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Thermoplastic Elastomers Blends Based on Linear Low Density Polyethylene, Ethylene-1-Octene Copolymers and Ground Rubber Tire

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Abstract: Blends of linear low density polyethylene (LLDPE) ethylene-1-octene copolymers (EOC), with different 1-octene (OC) content, and ground rubber tire (GRT) were prepared by melt mixing in a twin screw extruder. Five different compositions of LLDPE/EOC/GRT blends were processed in the extruder to evaluate the effect of EOC addition to the LLDPE/GRT blends. The addition of EOC to LLDPE/GRT blends improves the mechanical properties. Besides, the replacement of 5% of GRT by EOC grades (OC = 20 or 30 wt %) in the 50/50 LLDPE/GRT blend, leads to a significant increase of ultimate tensile properties. The EOC comonomer content affects the properties of LLDPE/EOC and LLDPE/EOC/GRT blends. Dynamical-mechanical analyses showed that, with the addition of EOC to LLDPE/GRT blends, the Tg of GRT and the Tg of EOC are closer. This effect is more pronounced when the EOC with the highest content of comonomer (30 wt %) is added to LLDPE/GRT blend. In this case, only one peak related to the Tg of the rubber phase can be visualized in the amorphous region. These findings indicate that EOC may act as compatibilizer agent for LLDPE/GRT blends.

Keywords: *Blend, linear low density polyethylene, ground rubber tire, ethylene-1-octene copolymers, compatibilizer, mechanical properties.*

Introduction

Nowadays, there is a great concern over the environment protection and biodiversity conservation. Consequently, new policies and techniques related to energy conservation, substitution of materials obtained from non-renewable sources and adequate solid waste management have been introduced in most countries. There is a big amount of discarded tires every year in the world. In order to maintain ecological balance, it is necessary to reduce the serious environmental problem caused by waste rubber. The main recycling approach of waste rubber is to make powdered rubber[1].

Vulcanized rubber tire is available in different sizes and can be obtained by cryogenic or room temperature methods. The cryogenic process allows smaller particles to be obtained, resulting in materials with better properties with respect to those obtained through grinding at room temperature[2,3].

Ground rubber tire (GRT) is mostly used in less demanding applications. There is a need to find some value-added applications for GRT based products. Recycling of GRT by mixing with thermoplastic polymers is a perspective branch of rubber recycling. It has been used for preparation of polymer blends with thermoplastic resins in order to obtain impact-resistant plastics. However, the resulting compositions exhibit poor mechanical properties due to the insufficient adhesion between the rubber particles and the polymer matrix. Several approaches have been used in order to improve the adhesion between GRT and the thermoplastic resin[2,4,5].

Ground rubber tire has also been used for preparing thermoplastic elastomers (TPEs) and thermoplastic vulcanizates (TPVs). The major criterion for the formation of thermoplastic elastomers is that the two components must be thermodynamically incompatible, but not so dissimilar that intermixing cannot be accomplished. In order to achieve this condition, one or more compatibilizers should be introduced into the system. As incorporated into the mixture, compatibilizers can reduce the surface tension between the matrix and the disperse phase by reducing its particle size. They can also enhance adhesion between the blends components[6].

Methods of reactive and non-reactive compatibilization have been described in the literature. Reactive methods require the compatibilizers and blends components to have a reactive group which can form in situ primary chemical bonds. The formed compatibilization agent reduces the interfacial tension between the immiscible blend components, enhances the adhesion between the phases and, as a consequence imparts to the blend satisfactory mechanical properties. In physical blending, the compatibilizing agent is chemically synthesized prior to the blending operation and added to the blend as a non-reactive component. Due

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to its chemical and molecular characteristics it is able to locate at the interface, reduces the interfacial tension between the blends components and promotes adhesion between the phases[6].

Several attempts have been made in order to compatibilize GRT and thermoplastic blends. Reactive and non-reactive compatibilization methods, GRT surface modifications based on acid treatments, UV or gamma irradiation, plasma or corona charge, and new methods for preparation of these blends such as: solid-state shear pulverization and solid state mechanochemical millings have been described in the literature[2,7,8]. The resulting materials present mechanical properties more or less similar to those presented by thermoplastic elastomers. Various thermoplastics have been investigated, either neat or scrap. Polyethylene is one of the most used polymers in these blends.

Hrdlicka et al.[9] tested several approaches in order to improve the mechanical properties of the GRT and low density polyethylene (LDPE) blends. Combination of mastication of ground rubber prior to use and incorporation of ethylene-propylene-diene terpolymer (EPDM) for compatibilization led to obtaining properties similar to those presented by thermoplastic vulcanizates materials. Partial crosslinking of LDPE employing dicumyl peroxide and a sulfur system was also studied. Peroxide cure gave positive results only for basic blend of ground rubber and LDPE and sulfur cure system led to a moderate increase of the tensile strength.

Nevatia et al.[10] found that utilization of a sulfur-accelerator system provides better results than a peroxide system for dynamic crosslinking of scrap LDPE and reclaimed rubber blends.

Kumar et al.[11] investigated TPEs based on GRT untreated or thermomechanically decomposed, LDPE and fresh rubber prepared with and without dynamic curing via sulfur or peroxide. The best performance was achieved by recipes containing decomposed GRT and EPDM after dynamic vulcanization with sulfur.

Grigoryeva et al.[8] prepared thermoplastic elastomers based on recycled high density polyethylene (HDPE), EPDM and GRT treated with bitumen. They concluded that bitumen acts simultaneously as a curing agent for the rubber components (EPDM/GRT) and as a compatibilizer for the blend components.

Naskar et al.[4] developed thermoplastic elastomers based on rubber plastic blends wherein the rubber phase consisted of a mixture of EPDM and GRT and the plastic phase consisted of acrylic-modified high density polyethylene. The reason behind this approach is that the incorporation of a fresh rubber like EPDM in the GRT-plastics blend, followed by dynamic vulcanization, could produce thermoplastic elastomers with desired properties. It was found that the 60:40 rubber/plastic blends behaved as a thermoplastic elastomer.

Guo et al.[12] dealt with thermoplastic elastomers from scrap rubber powder and linear low density polyethylene (LLDPE) treated with a dual compatibilizer consisting of LLDPE grafted with maleic anhydride, methyl methacrylate and butyl acrylate and epoxydized natural rubber (ENR). The mechanical properties, especially elongation at break were significantly improved after compatibilization.

Oliphant and Baker[13] precoated the cryogenic ground rubber tire with ethylene-acrylic acid copolymer and then mixed it afterwards with LLDPE and HDPE matrices. A significant improvement of the LLDPE impact and tensile strength was observed. However, the mechanical properties resulting from the processing of HDPE with GRT particles were very poor. This result was attributed to the large size of GRT particles which prevented a strong adhesion. In this case, moderate adhesion was not sufficient to produce useful composites.

Costa et al.[14] studied the thermal and rheological behavior of LLDPE/EPDM and LLDPE/EPDM/GRT blends. Their results indicated that there was no expressive reduction of thermal and rheological properties when EPDM was partly replaced by GRT. These results were attributed to a possible formation of a composite of GRT-EPDM particles tending to forming a shell around a LLDPE inclusion.

Qin et al.[15] found that the LLDPE/GRT blend contained styrene-butadiene-styrene (SBS) copolymer as a compatibilizer presented good mechanical properties. They also verified that satisfactory properties could be obtained even using high contents of GRT. Atomic force microscopy (AFM) and differential scanning calorimetry (DSC) results showed that good adhesion between the rubber particles and the surrounding LDPE matrix was achieved in the blend.

Li et al.[5] used various compatilizers, such as: ethylene-propylene copolymer (EPR), EPDM and an ethylene-1-octene copolymer (EOC), ENG 8003 for preparing GRT/HDPE blends with or without dynamic vulcanization using dicumyl peroxide. Highest tensile strength and elongation at break were found in the dynamically vulcanized GRT/HDPE/EOC ternary blends. Their results suggest that the metallocene copolymer promoted an enhanced adhesion between GRT and polymer matrix.

Nguyen[6] studied the possibility of using an ethylene-1-octene copolymer, Exact 0210 plastomer, as compatibilizer for blends of LDPE and recycled rubber. The blends were prepared by melt mixing in a Brabender using two concentrations of LDPE, respectively 5 and 15 wt%. A commercial recycled thermoplastic elastomer was used as a reference material. It was verified that there is a critical concentration of compatibilizer for each blend composition. At this concentration, maximum values of tensile strength and elongation at break were obtained. This result was attributed to the balance of viscous forces tending to breaking the dispersed drop and interfacial tension forces tending to resisting deformation and disintegration. Analysis of tensile properties indicated that blends containing 15% of LDPE and 10% of compatibilizer had tensile properties similar to those presented by the reference material. However, their tear strength was lower than that of reference material.

Linear low density polyethylene is a widely used resin in the packaging industry due to its excellent mechanical properties. Generally, LLDPE is mixed with other polyolefins in order to reduce costs or to improve its processability.

To our knowledge, there is not much in the literature regarding the effect of the addition of metallocene copolymers to the GRT-LLDPE blends. Therefore, the aim of this study is to evaluate the effect of the addition of three different grades of poly (ethylene-co-1-octene) elastomers with different comonomer content on the thermal and mechanical properties of GRT-LLDPE blends.

Experimental Procedure

Linear low density polyethylene (LLDPE), MFI = 2.3 g/10 min – ASTM D1238, at 190 °C was kindly donated by Politeno Comércio e Indústria S. A. Ground rubber tire (GRT) with average particle size equal to 40 mesh was supplied by Artgoma do Brasil LTDA. Ethylene-1-octene copolymers (EOCs) with different comonomer content were supplied by Dupont Dow Elastomers. The relevant properties of these copolymers are presented in Table 1[16].

The LLDPE/GRT/EOC blends (50/0/50, 50/25/25, 50/35/15, 50/45/5, 50/50/0 wt %) were prepared in a twin screw extruder (Extrusão Brasil-Model DRC) with 22 mm diameter and a length-to-diameter (L/D) ratio equal to 36. The temperature profile from the feed to the metering zone was set at 60/210/225/225/220 °C. The screw rotor speed was set at 350 rpm.

Melt flow index (MFI) values of the materials were determined following ASTM D 1238 using a Tinius-Olsen Extrusion Plastometer Model MP993.

Tensile properties were measured using an Emic Universal Testing Machine, Model DL 2000 with a 5 KN load cell. An extensometer (TRD 15) was attached to the machine for the measurement of elongation. Tests were conducted in accordance to the ASTM D 638 using Type I test specimens dimensions. A crosshead speed of 10 mm/min was employed and the average of at least 7 specimens was taken for each sample. All the specimens were prepared by injection molding using a Battenfeld plus 35 injection molding machine. The following experimental conditions were used in this procedure: injection temperature = 200 °C; injection pressure = 40 bar; cooling time = 30 s; mold temperature = room temperature.

The dynamic mechanical properties were measured using a TA Instruments, Dynamical Mechanical Analyzer (DMA) Model 2980 at a strain percent of 0.01% and a frequency of 1 Hz. Injection molded samples with dimensions equal to 35.00 × 12.35 × 3.20 mm obtained under experimental conditions similar to those used in the preparation of specimens for mechanical characterization were used for testing. The samples were analyzed in a temperature range of –100 to 150 °C at a heating rate of 3 °C/min.

Results and Discussion

Commercial linear low density polyethylene (LLDPE) produced by Ziegler-Natta catalyst technology is available in a range of densities from 0.900 to approximately 0.935 g/cm^3, depending of the amount of comonomer. The LLDPE used in this work is an ethylene-1-butene copolymer and presents short branches on the linear polymer backbone[17].

The morphology and the physical properties of LLDPE are highly dependent on the content and distribution of short branches. The crystalline lamellae of LLDPE are thicker than the lamellae of LDPE. Consequently, LLDPE has superior mechanical properties and higher melting temperature than LDPE[17].

Ethylene-1-octene copolymers (EOCs) produced by constrained geometry metallocene catalyst technology exhibits a molecular structure with narrow molecular weight and uniformity of comonomer distribution. The shear sensitivity of these copolymers can be controlled to the desirable level through selective incorporation of long chain branching. Copolymers with more than 20 wt% of octene are elastomeric and due to the chemical similarity and easy processability can be widely used to toughen polyolefin polymers[17].

There is evidence in the literature that the comonomer content of the metallocene ethylene- α -olefin copolymers has a strong effect on the properties of high impact polypropylene/LDPE blends and on the properties of polypropylene-ethylene random copolymer / EOCs blends[18].

The grades of EOCs used in this work present the same MFI values and different comonomer content (Table 1). Therefore, it should be interesting to investigate if the properties of the LLDPE/EOC/GRT blends will also be affected by the comonomer content.

Melt flow index (MFI) is an empirically defined parameter, inversely proportional to the melt viscosity at a temperature and shear rate specified by the operating conditions of measurement. Although it is not a fundamental property of a polymer, this parameter has been widely used in the industry in order to characterize the flow properties of the polymers[19]. The results for MFI determination of LLDPE and EOCs processed in the extruder and of the polymer blends: LLDPE/EOC and LLDPE/EOC/GRT are shown in Figure 1.

It can be seen that the MFI values of LLDPE, ENG 8480 and ENG 8003 showed a little decrease after processing in the extruder. This result suggests that the severe conditions of shear and temperature led to the

Table 1. Specification of the raw materials.

Material	MFI (g/10min)	OC (wt %)	Xc (%)	Tm (%)	Tg (%)
LLDPE	2.3	-	-	120	-
ENG 8480	1.0	20	33	99	–31
ENG 8003	1.0	30	25	77	–46
ENG 8100	1.0	38	18	60	–52

OC - Octene Content; Xc - Cristallinity degree; Tm - Melting Temperature; Tg - Glass Transition Temperature.

formation of free radicals and crosslinking of the polymer chains due to the great amount of secondary carbons.

The MFI value of ENG 8100, however, presented a slight increase after processing. As this metallocene copolymer presents the highest content of comonomer, this result suggests that there was a preponderance of degradation reactions, possibly due to the increase of tertiary hydrogen concentration resulting from the higher concentration of tie molecules in the amorphous phase.

Tensile properties were determined in order to give some indication of the balance of the properties achieved with various blends. Figures 2-6 summarize the mechanical properties of the LLDPE, of the three grades of EOCs and of the different blends.

Figure 2 shows that the thermoplastic elastomers present higher values of strength at break and elongation at break than LLDPE. ENG 8480 and ENG 8003 show approximately the same mechanical behavior. ENG 8100, however, has the highest value of elongation at break due to the highest concentration of 1-octene comonomer. The lower strength at break presented by this EOC grade may be attributed to the lower crystallinity degree of this grade. It has been reported that an increase of the comonomer content produces softer materials due to the increasing difficulty of chain crystallization[20].

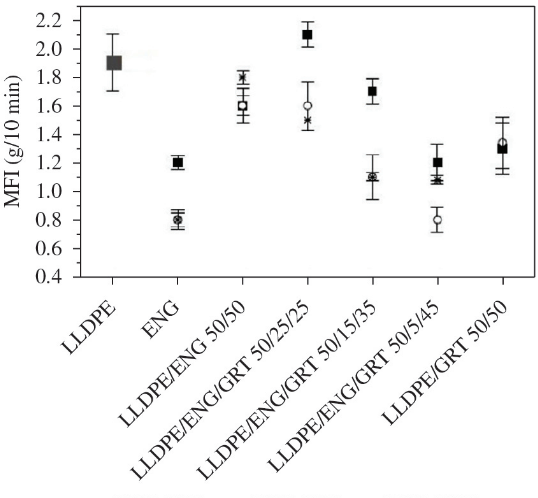

Figure 1. Melt flow index (MFI) values of the materials.

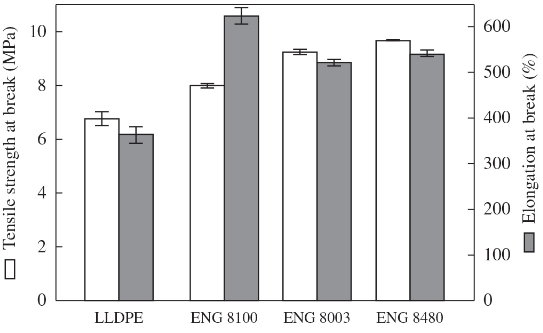

Figure 2. Mechanical properties of LLDPE, ENG 8100, ENG 8003 and ENG 8480.

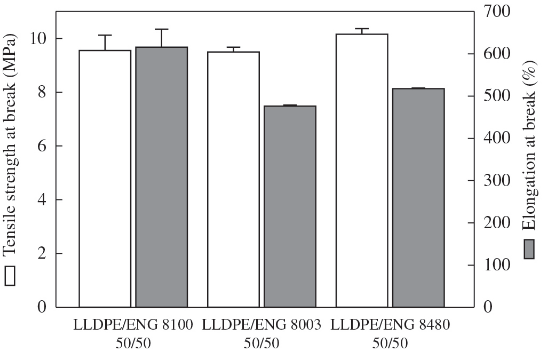

Figure 3. Mechanical properties of 50/50 LDPE/ EOCs blends.

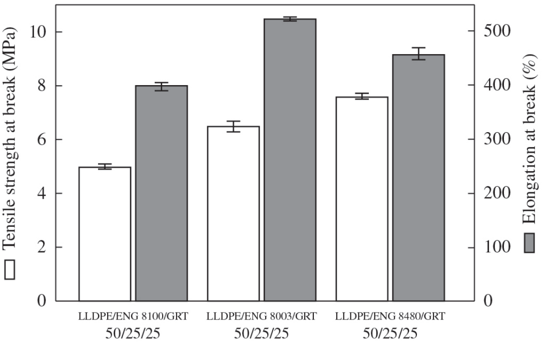

Figure 4. Mechanical properties of 50/25/25 LLDPE/ EOCs / GRT blends.

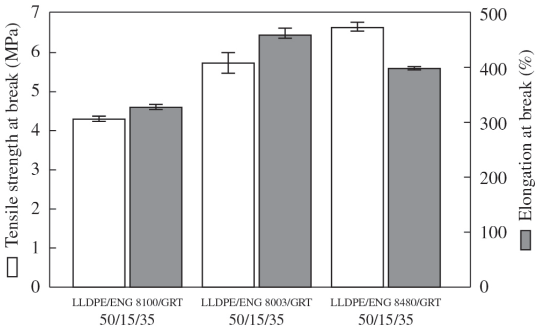

Figure 5. Mechanical properties of 50/15/35 LLDPE/EOCs/ GRT blends.

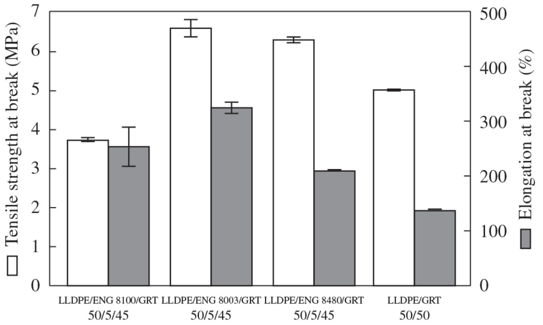

Figure 6. Mechanical properties of 50/5/45 LLDPE/EOCs/GRT blends and 50/50 LLDPE/GRT blend.

Table 1 shows that the crystallinity degree of EOCs grades decreases with the incorporation of higher content of comonomer.

Figure 3 shows that all blends presents higher values of elongation at break and tensile strength at break than those presented by LLDPE. This result is an indication that 50/50 LLDPE/EOCs blends show the good mechanical properties presented by the thermoplastic elastomers.

The values of tensile strength and elongation at break of LLDPE/ ENG 8003 and LLDPE/ENG 8480 blends are quite similar to those presented by Engage 8003 and Engage 8480. The LLDPE/ ENG 8100 blend presents the highest value of elongation at break due to the highest content of comonomer. However, this blend presents values of tensile strength approximately similar to those presented by the LLDPE/ENG 8003 and LLDPE/ENG 8480 blends. Perhaps, this result may be attributed to the better interfacial adhesion between LLDPE and this grade of EOC**.** Morphological analysis should be performed in order to elucidate this result.

Figures 4-6 show that when the content of GRT in the LLDPE/EOCs/GRT blends increases the elongation at break of these blends decrease. The ultimate strength of the blends also tends to decreasing with the increase of GRT concentration in the blends. However, the strength at break of 50/5/45 LLDPE/ENG 8003/GRT blend was higher than the strength at break of 50/15/35 LLDPE/ ENG 8003 /GRT blend.

Figure 6 makes evident the dramatic deterioration of the mechanical properties that occurs when 50 wt % of GRT is added to LLDPE. The poor adhesion between GRT and the polymer matrix and the large particle size of the rubber facilitate the propagation of cracks and leads to a pronounced decline of the mechanical properties.

Figure 6 also shows that the addition of a small concentration of all EOCs grades to the 50/45 LLDPE/ GRT blend leads to a significant increasing of the elongation at break. The addition of ENG 8003 and ENG 8480 to LLDPE also leads to a significant increase of the tensile strength at break. These results suggest that EOCs act as compatibilizer agents to the LLDPE/GRT blends and may indicate that EOCs can encapsulate the surface of the disperse GRT particles improving their dispersion in the LLDPE matrix. This compatibilizing effect of ethylene-1-octene copolymers was also observed by Li et al.[5] in a study of HDPE/GRT blends and by Nguyen[6] in a study of LDPE/recycled rubber blends.

Inspection of Figure 6 shows that a pronounced improvement of the mechanical properties of the LLDPE/ GRT blends occurs when the ENG 8003 is added to the blends.

Lee et al.[18] verified in a study of polypropylene-ethylene random copolymer (PP-CP) and EOC blends that the rubber particle size decreased as the octene content in the ethylene-α-olefin random copolymer increased. As the rheological properties of all EOCs and PP-CP/ EOC blends were identical, they inferred that interfacial interaction between PP-CP and EOCs increases as the octene content in EOC increases. Apparently, this finding is in agreement with our results which demonstrated that LLDPE/ENG 8100 blend presents the best mechanical properties. However, the Engage grades with lower content of comonomer were more efficient as compatibilizers agents for LLDPE/GRT blends than the Engage 8100. A study of morphology of these polymer blends is necessary in order to obtain more conclusive results about the effect of octene content on the properties of LLDPE/EOCs and LLDPE/EOCs/GRT blends.

Dynamic mechanical measurements can give information about the interaction between different components in the blend. The position of the primary peaks in the damping curve (tan δ *versus* temperature) can provide information about the molecular interaction between the components of the blends at the molecular level. Figure 7 shows the damping behavior of LLDPE, ENG 8480, LLDPE/ENG 8480 blend, LLDPE/ENG 8480/GRT blends and LLDPE/GRT blend.

Figure 8 presents the damping behavior of LLDPE, ENG 8003, LLDPE/ENG 8003/ GRT blends and LLDPE/ GRT blend.

The damping curve of LLDPE presents two secondary relaxations above the glass transition temperature: the α-relaxation around 80 °C and the β-relaxation between –40 °C and 20 °C. The α-relaxation is attributed to the movements of the chains in the crystalline region. After suffering some recrystallization processes, these chains will definitively melt at the primary relaxation. The β-relaxation occurs due to the movements of the short chain branches. It may also be attributed to the movements of some chain segments in the interfacial region[21].

The DMTA ENG 8480 curve (Figure 7) and the DMTA ENG 8003 curve (Figure 8) presents two peak

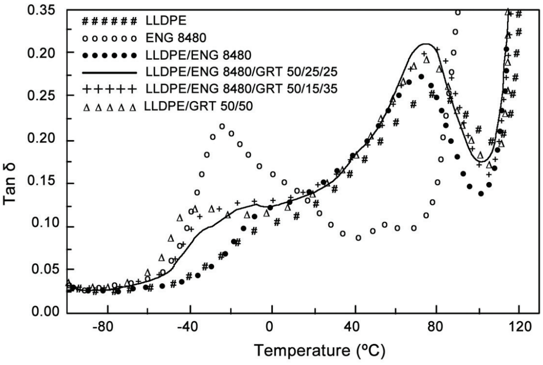

Figure 7. Damping behavior of the materials.

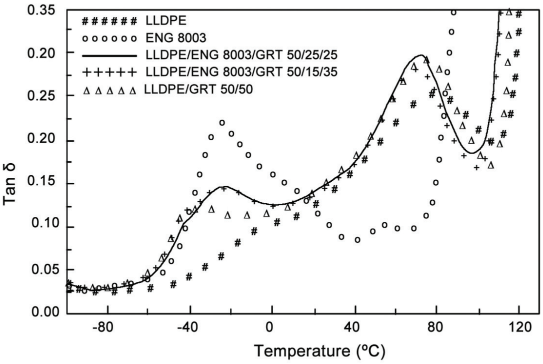

Figure 8. Damping behavior of the materials.

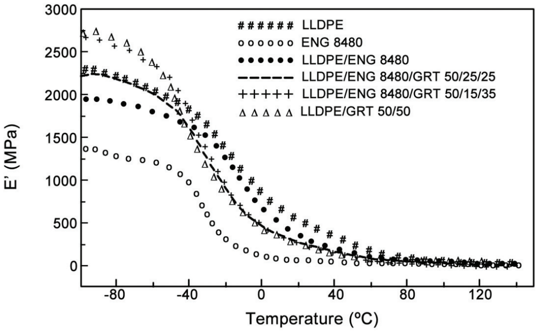

Figure 9. Storage modulus of the materials.

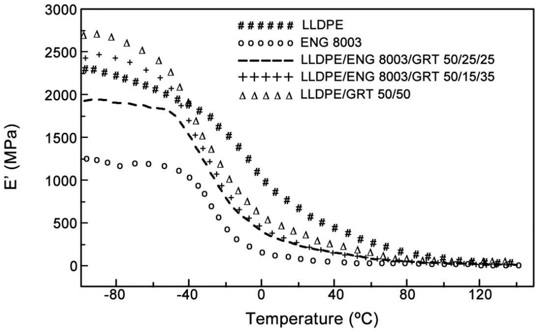

Figure 10. Storage modulus of the materials.

relaxations: one around – 30 °C, that may be assigned to the glass transition temperature (Tg) and other around 55 °C related to the movements of the chains in the crystalline region.

The LLDPE/ENG 8480 DMTA curves show that Tg peak of the elastomeric phase shifts towards higher temperatures. The curves also show that LLDPE α- relaxation position shifts about 10 °C downwards. These findings may be an indication of EOCs and LLDPE interactions at a molecular level.

The 50/50 LLDPE/GRT blend shows a low temperature relaxation peak around –40 °C related to the Tg of rubber phase. With the addition of Engage grades to these blends the Tg of GRT and the Tg of both the EOCs grades: ENG 8480 and ENG 8003 becomes closer. This effect is more pronounced when the Engage 8003 is added to LLDPE/GRT blend. In this case, only one peak related to the glass transition of rubber phase can be visualized in the amorphous region. The LLDPE α-relaxation peak position shifts about 5 °C downwards and becomes closer to the Tg peak of GRT. These findings suggest that the ENG 8480 and ENG 8003 may act as compatibilizer agents to LLDPE/GRT blends.

Figure 9 shows the storage modulus (E`) *versus* temperature curves of LLDPE, ENG 8480, LLDPE/ENG 8480 blend, LLDPE/ENG 8480/GRT blends and LLDPE/GRT blend.

Figure 10 shows the storage modulus (E`) *versus* temperature curves of LLDPE, ENG 8003, LLDPE/ENG 8003/GRT and LLDPE/GRT blends.

In the low temperature region, the storage modulus value of LLDPE is higher than those presented by the EOCs grades. LLDPE is an ethylene-1-butene copolymer with short ramifications and presents a typical thermoplastic behavior. The storage modulus of ENG 8003 is lower than the elastic modulus of ENG 8480 due to its higher content of 1-octene comonomer.

The addition of GRT to the LLDPE matrix increases the storage modulus in the range of temperatures below the glass transition temperature of GRT. This effect may be attributed to the limited movement of the chains in the amorphous phase imposed by the GRT composed by inorganic particles and crosslinked rubber. The large E´drop in the rubbery state presented in the curves related to LLDPE//GRT blends (Figures 9 and 10) may be a result of the reinforcing effect of the GRT particles.

The results of DMTA analyses may be an indication that the GRT particles are partially encapsulated by the EOCs particles. The morphology of the blends should be evaluated in order to have more conclusive results.

Conclusions

The addition of 5 wt % of ethylene-1-octene copolymers (EOCs), ENG 8480 or ENG 8003 to the 50/45 LLDPE/GRT blend leads to a significant increasing of the ultimate tensile properties. Therefore, the reuse of waste tire in compositions of thermoplastic elastomers using LLDPE as matrix is possible. The content of comonomer in EOCs grades affects the mechanical behavior of LLDPE/EOC and LLDPE/EOC/GRT blends. With the addition of EOCs to these blends, the Tg of the GRT and the Tg of both EOCs grades (ENG 8480 and ENG 8003) become closer and the LLDPE α-relaxation peak position becomes closer to the Tg peak of GRT. This effect is more pronounced when the ENG 8003 is added to the LLDPE/GRT blend. These results indicate that EOCs act as compatibilizer agents for LLDPE/GRT blends.

References

1. Fang, Y.; Zhan, M. & Wang,Y. – Materials and Design, **22**, p.123 (2001). http://dx.doi.org/10.1016/S0261-3069(00)00052-2
2. Carné, P. C. – "*Studying of compatibilization methods for high density polyethylene and ground rubber tire: Exploring new routes to recycle scrap tyres"*, Dissertation, Polytechnical University of Catalonia, Spain (2009).
3. Pistor, V.; Ornaghi, F. G.; Fiorio, R. & Zaterra, A. J.- J. Elast. Plast., **42**, p.417 (2010). http://dx.doi.org/10.1177/0095244310379175
4. Naskar, A. K.; Bhowmick, A. K. & De, S. K. - Polym. Eng. Sci., **41**, p.1087 (2001). http://dx.doi.org/10.1002/pen.10809
5. Li, Y., Zhang, Y. & Zhang, Y. X. – Polym. Test, **22**, p.859 (2003). http://dx.doi.org/10.1016/S0142-9418(03)00022-9
6. Nguyen, M. H. – "*Compatibilization of rubber/polyethylene blends"*, Master Thesis, Lulea University of Technology, Sweden (2008).
7. Sonnier, R.; Leroy, E.; Clerc. L.; Bergeret, A.; Lopez-Cuesta, J. M.; Bretelle, A. S. & Ienny, P. - Polym. Test., **27**, p.901 (2008). http://dx.doi.org/10.1016/j.polymertesting.2008.07.003

8. Grigoryeva, O. P.; Fainleib, A.; Tolstov, A. L.; Starostenko, O. M.; Lievana, E. & Karger-Kocsis J. – J. Appl. Polym. Sci., **95**, p.659 (2005). http://dx.doi.org/10.1002/app.21177
9. Hrdlicka, Z.; Kuta, A. & Hajek, J. – Polymery, **55**, p.832 (2010).
10. Nevatia, P.; Banerjee, T. S.; Rutta, B.; Jha, A.; Naskar, A. K. & Bhowmick, A. K. – J. Appl. Polym. Sci., **83**, p.835 (2002). http://dx.doi.org/10.1002/app.10115
11. Kumar, C. R.; Fuhrmann, I. & Karger-Kocsis, J. – Polym. Degrad. Stab. , **76**, p.137 (2002). http://dx.doi.org/10.1016/S0141-3910(02)00007-1
12. Guo, B.; Cao, Y., Jia, D. & Qin, Q. – Macromol. Mater. Eng., **289**, p.360 (2004). http://dx.doi.org/10.1002/mame.200300311
13. Oliphant, K. & Baker, W. E. – Polym. Eng. Sci., **33**, p.166 (2003). http://dx.doi.org/10.1002/pen.760330307
14. Costa, H. M. &Ramos, V. D. – Polym. Test., **27**, p.27 (2008).
15. Qin, J.; Ding, H., Wang, Y., Xie, M. & Yu, Z. – Polym. Plast. Technol. Eng., **47**, p.199 (2008). http://dx.doi.org/10.1080/03602550701816217
16. Leyva, M. E.; Oliveira, M. G.; Rocha, M. C. G. & Forte, M. M. C. – "*Propriedades-dinâmico mecânicas de elastômeros termoplásticos a base de pó de pneu reciclado", in:* Anais do 9º Congresso Brasileiro de Polímeros, p.89, Campina Grande, Paraíba (2007).
17. Shan, H. & White J. L. – Polym. Eng. Sci., **48,** p.2297 (2008). http://dx.doi.org/10.1002/pen.21109
18. Lee, H.; Kim, D. H. & Son, Y. – J. Appl. Polym. Sci., **103**, p.1133 (2007). http://dx.doi.org/10.1002/app.24644
19. Rocha, M. C. G.; Coutinho, F. M. B. & Balke, S. – Polímeros, Jul/Set, p.33 (1994).
20. Quijada, R.; Rupont, J.; Miranda, M. S. L.; Sapioni, R. B. & Galland, G. B. – Macromol. Chem. Phys., **196**, p.3991 (1995). http://dx.doi.org/10.1002/macp.1995.021961210
21. Starck, P. – Eur. Polym. J., **33**, p.339 (1997). http://dx.doi.org/10.1016/S0014-3057(96)00178-4

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