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Abstract

Despite the fact that more and more methods and solutions are used in the recycling of polymers, there are still some problems, especially in the recycling of cross-linked materials such as rubber. Usually the biggest problem is the lack of compatibility between the cross-linked rubber and the thermoplastic matrix. In this study we applied ground tire rubber (GTR) as recycled material. The GTR was embedded into polyethylene (PE) and polyethylene/ethylene-vinyl acetate (PE/EVA) matrices. In order to increase the compatibility of the components electron beam (EB) irradiation was applied. The results showed that the irradiation has a beneficial effect in the polymer-GTR interfacial connection. The EB treatment increased not only the tensile strength but also the elongation at break. The irradiation had also positive effect on the impact strength properties.

Keywords: Electron beam, recycling, ground tire rubber

1. Introduction

One of the main problems of the recycling of technical polymers is the thermodynamical incompatibility. The change of the Gibbs “free energy” during the mixing - determined by the changes of enthalpy and entropy - should be directed towards the miscibility (Brandrup et al., 1996). In most cases, even between closely related polymers, the compatibility is on low level which leads to phase separation and weak adhesion between the phases. Radiation treatment may help in this problem making the polymers more compatible by the chance of creating covalent bonds between the polymer phases (Burillo et al., 2002; Ronkay et al., 2010; Szebényi and Romhány, 2010).

In most of the developed countries the utilization of waste tires has become highly required recently. In case of the rubber recycling technologies the tires are usually ground (ground tire rubber, GTR). The rubber properties of GTR could be utilized by mixing the GTR with thermoplastic polyolefins. The incorporation of GTR into thermoplastic polymer matrices results in rubber-like materials with limited mechanical performance. These reduced mechanical properties are caused mainly by the before mentioned incompatibility (Ausias et al., 2007; Grigoeyeva et al., 2006; Li et al., 2004; Radesh Kumar et al., 2002; Wagenknecht et al., 2006).

Among the thermoplastic polymers, the production of polyethylene is one of the largest in the world. Because of the relatively simply build-up of the PE molecules, the recycling is easier than for other polymers. The use of GTR particles in PE matrix could produce great advantage for rubber recycling: the thermoplastic processability. Before producing GTR containing recycled thermoplastic materials it is advisable to investigate the interaction of the GTR and neat polymer matrix. There are some studies that are dealing with the coupling of the GTR and polyolefin matrices. The polyolefins – especially the PE – are chemically non-polar, low-affinity materials. By filling these matrices some reactive agents (peroxides, anhydrides) are proposed to improve the compatibility of the two phases (Fávaro et al., 2010; Scaffaro et al., 2005; Sonnier et al., 2007; Sonnier et al., 2008; Tz. Dintcheva et al., 2011). An alternative way is to mix PE with ethylene vinyl acetate copolymer (EVA). In this case the matrix becomes more polar so there is a chance to have better interaction with the GTR. Moreover the mechanical behavior of the EVA is closer to the rubbers (Li et al., 2004; Meszaros et al., 2008).

High energy irradiation treatment has been already used successfully as compatibilizing technology (Abou Zeid et al., 2008; Burillo et al., 2002; Sonnier et al., 2006). In these cases the irradiation has double effect. Firstly it produces free radicals on the surface of the GTR particles which can attack the PE, forming covalent bonds between the two phases. On the other hand the irradiation induces the crosslinking of PE which improves the shape memory behavior and other properties of the material. The addition of these two effects can result more rubber-like recycled materials.

In this study polyethylene (50-70 weight%) as thermoplastic olefin, 30 weight% of GTR and ethylene vinyl acetate copolymer (EVA) (20 weight%) as rubber-like compatiblizing material were used. The continuous melt-mixing of the samples was made in a twin-screw extruder and then the test specimens were injection molded. The injection molded samples were than treated by high energy electron beam. On the specimens tensile tests, falling weight impact

tests, hardness measurements, and dynamic mechanical thermal analysis (DMTA) were carried out.

2. Experimental

Ground tire rubber powder (GTR) was produced by mechanical grinding from automobile tires at ambient temperature by C.S.O. Ltd. (Hungary). The GTR was screened and classified. For this study the powder particles between size 0.25 and 0.5 mm were selected. The GTR content in the blends was fixed at 30 weight%. As matrix material injection molding grade LDPE (Tipolen OF 2019, TVK, Hungary) with $MVR_{190^oC/2.16\ kg}$=26 cm^3/10 min was used. Ethylene vinyl acetate copolymer (EVA) (IBUCELL K-100, H. B. Fuller Co.) with $MVR_{190^oC/2.16\ kg}$= 10 cm^3/10 min was used as a compatibilizer. The Table 1 shows the composition of the tested materials.

Table 1 Composition of the tested materials

	LDPE [weight%]	**GTR [weight%]**	**EVA [weight%]**
PE	100	0	0
EVA	0	0	100
PEGTR30	70	30	0
PEGTR30EVA20	50	30	20

After pre-mixing of the components mechanically, the mixtures were melt-mixed in a Brabender Plasti-Corder PL 2100 type twin screw extruder. Extrusion temperatures were set between 165…175ºC and the number of revolutions was 10 rpm. The extruded materials were subsequently granulated. Dumbbell type specimens (4x10 mm of cross section) for tensile and plaque specimens (with the dimensions of 80x80x2 mm) for instrumented falling weight impact (IFWI) tests were injection molded from the granulated blends in an Arburg Allrounder 320C 600-250 injection molding machine.

The tensile and instrumented falling weight impact (IFWI) specimens were EB treated on a LUE-8-5V (NIEFA) type electron accelerator, in air, by a dose 50; 100; 150 and 200 kGy. Dynamic mechanical thermal analysis (DMTA) was performed on rectangular specimens (of (20x4x4 mm) cut from the dumbbell type specimens in three point bending mode on a Perkin Elmer DMA 7e at a frequency of 1 Hz and heating rate of 2ºC/min. The temperature range was -80 to 35ºC.

The cyclic tensile tests were performed on a Zwick Z020 universal testing machine. Over the usual static mechanical tests, cyclic tensile tests are often used for thermoplastic polymers and their blends in order to determine their viscoelastic characteristics. Cyclic investigation is performed at a constant loading rate – only the direction changes according to uploading and unloading. In this study one cycle was set prior to a usual tensile test. During the cycle a crosshead speed of 5 mm/min was applied up to 25 N, then unloading at 5 mm/min to zero force, where 15 sec relaxation time was set. Thereafter a tensile test was carried out at a loading rate of 50 mm/min. The tensile modulus was determined in the strain range of 0.1…0.5% at the beginning of the cycle.

IFWI tests were performed on a Fractovis 6785 instrument (Ceast, Italy) using the following settings: maximal energy: 229.05 J; diameter of the dart: 20 mm; diameter of the support rig: 40 mm; weight of the dart: 23.62 kg and drop height: 1 m. All mechanical tests were performed at 23°C. From the results the perforation energy were calculated (total absorbed energy/specimen thickness).

The Shore D hardness was measured by a Zwick Roell HO4 3150 type equipment at room temperature.

3. Results and Discussion

Fig. 1 shows the tensile strength of the investigated materials. It can be seen that by increasing of the EB dose the tensile strength also increases in all cases. The pure PE has the highest values, by addition GTR and EVA to the system the values decreases by around 25%. For different compositions the increments are also different as a function of the dose. In case of the PE 50 kGy is enough to increase the tensile strength significantly; further irradiation does not cause significant effect in this property. For the GTR loaded materials the values are increasing smoothly with increasing irradiation dose. At the PEGTR30 the increment is close to 10%; at the EVA containing one the change is more than 20%.

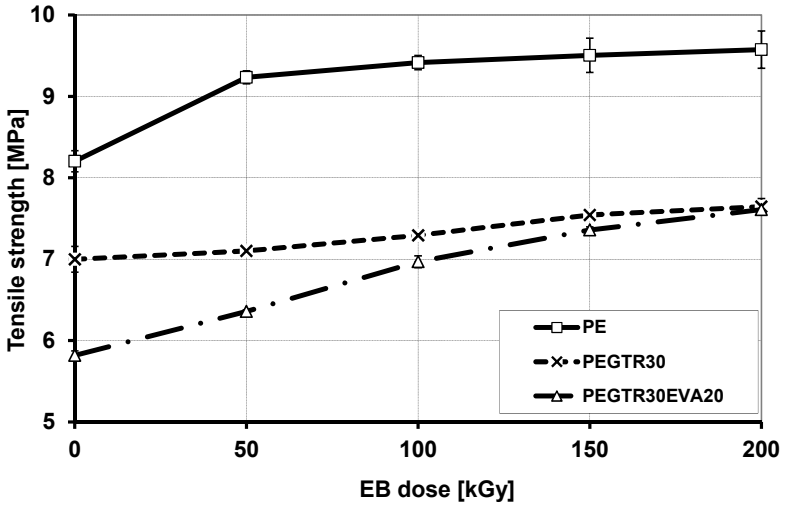

Fig. 1 Tensile strength of the GTR containing thermoplastics as a function of the EB dose

In case of the elongation at break (Fig. 2) the beneficial effects of the irradiation and the EVA can also be observed. Above 100 kGy the elongation at break of PE starts to decrease while in the other materials some further increase may be observed. This can be explained by the crosslinking of the PE which results in lower elongation at break, but in the GTR containing materials better interfacial connection is reflected by increasing doses. Without coupling material the presence of GRT causes 40% decrement in the elongation at break. If there was also EVA in the system the elongation at break was close to the value of neat PE values and at higher doses this mixture shows the highest values.

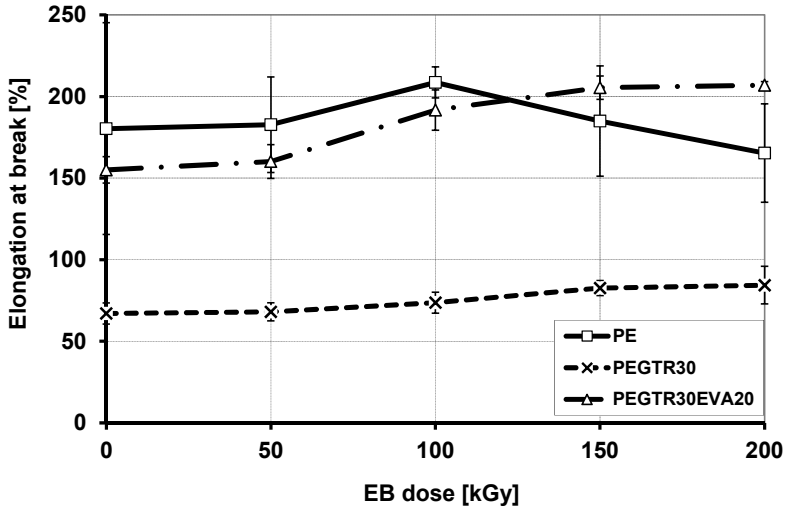

Fig. 2 Elongation at break of the GTR containing thermoplastics as a function of the EB dose

From the viewpoint of the tensile modulus (Fig. 3) the effect of the electron beam irradiation is different in case of the pure PE and the GTR filled materials. In case of neat PE the

modulus increases at the beginning, after 100 kGy it starts decreasing. In contrast, at the GTR containing ones only 50 kGy EB dose reduces the modulus significantly but further irradiation does not affects this property. The composition has also very strong effect. As it is expected the incorporation of GTR decreased the values and by adding EVA to the blend, further decrement can be observed. Thereby the materials became more rubber-like.

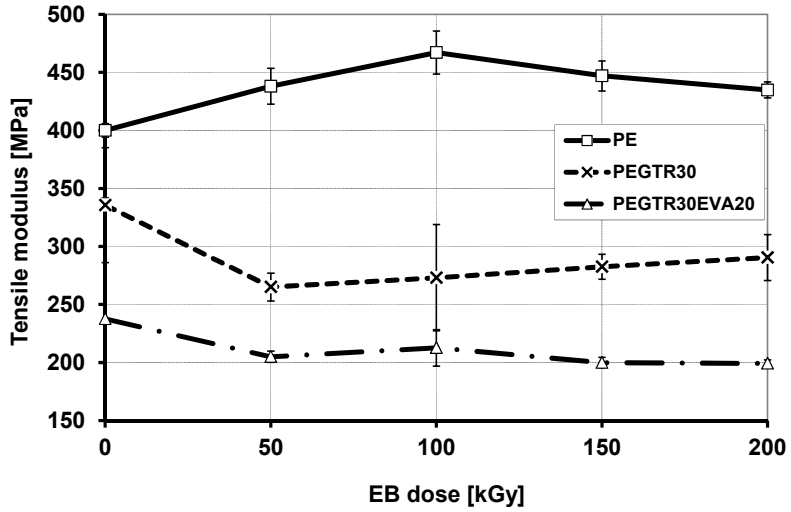

Fig. 3 Tensile modulus of the GTR containing thermoplastics as a function of the EB dose

The results of the cyclic tests are presented in Fig. 4. The differences in the hysteresis loop of the materials - irradiated by 150 kGy doses - can easily be distinguished. The curves of the GTR containing blends are between the PE and EVA. The hysteresis area of the PEGTR30EVA20 is larger and the instantaneous elastic-, and the total deformation are also higher than for PEGTR30. Note that the higher hysteresis area means higher dumping property.

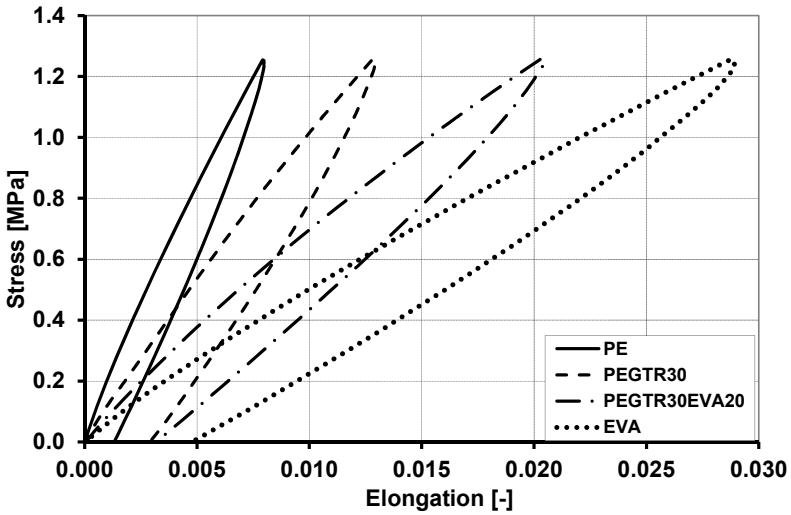

Fig. 4 Hysteresis cycles of the recycled rubber containing thermoplastics after 150 kGy EB treatment

Fig. 5 shows the perforation energy values (calculated from IFWI tests) as a function of the dose of EB treatment. The perforation energy of PE increases by increasing EB dose. This reflects the effect of radiation induced cross-linking. The GTR containing blends also have higher perforation energies by increasing dose. In our interpretation, this is a clear sign of the EB-induced compatibilization between the thermoplastic matrix and recycled rubber. Interestingly, the EVA – although also subjected to cross-linking – becomes more rigid in same dose range.

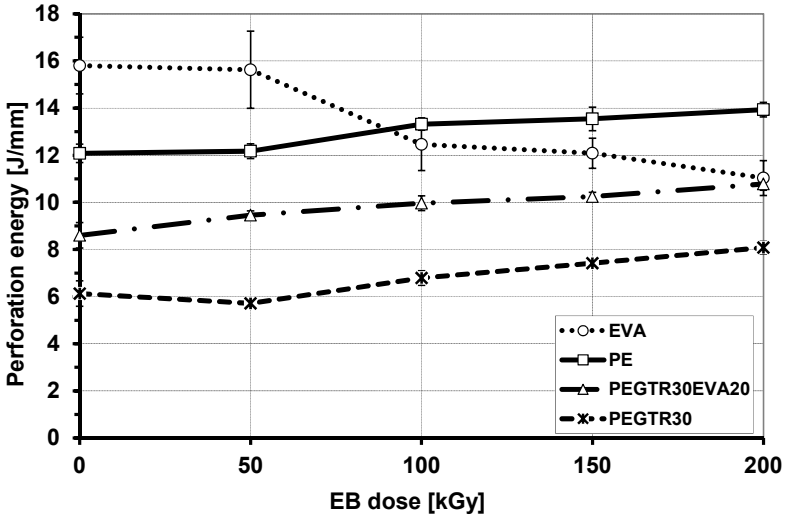

Fig. 5 Fracture (perforation) energy of the recycled rubber containing thermoplastics as a function of the EB dose

The result of the hardness tests (Fig. 6) is a rough approximation of the cross-linking state of the materials. Regarding to the irradiated materials a modest increase can be observed as a general trend, by increasing EB dose, so the cross-linking effect of the EB irradiation is proven in all cases. At lower doses the EB treatment affected more the pure EVA which is in correlation with the perforation energy results.

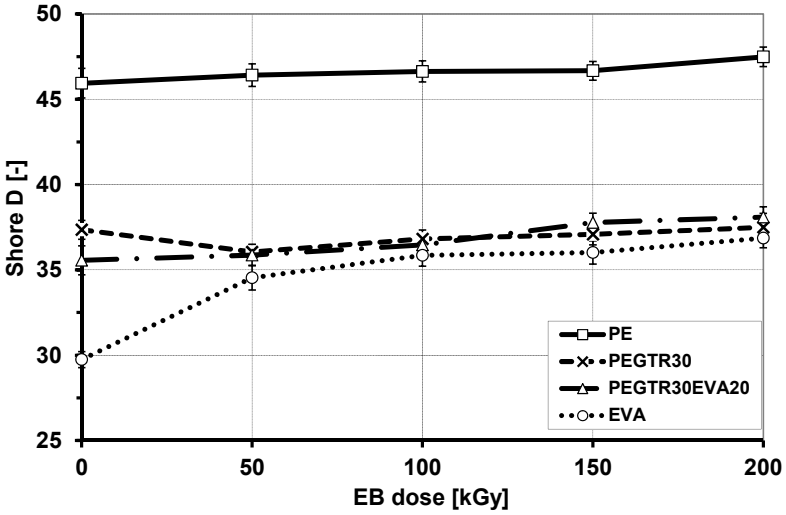

Fig. 6 Hardness (Shore D) of the recycled rubber containing thermoplastics as a function of the EB dose

In the dynamic mechanical testing the loss tangent (tan δ) is reflecting best the differences in viscoelastic properties. In Fig. 7, the tan δ curves of the 150 kGy EB irradiated samples are presented. The pure EVA copolymer shows a significant relaxation peak at -13.2°C which corresponds to the glass transition temperature of the amorphous phase of EVA. The tan δ curves of the PE and its blends with GTR are flatter. However due to the incorporation of rubber particles, a new relaxation site can be observed around -50°C. In case of this peak there is a slight shift towards higher temperatures if EVA is added to the PEGTR30 blend. This phenomenon refers to the increased compatibility of the components.

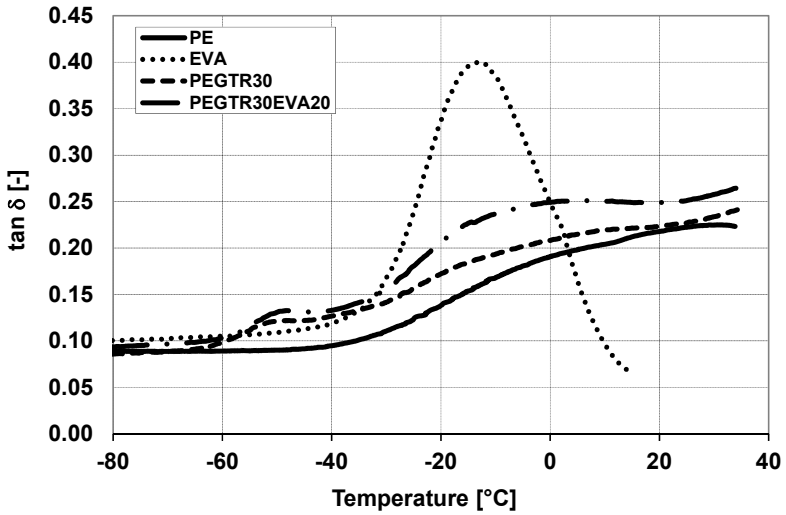

Fig. 7 The loss tangent of the recycled rubber containing thermoplastics after 150 kGy EB treatment

In Fig. 8 one can see that the glass transition regions of the EVA and recycled rubber containing blends are shifted toward the higher temperatures with increasing dose. This is

showing a certain intensification of the connections on the interface. The modest decrease of the absolute level of the tan δ curves with increasing dose at the glass transition indicates an increasing limitation of the chains flexibility.

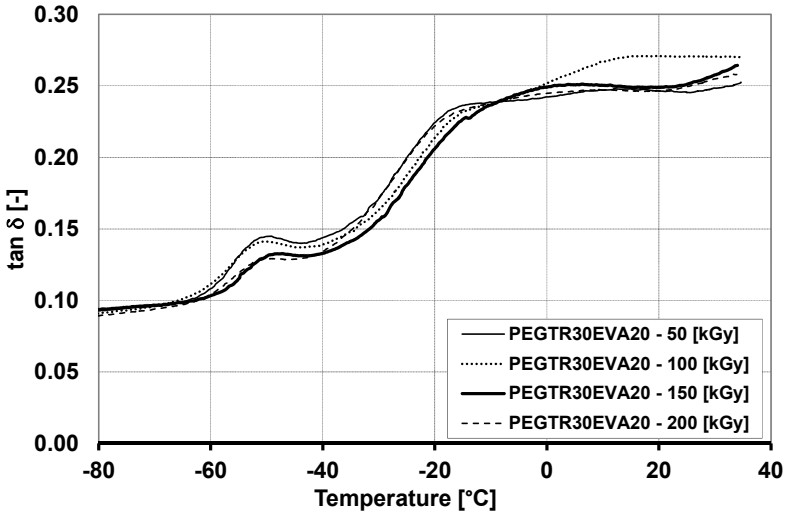

Fig. 8 The loss tangent of the PEGTR30EVA20 blends treated with different EB dose

4. Conclusion

The EB treatment of the GTR containing polyolefin matrix blends showed significant benefits. The 200 kGy EB dose (in air) resulted in a better tensile strength and increased elongation at break, without changing the tensile modulus which provides more rubber-like properties. The results of the cyclic and falling weight impact tests showed that the application of GTR and EB together is advantageous from the point of view of the energy absorbing capability of PE/EVA thermoplastic polymer matrix. The modest change in hardness proves the cross-linking effect caused by the EB treatment in all cases. The dynamic mechanical analysis confirmed the compatibilization effect of EVA and EB between the GTR and (thermoplastic) polymer matrix.

Acknowledgement

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Figure Legends

Tables

Highlights

>In this study ground tire rubber was incorporated into polyethylene (LDPE) matrix. >Compatibilizing effects of irradiation and ethylene-vinyl acetate were investigated. >The samples were manufactured by twin-screw extrusion and injection molding. >Both compatibilizing methods improved the rubber-like properties of the blends. >This improvement was especially significant when they were applied together.