INFLUENCE OF MALEATED ETHYLENE PROPYLENE DIENE TERPOLYMER COMPATIBILIZATION AGENT ON PHYSICAL-MECHANICAL PROPERTIES OF POLYMERIC COMPOSITES BASED ON CURED RUBBER POWDER AND HIGH DENSITY POLYETHYLENE

Mariana Daniela BERECHET[1], Maria Daniela STELESCU[2], DANA GURĂU[3]

This paper investigates the compatibilization action of maleated ethylene-propylene-diene terpolymer ionomer on polymeric composites based on high density polyethylene and cured rubber powder. Two types of cured rubber powder obtained from rubber wastes were used. Composites were developed using the melt mixing technique. Physical-mechanical characteristics of polymeric composites depend on the type and amount of components in blends. The optimal amount of compatibilization agent was selected for developed polymeric composites. The resulted polymer composites can be used in the manufacture of a large range of products, such as hoses, gaskets, shoe heels, joint packings, slab pavements in sports halls etc.

Keywords: HDPE, rubber powder, EPDM-g-AM, mechanical properties

1. Introduction

Rubber wastes resulting from the manufacture of tyres, mechanical rubber goods, etc., are generally non-biodegradable, being thus a major environmental problem. Some ways to recycle rubber wastes were studied, such as: preparation of reclaimed rubber, introduction of rubber powders into the rubber blends, etc. A promising application for recycled rubber powder is in the production of composite materials of thermoplastic elastomer type, whose properties are similar to elastomer and whose processing technology is similar to plastic (injection, extrusion, etc.), on high productivity automated lines, significantly increasing work productivity. Mixing of a dispersed elastic (rubber powder) and thermoplastic filler (polyethylene, polypropylene, polystyrene etc) in a melt is the simplest method for their production [1-2].

[1] Engineer, National Research and Development Institute for Textile and Leather- Division Leather and Footwear Research Institute, e-mail: marianadanielaberechet@yahoo.co.uk
[2] Senior Researcher II, National Research and Development Institute for Textile and Leather-Division Leather and Footwear Research Institute, e-mail: dmstelescu@yahoo.com
[3] Research Assistant, National Research and Development Institute for Textile and Leather-Division Leather and Footwear Research Institute, e-mail: dana.gurau@icpi.ro

The main factor affecting the mechanical properties of materials containing a dispersed ingredient is adhesive interaction at the matrix/filler boundary. Adhesive interaction of components of the blend depends on their compatibility, which is determined by the chemical structure of polymer and filler. To improve the properties of thermoplastic elastomers, different additives are introduced to enhance adhesive interaction [3-4].

This paper presents a study on the possibilities to use rubber wastes as flexible fillers in thermoplastic polymers. To produce polymer composites, high density polyethylene (HDPE) Hostalen GC 7260 and two kinds of rubber powder obtained from the rubber wastes resulting from rubber goods manufacturing were used. To improve the properties of polymer composites, an ionomer based on maleated ethylene propylene diene terpolymer (EPDM-g-AM) is introduced to enhance adhesive interaction. The effect of amount of EPDM-g-MA compatibilizing agent on physical-mechanical properties of HDPE/waste rubber powder blends was studied.

This is an efficient procedure for rubber waste reclamation as a result of: employing polymer composites as substitutes for thermoplastics - thus resulting in material savings, rubber waste recycling, no wastes resulted from polymer composite processing, because the fleshes and refuse can be recycled. These composites can be processed by some techniques similar to those for plastics and rubber blends (pressing, injection, extrusion, etc.) [5, 6].

2. Experimental

In preparing the above polymer composites the following materials were used:

- High density polyethylene – Hostalen GC 7260 (from BASELL): density 0.962 g/cm^3, MFI 23.0 g/10 min at 190°C/2.16 kg, Vicat softening temperature B/50 of 72°C.
- Two kinds of rubber powder made by grinding rubber wastes resulted from rubber goods manufacturing: type RP1 – natural rubber (NR) powder and type RP2 – styrene-butadiene rubber (SBR) powder. They were subjected to chemical tests and the results are shown in **Table 1**. *Acetone extract* value (5.36% and 14.86%, respectively) reveals such matter as free sulphur, curing accelerators, antioxidants, resins, plasticizers, lubricants and monomers being present in the elastomers. *Ash* value (13.24% and 26.57%, respectively) reveals the presence of such fillers as metal oxides (zinc oxide), chalk precipitate and other passive fillers; as a remark, it is known that as a result of the calcination operation, calcium carbonate ($CaCO_3$) - a frequently used filler in the rubber industry – turns into calcium oxide (CaO). *HCl insoluble matter* value (0.03% and 0.96%, respectively) reveals the presence of an active filler such as silica

precipitate in the rubber blends used in preparing rubber waste powder – low values indicate that there is only a low amount of active filler in the powder, which may be due to sulphur and curing accelerators [7].

- Compatibilizing agent EPDM-g-AM was used to improve the properties of the HDPE/rubber powder polymer composites; EPDM-g-MA elastomers exhibit the peculiar features of EPDM elastomers, but they can react with divalent metal oxides salts leading to crosslinking by ionic bonds. In this study EPDM-g-MA elastomer Royaltul 498 containing 1% MA having amorphous structure and as neutralizing agents of the ionic groups - zinc oxide in the presence of stearic acid were used. Mooney viscosity (ML 1+4 125ºC): 130, Tg = - 46ºC and density 0.89 g/cm^3.

Table 1

Rubber powder characteristics

Characteristic	**RP1 (NR)**	**RP2 (SBR)**
Acetone extract, %	5.36	14.86
Ash, %	13.24	26.57
Insoluble matter in HCl, %	0.03	0.96

Polymer composites based on rubber wastes and high density polyethylene were prepared by melt blending at a temperature closed to the melting point of the thermoplastic matrix, on an electrically heated laboratory roller, with the following process variables: temperature – 140-150^{o}C, friction – 1:1.24. The ingredients were weighed according to the processing formulations (see **Table 2** and **Table 3).** The blend constituents were added in the following sequence: roll binding of HDPE (5'), embedding EPDM-g-AM, zinc oxide and stearic acid (2'), introducing rubber powder (5'), homogenizing the blend and removing it from roll in 2 mm thick sheets (3').

Plates for the physical-mechanical tests were obtained by compression molding into 2x150x150 mm sheets on a laboratory electrical press at a temperature of 160^{o}C and pressure of 150 MPa for 10 minutes. The molded samples were stored away from light, at room temperature.

Table 2

Formulations of the polymer composites based on HDPE/EPDM-g-AM/vulcanized NR rubber powder

Ingredients	**P50**	**PI1**	**PI2**	**PI3**	**PI4**	**I**
EPDM-g-AM Royaltuf 498, g	-	10	20	30	40	100
Stearic acid, g	-	0.2	0.4	0.6	0.8	2
Zinc oxide, g	-	2	4	6	8	20
Natural rubber powder PR1, g	200	200	200	200	200	-
HDPE Hostalen GC 7260, g	200	190	180	170	160	-

Table 3

Formulations of the polymer composites based on HDPE/EPDM-g-AM/vulcanized SBR rubber powder

Ingredients	**N50**	**NI1**	**NI2**	**NI3**	**NI4**
EPDM-g-AM Royaltuf 498, g	-	10	20	30	40
Stearic acid, g	-	0.2	0.4	0.6	0.8
Zinc oxide, g	-	2	4	6	8
SBR rubber powder PR2, g	200	200	200	200	200
HDPE Hostalen GC 7260, g	200	190	180	170	160

Mechanical properties of samples were measured on a Schopper tensile tester with a nominal rate of the traverse of the moving grip of 460 mm/min. Modulus at 100% strain, tensile strength and elongation at break tests were carried out according to the conditions described in ISO 37/2012, on dumb-bell shaped specimens of Type 2. Tearing strength tests were carried out using angular test pieces (type II), according to SR EN 12771/2003. The hardness of these materials was measured using the Shore A scale with samples of 6 mm thickness, by using a hardener tester according to ISO 7619-1/2011. Elasticity was evaluated with a Schoob test machine using 6 mm thick samples, according to ISO 4662/2009. Residual elongation is the elongation of a specimen measured 1 minute after rupture in a tensile test. It was calculated using formula 1:

$$\text{Residual elongation (\%)} = [(L-L_0)/L_0] \times 100 \quad (1)$$

where: L_0 is the initial length between two marks and L is the length between the marks 1 minute after the sample broke in a tensile test.

Accelerated ageing trial was done according to SR ISO 188/2007 using the hot air circulation oven method. Similar samples to those used for tensile testing and for hardness determination were used. Test duration was of 7 days and temperature of 70±1ºC. The results were compared with those from samples not subjected to ageing.

For rubber powder, the ash was determined in accordance with method A of ISO 247:2006 and the acetone extract was determined, in accordance with method A of ISO 1407:2011.

3. Results and discussion

HDPE is one of the large-consumption polymers and it is difficult to make a polymer blend or a composite due to its non-polar characteristics. Because the non-polar characteristics of HDPE often result in poor interfacial adhesion properties with other materials, a third material is used to increase the compatibility between the two components [5-6].

The compatibilization agent is generally a co-polymer, preferably a block copolymer containing chain units similar to both blend constituents. There is a variety of variables acting on the interface saturation such as: homopolymer molecular weight, copolymer molecular weights, polymer structure details, how the compatibilization agent is added, processing conditions, copolymer affinity for the disperse phase, copolymer orientation at the interface, etc., [5-7].

In this study, the aim of adding EPDM-g-MA to the matrix was to increase the compatibility of vulcanized rubber waste powder and the HDPE matrix. To see the effect of adding this material on the mechanical properties of HDPE matrix, 5, 10, 15 and 20 wt% EPDM-g-MA was added to a HDPE matrix. Then, the mechanical properties of HDPE/EPDM-g-AM/vulcanized rubber powder ternary compounds were compared with pure HDPE, the EPDM-g-MA blend (I) and HDPE/vulcanized rubber powder binary compound (P50 and N50, respectively).

The physical-mechanical properties of blends based on HDPE/EPDM-g-AM/vulcanized rubber powder obtained is presented in Table 4 and Table 5.

As it can be seen from Tables 4-5, upon adding 5 wt% EPDM -g-MA to a HDPE matrix, a decrease in hardness (by 8 ºShA and 2 ºShA respectively), tensile strength (by 32.2% and 39.7% respectively) and tear strength (by 30.7% and 18%, respectively), and an increase in elongation at break (by 189.4% and 13% respectively) occur. This is due to the fact that properties of polymeric composites depend on the characteristics of components. Upon further increase of EPDM-g-AM amount in composites, an increase in tensile strength and tear strength is noticed, by the formation of a maximum and then a slight decrease of these characteristics, while elongation at break forms a minimum. According to obtained characteristics, it can be said that in order to obtain optimal values for tensile strength and tear strength, the polymeric composites must contain an optimal concentration of compatibilization agent of 10-15wt% EPDM-g-MA to HDPE matrix.

Table 4

Physical-mechanical characteristics for the polymer composites based on HDPE/EPDM-g-AM/vulcanized NR rubber powder

Ref. no.	Ingredient	P50	PI1	PI2	PI3	PI4	I	HDPE
	Physical-mechanical characteristics measured in normal conditions							
1	Hardness, ºShA	96	88	94	95	93	62	90
2	Elasticity, %	16	20	20	20	22	40	24
3	100% Modulus, N/mm^2	8.8	4.3	7.5	7.2	6.5	1.5	-
4	300% Modulus, N/mm^2	-	5.5	-	-	-	2.5	-
5	Tensile strength, N/mm^2	8.7	5.9	7.3	7.2	6.5	5	33.4
6	Elongation at break, %	113	327	127	140	273	520	40
7	Residual elongation, %	43	63	31	40	65	42	20

8	Tear strength, N/mm	75	52	67.5	69	65	32.5	148
	Physical-mechanical characteristics measured after accelerated ageing (168hx70ºC)							
1	Hardness, ºShA	95	88	94	95	93	61	
2	100% Modulus, N/mm^2	-	4.7	-	7.8	6.5	38	
3	Tensile strength, N/mm^2	8.9	5.6	7.2	7.8	6.5	4.3	
3	Tear strength, N/mm	68	53.5	61	65	59	31	

In literature, experimental and theoretical studies have reported the interfacial saturation reached by copolymer addition. Thus, the disperse phase area sizes have been revealed to decrease with the increase in the grafted copolymer percentage. The average area size has decreased with the increase in the compatibilization agent level up to an equilibrium point which can be considered to be the so-called critical micelle concentration (CMC), where the micelles are formed. By adding further copolymer above the CMC has led to micelle formation decreases often the overall performance of the blend system [6-9]. Given the literature studies and obtained results (Tables 4-5), for such blends a level of 10-15wt% EPDM-g-MA added to a HDPE matrix may be concluded to be the best one to improve polymer composites based on HDPE/EPDM-g-AM/vulcanized rubber powder characteristics. It can be the EPDM-g-AM critical micelle concentration (CMC) for such blends.

Behavior of obtained polymeric composites to accelerated ageing is very good because hardness variation is 1ºShA, and tensile and tear strength variation is less than 10%.

Table 5

Physical-mechanical characteristics for the polymer composites based on HDPE/EPDM-g-AM/vulcanized SBR rubber powder

Ref. no.	Physical-mechanical characteristics	N50	NI1	NI2	NI3	NI4
I	*Physical-mechanical characteristics measured in normal conditions*					
1	Hardness, ºShA	96	93	95	95	95
2	Elasticity, %	20	20	22	20	20
3	Tensile strength, N/mm^2	12.6	7.6	11.8	10.4	9.3
4	Elongation at break, %	53	60	60	60	60
5	Residual elongation, %	8	12	11	15	19
6	Tear strength, N/mm	44	52	65	69	65
II	*Physical-mechanical characteristics measured after accelerated ageing (168hx70ºC)*					
1	Hardness, ºShA	97	94	96	95	95
2	Tensile strength, N/mm^2	13	8.2	12.5	11	11
3	Tear strength, N/mm	45	48	60	63	62

Comparing characteristics of polymeric composites containing natural rubber powder (Table 4) with those containing SBR rubber powder (Table 5), it is noticed that composites containing natural rubber powder have higher elongation at break and tear strength than those containing SBR rubber powder, tensile

strength is lower, and hardness and elasticity have comparable values. These effects prove that properties of polymeric blends are additional and depend on the characteristics of component polymers and on their molar fractions; these characteristics of polymer blends are reported by several researchers [8-10].

4. Conclusions

Blending ground rubber with thermoplastic polymers is a very cost effective and efficient method for recycling rubber waste. In this paper, new polymer composites were prepared from the rubber powder and HDPE by melt blending. To improve the properties of polymer composites, an ionomer based on maleated ethylene propylene diene terpolymer (EPDM-g-AM) is introduced to enhance adhesive interaction. The effect of amount of EPDM-g-MA compatibilizing agent on physical-mechanical properties of HDPE/waste rubber powder blends was studied. For such blends, a level of 10-15wt% EPDM-g-MA added to a HDPE matrix may be concluded to be the best one to improve the polymer composites based on HDPE/EPDM-g-AM/vulcanized rubber powder characteristics. It can be the EPDM-g-AM critical micelle concentration (CMC) for such a blend.

The resulted thermoplastic polymer composites can be processed by extrusion, injection, or compression molding. The use of such polymer composites removes curing operation with high power expenditure and noxious gas release. Furthermore, the processing is highly reduced, resulting thus in lower costs, both due to using lower cost materials and simplified processing equipment in continuous flow. The resulted polymer composites can be used in the manufacture of a large range of products, such as hoses, gaskets, shoe heels, joint packings, slab pavements in sport halls, etc., with competitive characteristics - as compared to the similar products from virgin materials [11-12].

R E F E R E N C E S

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