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COMPATIBILIZATION OF POLYMERIC COMPOSITION FILLED WITH GROUND TIRE RUBBER – SHORT REVIEW

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Abstract. Waste rubber is recognized as a valuable materials resource and searching for new recycling methods is the main activity of many research institutions and companies. During last years only few scientific papers concerning foamed polymer compositions filled with ground tire rubber were published. The paper reviews the progress in compatibilization and foaming of polymeric compositions filled with a ground tire rubber.

Keywords: ground tire rubber, rubber recycling, foaming, polymer composition, compatibilization.

1. Introduction

Tires are one of the most problematic sources of waste, due to their large volume produced and durability. According to European Tyre & Rubber Manufactures` Association (ETRMA) in European Union 3.4 mln of end-of-life tires were generated in 2013 [1]. In Poland around 200 000 tons of worn tires are generated annually, which gives our country the sixth position in European Union [2, 3]. Development of automotive industry and increasing traffic affected towards the searching of new methods and technology to recovery and recycling of waste rubber [4]. Furthermore, the growing interesting of pro-ecologic technology is based on reused materials such as waste rubber, besides economic factors, the significant influence have the environment protection legislations [5]. The required recovery level of used tires in Poland in 2008-2014 is about 75 %, only 15 % of which is material recycling. However, using of waste rubber as the alternative fuel in cement kilns and power plants, allows to recovery only ca. 37 % of energy used to producing of new tires [6].

Currently, the size reduction method in the form of grinding is among the most commonly applied end-of-life recycling technologies. Mechanical disintegration of the waste rubber is conducted at ambient temperature (the most commonly used method) or cryogenic conditions (liquid nitrogen as a freezing medium) until the required particle size has been reached [7]. In Fig. 1 the comparison between the shape of grinding rubber particles obtained by a cryogenic technique and ambient grinding is presented. Ground tire rubber (GTR) obtained *via* ambient grinding possesses more extended surface than the ground rubber obtained *via* cryogenic technique, which has significant influence on interphase interaction between matrix and waste rubber.

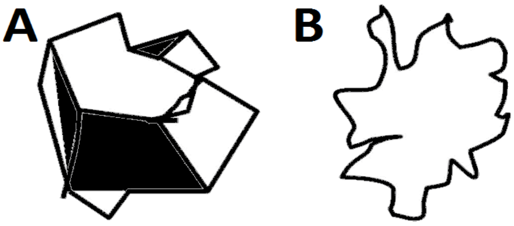

Fig. 1. Surface of ground tire rubber obtained *via* cryogenic technique (a) and ambient grinding (b) [7]

The disintegrated waste rubber containing the high quality material can be used as a filler in thermoplastic compositions [8, 9], thermoplastic elastomers [10, 11] and rubber compounds [12, 13] as well as a bitumen and concrete modifier [14] and as a substrate used in reclaiming/devulcanization [15, 16] or pyrolysis process [17]. Comprehensive work about using of ground tire rubber in polymeric compositions was recently published by Karger-Kocsis *et al.* [18].

The incorporation of larger amount of ground tire rubber (GTR) in polymeric compositions causes deterioration of mechanical properties of the compositions resulting from lower adhesion and lower interaction between polymer/GTR phases. Higher interaction between the substrates can be obtained by using of compatibilizers which improves the quality of the polymeric composition containing ground tire rubber. On the other hand, low compatibility between phases has the smaller influence on properties of a polymeric material with the cellular structure and it can be the advantage of this type of materials [19].

In the present work, a review describing the progress in research on compatibilization and foaming of polymeric compositions filled with ground tire rubber is presented.

2. Compatibilization of Polymer/Ground Tire Rubber Blends

Nowadays, many methods for compatibilization of polymer blends containing ground tire rubber are developed; however, the main directions of research in this area include reducing the size of the used ground tire rubber. The increase of physical and/or chemical interfacial interaction in the heterogeneous polymer blend is also possible by the use of surface modification or addition of compatibilizers. An example of this process may be partial devulcanization of waste rubber [20, 21], giving a rise to the interactions on the phase boundary between the matrix polymer and the ground tire rubber. In Fig. 2 the scheme of compatibilization of polymer phase and ground tire rubber phase by partial reclaiming/devulcanization of GTR is shown.

Fig. 3 shows the morphology of the samples subjected previously to the tensile test at a speed of 500 mm/min. There was observed the significant effect of the degree of devulcanization on the fracture mechanism of rubber SBR/devulcanize rubber blends, which corresponds to the scheme of compatibilization presented in Fig. 2.

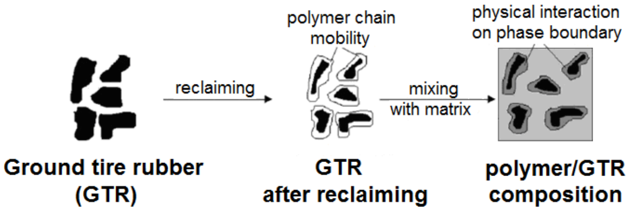

Fig. 2. Schematic view of compatibilization of polymeric compositions by the partial reclaiming of ground tire rubber [20]

Presented in Fig. 4 static and dynamic mechanical analysis confirms an increased compatibility of SBR/devulcanized blends with increasing devulcanization degree of waste rubber.

Effective method of compatibilization of plastomer/ground tire rubber blend is incorporation of the maleic anhydride grafted polyethylene (PE-g-MA) [22-24]. Fig. 5 shows the morphology of the samples previously subjected to the static tensile test at the speed of 50 mm/min. Blends of HDPE/GTR in ratio 50/50 wt % were modified by using PE-g-MA as a compatibilizer. In case of sample 50/50 HDPE/GTR, the plastomer phase was more ductile and showed lower adhesion to the cross-linked ground tire rubber than for sample HDPE/GTR/PE-g-MA 40/50/10 wt % that was confirmed by larger amounts of shredded pieces of the plastomer phase formed during tensile testing. The use of polyethylene grafted with maleic anhydride caused a significant increase of cohesive interfacial breaks between the plastomer and the ground tire rubber, which was also confirmed by the mechanical properties shown in Table 1. Proposal of schematic mechanism compatibilization of the plastomer/GTR bleds due to the reaction between maleic anhydride and hydroxyl group presented in carbon black is shown in Fig. 6. Maleic anhydride can also react with *i.e.* carboxyl group presented on the surface of ground tire rubber after reclaiming (controlled oxidation).

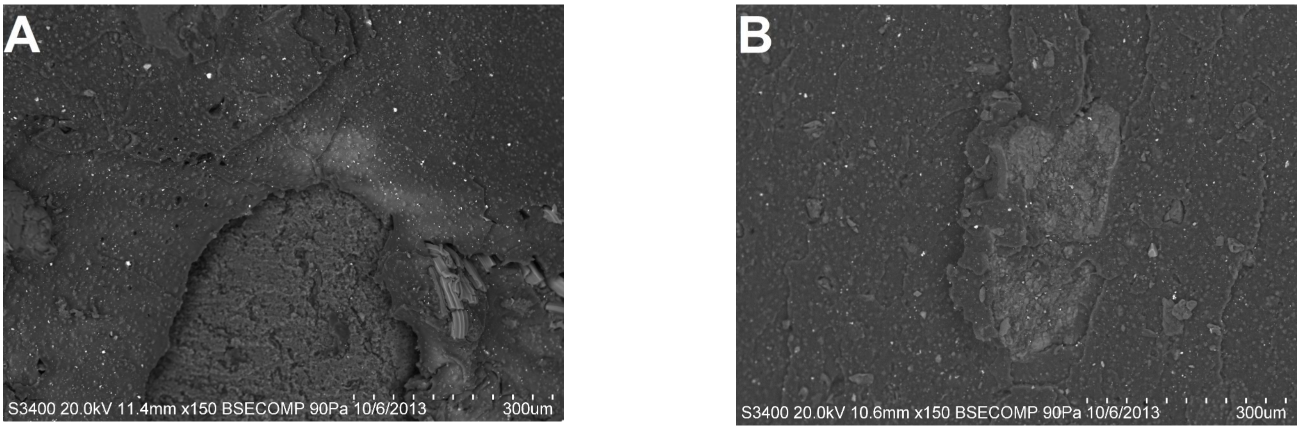

Fig. 3. SEM images of SBR vulcanizates with 50 phr of: GTR without devulcanization (a) and dGTR reclaimed at 453 K (b); magnification of 150x

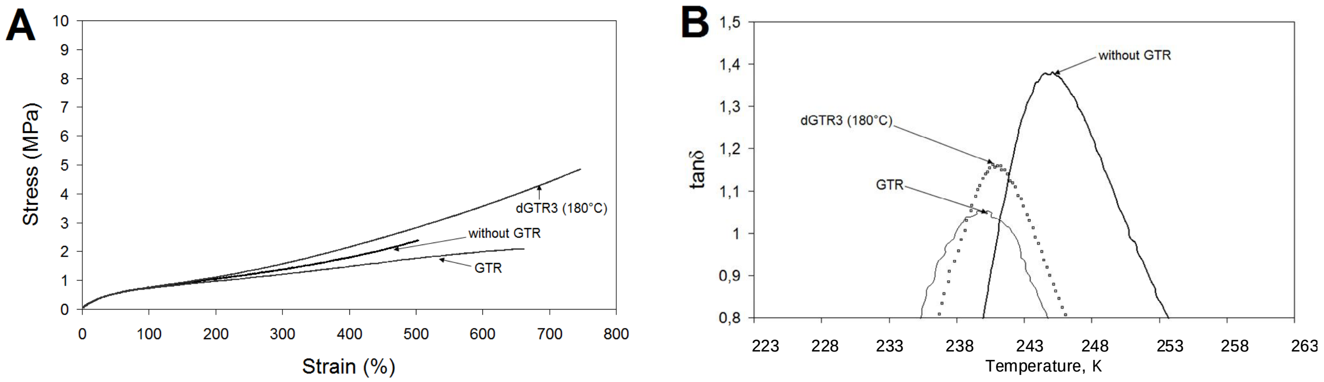

Fig. 4. Stress-strain curves (a) and loss tangent values (b) in temperature function determined for SBR vulcanizates with 50 phr of GTR without devulcanization and dGTR reclaimed at 453 K

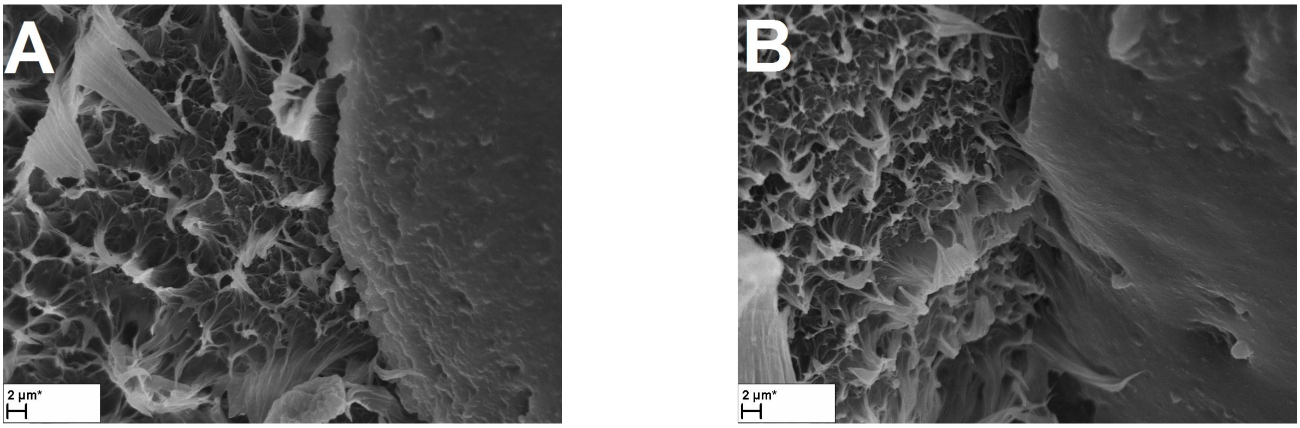

Fig. 5. SEM images of samples: HDPE/GTR 50/50 wt % (a) and HDPE/GTR/PE-g-MA 40/50/10 wt % (b); magnification of 5000x

Table 1

Properties of thermoplastic composition without and with PE-g-MA

Item	Sample	
	HDPE/GTR 50/50 % wt.	HDPE/GTR/PE-g-MA 40/50/10 wt %
Tensile strength, MPa	6.36 ± 0.33	7.35 ± 0.31
Elongation at break, %	10 ± 1	13 ± 1
Hardness, °ShD	43	43
Abrasion resistance, mm^3	169	127

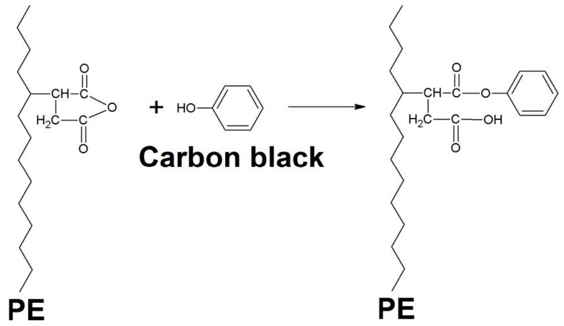

Fig. 6. Chemical reaction between PE-g-MA and carbon black content in the ground tire rubber [25]

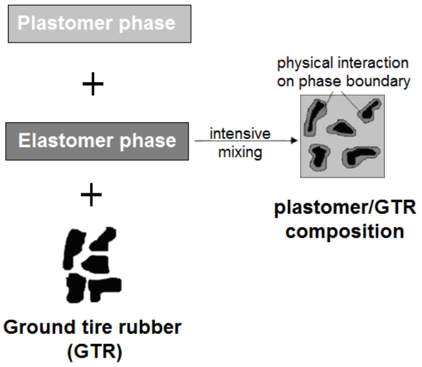

Fig. 7. Schematic diagrams of plastomer/GTR compositions compatibilization by using of elastomer

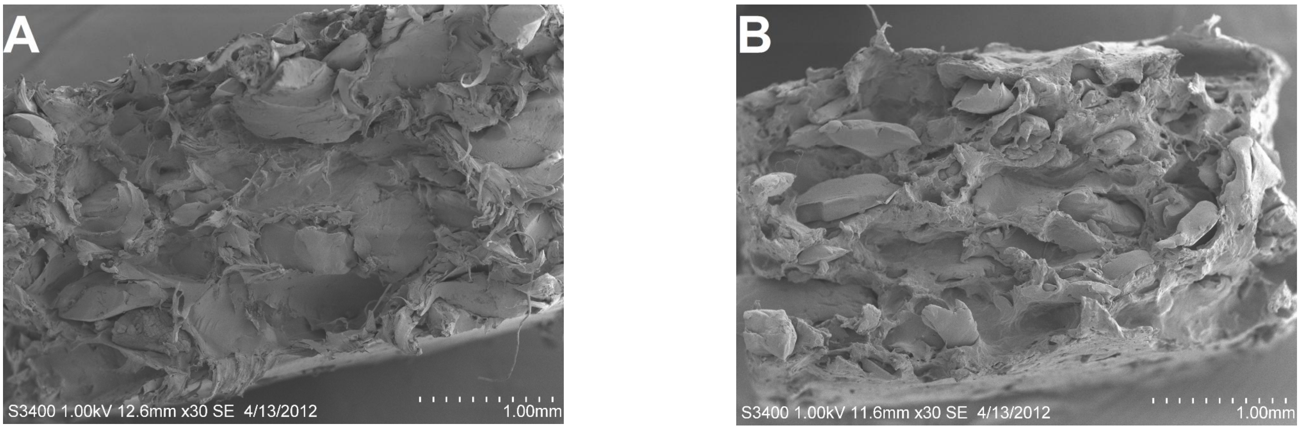

Fig. 8. SEM images of blends: LDPE/GTR/slightly cross-linked butyl rubber 40/50/10 wt % (a) and LDPE/GTR/slightly cross-linked butyl rubber 10/50/40 wt % (b)

Other commonly used method for compatibilization of the plastomer/ground tire rubber blends is incorporation of elastomers [26, 27] and thermoplastic elastomers [28, 29]. Based on the results obtained by other researchers [30-32], one can conclude that the incorporation of an elastomer, as the compostibilizer, the coating of ground tire rubber is strongly affected. Elastomer provides interphase between phase of the plastomer and ground tire rubber, which improve the mechanical properties of prepared blends. Scheme of compatibilization mechanism of the plastomer/ground tire rubber with elastomer is shown in Fig. 7.

In Fig. 8 SEM images of low density recycled polyethylene/GTR blends with the slightly cross-linked butyl rubber after tensile test are presented. It was observed that the increased content of butyl rubber in the obtained blends resulted in the higher number of microfractures in LDPE matrix, as observed on the surface of samples after breaking. The results suggest that butyl rubber is partially compatible with LDPE phase, whilst it is not compatible with the ground tire rubber [33, 34].

Moreover, in the published papers the information about methods of waste rubber modification is presented, *e.g.* by controlled oxidation [35, 36], ozonation [37], chlorination [38, 39], using of supercritical gases and liquids [40, 41], grafting monomers and acid anhydride using gamma and UV radiation [42, 43], plasma [44, 45], microwave [46, 47] and ultrasound [48, 49] treatment of waste rubber, *etc*. The modification of ground tire rubber improves the mechanical properties of polymer composition, which results from an increasing interfacial bonding between separate phases.

3. Foaming of Polymer/Ground Tire Rubber Blends

In the recent years, only a few researches [50-58] on the potential use of foamed thermoplastic compositions containing waste rubber, were published. The obtained results indicate that addition of 25 wt % of the ground tire rubber to polypropylene has beneficial influence on the cell size reduction in comparison to neat polypropylene caused by an enhanced viscosity of foamed blend. Moreover, ground tire rubber can act like a nucleating agent during forming of foam structure. Increasing the contribution of ground tire rubber (above 25 wt %) adversely affected the cellular structure obtained foams, which is due to weak interfacial bonding of the used components.

An interesting alternative for thermoplastic foams filled with GTR, constitutes foamed polyurethane materials containing the ground tire rubber [59, 60]. Advantage of these materials is the simple forming of polyurethane foam and diverse properties of obtained products that can be controlled by chemical structure of polyurethane or addition of some additives. Furthermore, the ground tire rubber and modified ground tire rubber possess the surface chemical groups (*i.e.* hydroxyl, carboxyl, aldehyde group, *etc*.), which can react with isocyanate groups of the polyurethanes. These reactions increase compatibility of polyurethane matrix and ground tire rubber.

4. Conclusions

Using of higher amount of ground tire rubber (GTR) in polymeric compositions caused deterioration of mechanical properties, due to a low adhesion and weak interactions of both phases. Using of comptibilizers in polymer/GTR blends can enhance the mechanical properties of obtained products. On the other hand an interesting alternative is foaming of polymer/GTR blends. The porous polymer structure overcomes the problem of weak interfacial interactions. Moreover the usage of this type of polymeric materials reduces production cost and have beneficial influence on environment (limiting use of fresh materials, reduction of carbon dioxide emissions). Further studies in this field, should be directed on optimalization of processing and characterization of obtained foamed materials properties that allows to estimate a correlation between cellular structure of polymer matrix and cross-linked structure of the ground tire rubber.

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СПІНЮВАННЯ ЯК АЛЬТЕРНАТИВА КОМПАТИБІЛІЗАЦІЇ ПОЛІМЕРНОЇ КОМПОЗИЦІЇ З НАПОВНЮВАЧЕМ ШИННА ГУМА – ОГЛЯД

Анотація. *Показано, що пошук нових методів перероблення гумових відходів, як цінної сировини, є головним видом діяльності багатьох науково-дослідних інститутів і компаній. Розглянуто компатибілізацію і спінювання полімерних композицій з наповнювачем шинна гума.*

Ключові слова: *гумова шина, гума утилізації, спінювання, полімерна композиція, компатибілізація.*