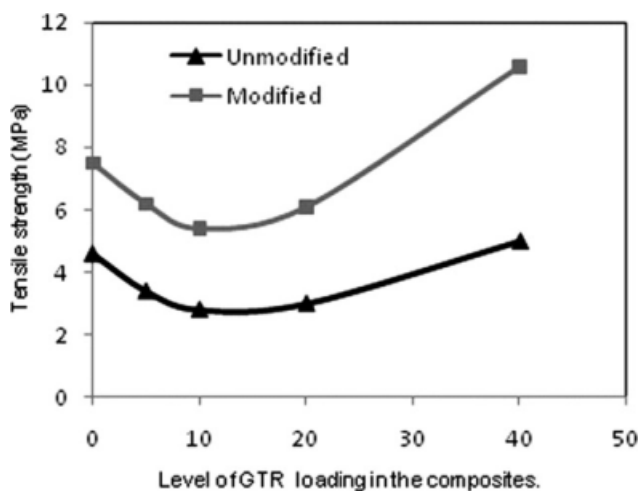
Table II shows the obtained results of measuring tensile strength, elongation at break, and hardness of the blends. These results show that introduction of 40 part NR into LLDPE leads to a great decrease of mechanical properties of LLDPE because of the poor compatibility between phases and formation of NR aggregates. Furthermore, the hardness of this blend is also lower than that of pure LLDPE.

The effect of GTR content on tensile strength and elongation at break is shown in Figures 2 and 3, respectively. These figures show that substitution of 5–10 wt % of NR phase with GTR decreases mechanical properties of LLDPE/NR blend. This is due to the poor adhesion between unmodified GTR and polymer matrix. In fact poor interfacial bonding causes making of voids at interfaces and growth of voids leads to crack formation and decreasing of tensile strength of the blends. On the other hand, in the presence of GTR particles that acts as fillers with low interactions with the matrix, the phase boundary occurring probably produce defects between the rubber molecular structures, which leads to a reduction in the tensile stress and elongation at break.<sup>18</sup> With increasing of GTR content to 20–40 wt %, tensile strength of the blends has increased. This may result from the carbon black presence in GTR that acts as active filler and increases the tensile strength. Similar results have been reported for blends based on NR/reclaimed rubber (RR) by Sombatsompop and Kumnuantip.<sup>18</sup> Figure 2 represents that substitution of NR phase with GTR decreases elongation at break due to crosslinked structure of the GTR.

Modification of GTR by MA and using DCP to provide vulcanization of rubber phases during reactive mixing of the blends causes a dramatically increase in mechanical properties (Figs. 2 and 3). For example, comparing of these results between modified (No. 10 in Table I) and unmodified (No. 5 in Table I) blends contain 20% GTR, which shows that the modified blend exhibits a tensile strength of 6.1 MPa which is two times that of unmodified blend. Modified blend also shows elongation at break equal to 201% which is 5.75 times that of similar unmodified blend. In fact reactive mixing of the components of the blend in the presence of MA and DCP increases the compatibility between phases and also ends to dynamic vulcanization of rubber phases in

TABLE II  
Mechanical Properties of the Blends

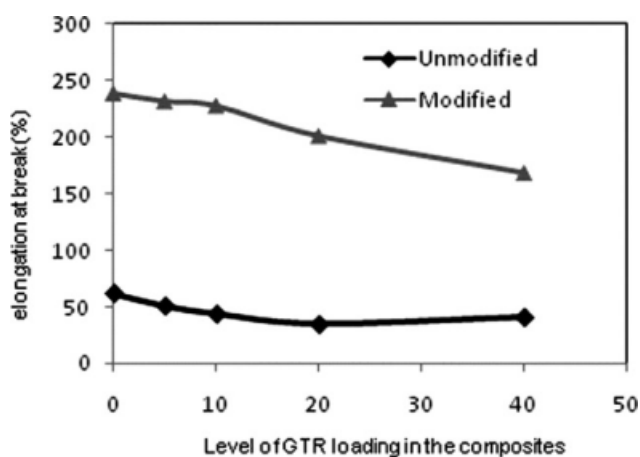
Properties	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Tensile strength (MPa)	12.6	4.6	3.4	2.8	3	5	7.5	6.2	5.4	6.1	10.6
Elongation at break (%)	499	62	51	44	35	41	239	232	228	201	168
Hardness (Shore A)	95	82	86	82	92	92	86	81	92	88	93



**Figure 2** Effect of GTR substitution of NR in the blend (60LLDPE/40NR) on tensile strength.

the blend. Reduction of interfacial tension and an increase in interfacial adhesion due to reactions occurring during melt mixing, allow the interface to withstand a greater stress before breaking<sup>19</sup> and causes improvement of mechanical properties. On the other hand, zinc oxide as a component of GTR can react with MA during melt mixing to produce a salt which may enhance tensile strength. Bhowmick and coworkers<sup>20</sup> pointed out the occurring of this reaction in thermoplastic elastomer based on HDPE/EPDM which contained maleated GTR.

The hardness of the LLDPE/NR blend has been increased by incorporation of GTR (Table II) which can be attributed to the higher hardness of GTR compared with the polymeric matrices and also to interfacial interaction between GTR and matrices in modified blends.

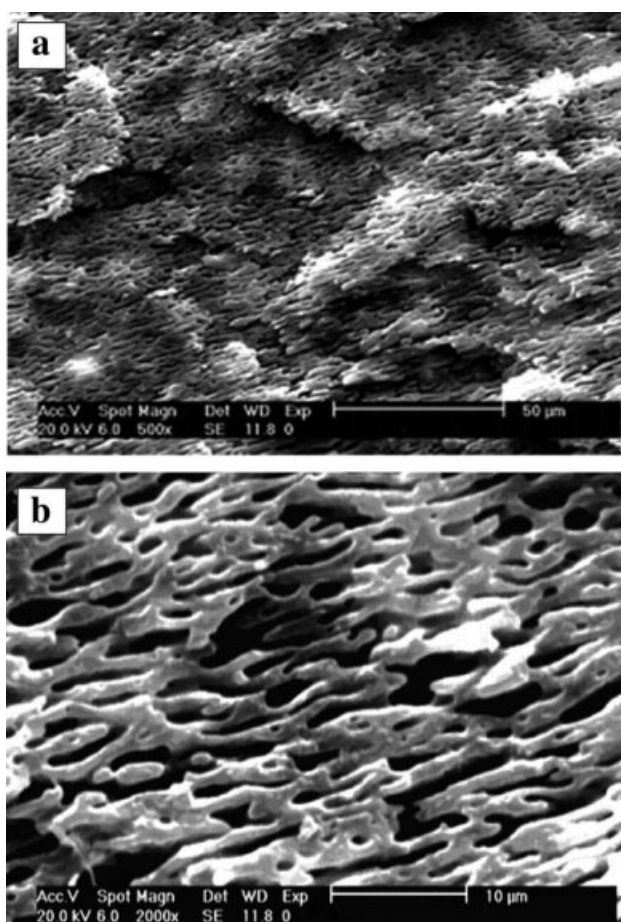


**Figure 3** Effect of GTR substitution of NR in the blend (60LLDPE/40NR) on elongation at break.

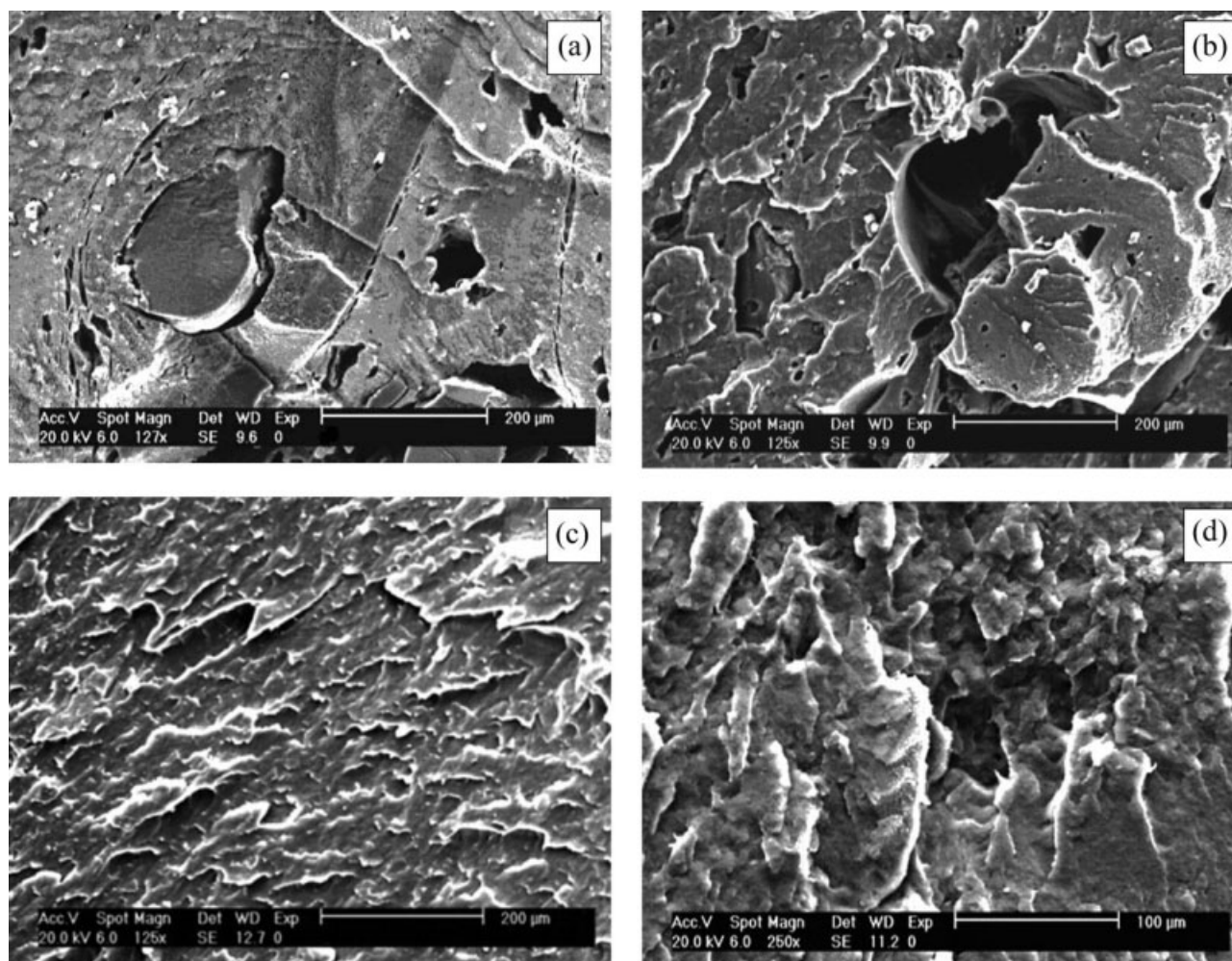
## Morphology

Figure 4(a,b) represents SEM micrographs of cryogenically fractured surface of LLDPE/NR blend, after extraction of the NR phase with toluene. In these micrographs, the dark domains are the voids left by the extracted rubber. A co-continuous morphology of LLDPE/NR (60/40) blend similar to the results reported by Dahlan and coworkers<sup>21</sup> is observed.

Figure 5(a,b) shows the SEM micrographs of unmodified LLDPE/NR blends containing 10 and 20 wt % GTR, respectively. It can be seen that GTR particles in these simple blends are very poorly bonded to the matrix. The SEM micrographs of modified LLDPE/NR blends containing 10 and 20 wt % GTR are shown in Figure 5(c,d), respectively. These micrographs show that GTR modification with MA and dynamic curing of rubber phases by DCP improves the bonding between the GTR and the matrix and also leads to a better shear induced distribution of GTR into the matrix.



**Figure 4** SEM micrographs of 60LLDPE/40NR blend with different magnification.



**Figure 5** SEM micrographs of LLDPE/NR/GTR: (a) unmodified (60/30/10); (b) unmodified (60/20/20); (c) modified (60/30/10); (d) modified (60/20/20).

### Rheological behavior

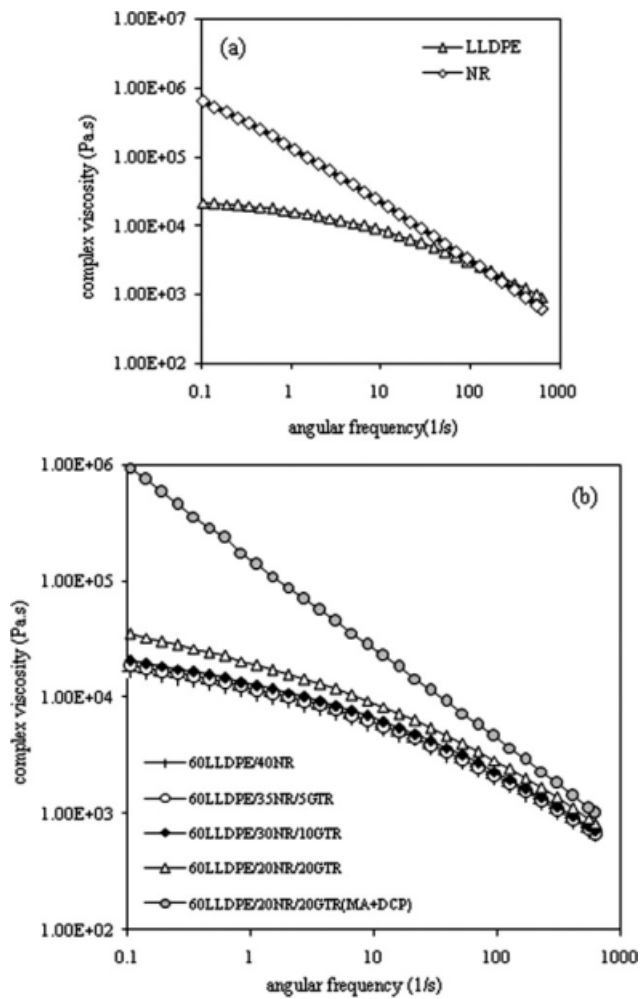
Variations of complex viscosity versus frequency obtained by RMS for the pure components, LLDPE and NR, and for some of the prepared blends are presented in Figure 6(a,b), respectively. LLDPE shows almost Newtonian flow characteristics within the frequency range lower than  $7 \text{ s}^{-1}$ . NR sample exhibits complex viscosity higher than that of the LLDPE at the mentioned range of frequency [Fig. 6(a)].

As it can be seen in Figure 6(b) all compositions exhibit a decrease in viscosity value with increasing frequency, which is the characteristic of pseudo plastic behavior of the blends. This figure also shows that by replacing up to 10% of NR by GTR in simple blends, the complex viscosity and its trend remain unchanged, and increasing the level of GTR to 20% causes a slightly increase in complex viscosity at low range of frequency in simple blend.

It is also clearly observed that at low frequency range, complex viscosity of the composition of

LLDPE/NR/GTR (60/20/20) contain, MA and DCP is dramatically higher than that of corresponding simple blend. This is believed to be due to the formation of the agglomerate structure by the dispersed rubber phases, consisting of NR and elastomeric part of GTR, which leads to the more resistance of the blend to flow at low frequencies. However, as the shear rate increases, the agglomerates are broken resulting in the reduction of the blend viscosity. The mentioned reasons cause a non-Newtonian behavior of this blend at low frequencies and a linear variation of viscosity at whole range of frequency. It is well known that this rheological behavior is in consistent with that of dynamic vulcanized thermoplastic elastomers.<sup>22</sup> On the other hand, melt mixing of NR/GTR/MA to produce initial masterbatch may generate macroradicals which initiate grafting of GTR on the backbone of NR. This reaction also enhances complex viscosity of the blend at low frequencies.

Figure 7(a,b) shows the variation of elastic modulus ( $G'$ ) versus frequency for pure LLDPE, NR, and



**Figure 6** Variation of the complex viscosity versus angular frequency (a) pure LLDPE and NR; (b) different blends sample.

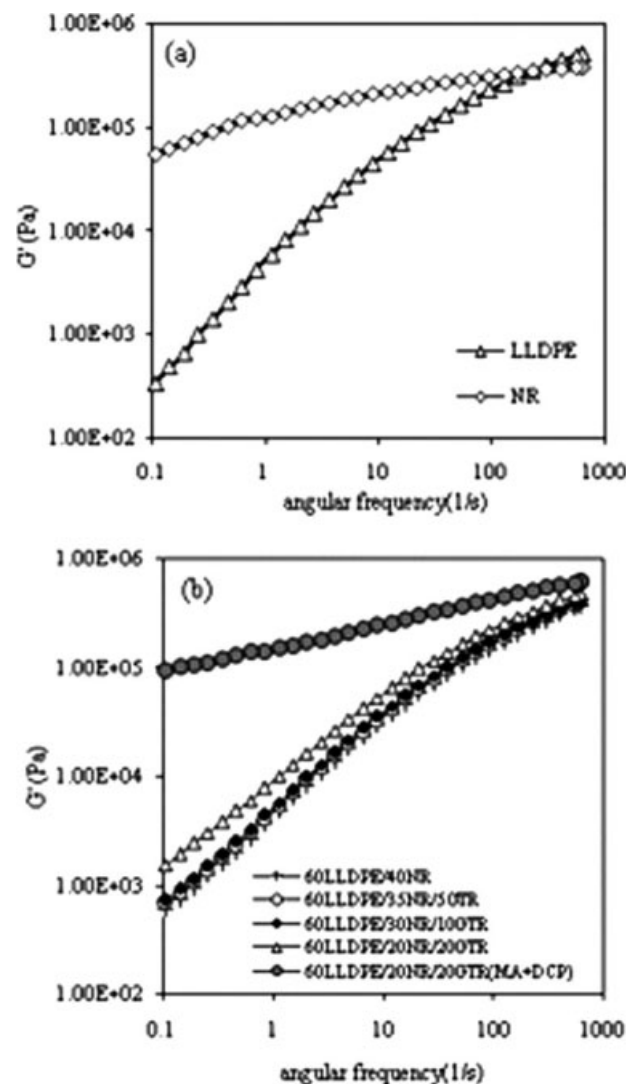
for some of the prepared blends, respectively. It can be observed that  $G'$  increases slightly according to level of GTR content. Comparison of  $G'$  of the blends leads to the same results as discussed for variation of shear viscosity. The elastic modulus for the composition of LLDPE/NR/GTR (60/20/20) contain, MA and DCP is dramatically higher than that of similar simple blend which it confirms formation of the structure similar to that of dynamic vulcanized thermoplastic elastomer in this composition. In fact formation of the rubber agglomerate structure due to crosslinking of the dispersed rubber phases consist of NR and elastomeric part of GTR, during melt mixing, causes an increase in the elastic modulus of the blend at low frequencies.

## CONCLUSION

The obtained results in this work show that using of NR (40%) in combination of LLDPE (60%) to produce TPE leads to a reduction of tensile properties

of LLDPE due to poor compatibility between NR and LLDPE.

Replacement of 5–10% of rubber phase by GTR leads to a further decrease in mechanical properties of the blend, however increasing of GTR content to 20–40 wt %, slightly increases tensile strength of the blend, which may be attributed to presence of carbon black in GTR that act as active filler. Employing of GTR in replacement of NR phase also decreases elongation at break due to crosslinked structure of the GTR. Reactive mixing of the LLDPE/NR/GTR compounds in the presence of MA and DCP increases the compatibility between phases and also ends to dynamic vulcanization of rubber phases in the blend which was confirmed by a distinctive rheological behavior and morphology of the blend, such that at low frequencies, complex shear viscosity, and storage modulus of the modified blend is



**Figure 7** Variation of elastic modulus versus angular frequency (a) pure LLDPE and NR; (b) different compound samples.

much higher than those of corresponding simple blend. Modified blends show morphology structure similar to TPV materials with good mechanical properties compared to unmodified blends.

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