DYNAMIC VULCANIZED THERMOPLASTIC ELASTOMERS BASED ON ETHYLENE-PROPYLENE TERPOLYMER AND POLYETHYLENE

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The paper presents the studies on the obtaining and characterization of new types of dynamically vulcanized thermoplastic elastomers based on ethylene-propylene terpolymer rubber and polyethylene. As a vulcanizing agent, a phenolic resin (0-15 parts per 100 parts rubber) was used in the presence of dehydrated stannous chloride. Mixtures were obtained by the dynamic vulcanization technique in a Plasti-Corder Brabender mixer at 80 rpm and a temperature of 170°C. Analyzing variations of physical-mechanical characteristics depending on the amount of resin introduced into the blends, it was observed that 100% modulus, tensile strength, and tear strength increased to an optimal point after which they tended to decrease. By dynamically crosslinking the elastomer in the thermoplastic polymer melt there was a significant improvement in the resistance to repeated flexures, behavior to permanent deformation at compression, and resistance to the action of toluene. New materials can be used in various fields such as: the footwear industry (soles, heels and plates), protection equipment, obtaining gaskets, hoses, technical rubber products for cars, etc.

Keywords: dynamic vulcanized thermoplastic elastomers, EPDM, physical-mechanical characteristics

INTRODUCTION

The thermoplastic elastomers (TPE) is a rubbery material with properties and functional performance similar to those of conventional vulcanized rubber at room temperature, yet it can be processed in a molten state as a thermoplastic polymer at elevated temperature (Walker and Rader, 1988; Legge *et al.*, 1987; Naskar, 2004). The unique characteristics of TPEs make them very useful and attractive alternatives to conventional elastomers in a variety of applications and markets, such as the automotive industry. Depending on the chemical composition, the main types of thermoplastic elastomers are: styrene butadiene elastomers (SBS), thermoplastic elastomers olefin (TPO), thermoplastic polyurethanes (TPU), thermoplastic vulcanizates (TPV), thermoplastic copolyesters (CPE), ionic thermoplastic elastomers (ETI) etc (Mirci, 2005; Stelescu, 2011). The TPVs represent the second largest group of soft thermoplastic elastomers, after styrenic-based block copolymers. The TPVs represent the second largest group of soft thermoplastic elastomers, after styrenic-based block copolymers. Commercial types of dynamic vulcanizates are commonly based on blends of unsaturated ethylene-propylene terpolymer elastomer (EPDM) and polypropylene (Stelescu, 2011; Puydac, 1991). A wide range of TPVs can be obtain, which differ from each other by the types of thermoplastic elastomers and polymers used, the blended elastomer ratio, the vulcanization system used, etc. The vulcanization systems used are selected depending on the type of elastomer used or the desired characteristics of the finished products. Thus, it is possible to use: (1) vulcanization with sulfur and vulcanization accelerators, crosslinking with peroxides in the presence of vulcanizing coagents, crosslinking with phenolic resins, etc. The amount and type of vulcanization agents used significantly influence the physico-mechanical, chemical and rheological properties of the obtained products - TPVs granules or finished products.

In this paper were analyzed new types of dynamic vulcanized thermoplastic elastomers based on ethylene-propylene terpolymer rubber and high density polyethylene in which a phenolic resin in the presence of dehydrated stannous chloride was used as a vulcanizing agent. The influence of the phenolic resin quantity on the physico-mechanical and chemical characteristics of the obtained thermoplastic vulcanizates was analyzed.

MATERIALS AND METHODS

Materials

The following raw materials were used: (1) EPDM Nordel NDR 47130 (ethylene content 67%, 5-ethylidene-2-norbornene (ENB) content 4.9%, crystallinity degree 9%, density 0.97 g/cm³, Mooney viscosity at 125°C: 130); (2) HDPE Hostalen GC 7260 (density 0.962 g/cm³, softening temperature Vicat B/50 of 72°C) (3) zinc oxide (97.1 % active ingredient) Werco Metal, Zlatna Romania, (4) phenolic resin Ribetak 75-30 (8,8% methyl and melting point of 85°C) and stannous chloride dehydrate (molecular weight 225.65, 98.6% purity) were used as a crosslinking agent, (5) antioxidant pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate Irganox 1010 (melting point of 40°C, 98 % active ingredient).

Method

Thermoplastic vulcanized are obtained by dynamically crosslinking an elastomer into a molten thermoplastic polymer under strong shear forces, when forming micron-sized cross-linked rubber particles finely dispersed in a thermoplastic matrix (Stelesc, 2011). Therefore, in order to obtain the blends is important to use internal mixer that allows efficient mixing of ingredients, due to the shear forces occurring during the rotation of the screws. At the same time, it is necessary to provide a suitable temperature for melting the thermoplastic polymer – the polyethylene.

Blends were obtained by mixing in a 70 cm³ Plasti-Corder PLV 330, Brabender equipment at 80 rpm, and temperature of 175°C. The mixing sequence involved, first adding the thermoplastic polymer into the mixer. After melting HDPE (3-4 min), EPDM rubber was embedded (3-4 min). When a homogeneous melt was achieved, the antioxidant and zinc oxide were added (1-2 min). Finally, phenolic resin and stannous chloride were added and the mixing process was continued for about 2 min. Blends were homogenized on a laboratory roller mill heated at 155-165°C. Plates required for physical-mechanical tests were obtained by pressing in an electrical press at 170°C, for 5 min and pressure of 150 MPa. After molding, the mix was cooled at room temperature under pressure. The blend formulations containing EPDM and HDPE are presented in Table 1.

Table 1. Formulations of the thermoplastic elastomers

Ingredients	Samples Codes						
	R0	R1	R2	R3	R4	R5	R6
EPDM (g)	60	60	60	60	60	60	60
HDPE (g)	40	40	40	40	40	40	40
ZnO	2	2	2	2	2	2	2
Phenolic resin (g)	0	4	8	12	16	20	24
SnCl ₂ x 2H ₂ O (g)	0	0.8	1.6	2.4	3.2	4	4.8
Antioxidant (g)	1	1	1	1	1	1	1

Specimen Characterization

Tensile properties were measured by means of a Schoppler tester. *Tensile strength* was determined using dumb-bell shaped specimens according to ISO 37/2012. Residual elongation is the elongation of a specimen measured 1 min after rupture in a tensile test. It was calculated using the formula:

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

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

Tear strength was measured according to EN 12771/2003 using angular test pieces (type II).

Hardness, in Shore A, was measured by means of a hardness tester according to ISO 7619-1/2011.

Elasticity was determined with a Schob type test machine (according to ISO 4662/2009).

Test specimens were cut off from plates of 150 x 150 x 2 mm³ or 50 x 50 x 6 mm³ by means of an automatic punching die.

Accelerated ageing tests were carried out according to ISO 188/2001 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±1°C. The results were compared with those from samples not subjected to ageing.

The densities of samples were measured according to ISO 2781/2010.

Abrasion resistance test was carried out according to ISO 4649/2010, the cylinder method using a pressure of 10 N. Abrasion resistance was expressed by relative volume loss in relation to calibrated abrasive paper. A wearing tester with abrasive cloth and abrasive based on normal electro-corundum on dressed cloth substrate with granulation of 212–80 µm (PE 80), whose abrasiveness must be of 180–220 mg control rubber. The samples used were obtained from rolled blends and pressed by cutting with a rotating die and have cylindrical shape, with a diameter of 16 mm and height of min. 6 mm.

Flexion resistance (Ross Flex) was determined according to SR 7645/1994. Samples were obtained by punching rubber plates and have rectangular shape. The test was performed using a Ross Flex equipment, monitoring crack marks on each sample at intervals of 1h, 2h, 4h, 8h, 24h, 48h, 72h, 96h.

The *permanent deformation in compression test* was carried out according to SR 8664:1970. Samples were obtained by punching rubber plates and have the shape of 6 mm thick discs. Determinations were performed for a compression of 25% at the temperature of 23°C for 22 h.

Determination of *toluene action* was performed according to ISO 1817/2015. The test pieces of known weight, m_0 , were immersed in toluene in diffusion test bottles and kept at room temperature for 22 hours. After immersion the samples were removed from the solvent and the wet surfaces were quickly dried using a tissue paper and re-weighted, m_i .

To calculate the percentage change in mass Δm_{100} the following formula was used (2):

$$\Delta m_{100} = \frac{m_i - m_0}{m_0} \times 100 \quad (2)$$

where m_0 is the initial mass of the test piece and m_i is the mass of the test piece after immersion.

To calculate the percentage change in volume ΔV_{100} the following formula was used (3):

$$\Delta V_{100} = \left(\frac{m_i - m_{i,w} + m_{s,w}}{m_0 - m_{0,w} + m_{s,w}} - 1 \right) \times 100 \quad (3)$$

where

$m_{0,w}$ is the initial mass of the test piece (plus sinker if used) in water;

$m_{i,w}$ is the mass of the test piece (plus sinker if used) after immersion in water;

$m_{s,w}$ is the mass of the sinker, if used, in water.

RESULTS AND DISCUSSION

Analyzing variations of physical-mechanical characteristics depending on the amount of resin introduced into the blends, the following are noticed: (1) the hardness varies with 2°Sh A and the elasticity with max 28.6% when increasing the amount of resin; (2) the tensile strength and tear strength increase to an optimum point that corresponds to an amount of about 8 parts per 100 parts of rubber (phr) resin incorporated into the blend, after which they tend to drop, (3) values of elongation at break and residual elongation, are lower than those control sample (without resin) due to elastomer cross-linking (Elias, 2008).

Table 2. Characteristics of blends

Characteristics	Samples Codes						
	R ₀	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆
Hardness, °Sh A	94	96	95	95	95	95	96
Elasticity, %	28	24	22	22	22	22	20
100 % modulus, N/mm ²	7	10.4	10.2	10.5	11.2	12.3	-
Tensile strength, N/mm ²	7.3	15.7	17.2	16.7	14.8	15.7	14.9
Elongation at break, %	607	273	240	207	200	173	100
Residual elongation, %	303	79	52	46	37	36	33
Tear strength, N/mm	71	107	108	106.5	101	99	100

Blends R₀ and R₂ have been selected. For these, other characteristics were determined in order to define field of application, these were: resistance to accelerated aging, abrasion resistance, permanent compression deformation, behavior at Ross Flex repeated flexing, toluene action testing (see Figure 1 and Table 3).

Figure 1 show both mixtures exhibited very good behavior after accelerated aging. The non-resin (R₀) control mixture showed a decrease in tensile and tears strength. Instead, R₂ showed an increase in tensile and tears strength, probably continuing the cross-linking due to maintaining of high temperature.

Analyzing the characteristics presented in Table 3, we can see the following: (a) the specific weight increases by dynamic crosslinking of the elastomer with phenolic resin, leading to more compact blends with a better macromolecule packaging; (b) abrasion resistance values are very good, which recommends the use of these polymer alloys in a large number of industrial applications; (c) R₂ sample shows a very good resistance to repeated flexions, much better than R₀, the control sample (same composition with R₂ but not dynamically crosslinked); (d) the best behavior at permanent deformation at 25% compression was obtained for sample R₂ - 2.2 times better than the control sample R₀; this indicates that the dynamic crosslinking of the elastomer has led to a significant improvement in this feature; (e) the same behavior was observed for toluene resistance,

namely the mass and volume variation after 72 h immersion in toluene was about 2 times lower for the sample R_2 than for the R_0 sample, indicating that the sample in which elastomer has been dynamically crosslinked has a higher resistance to the action of toluene than that in which the elastomer is not reticulated (Stelescu *et al.*, 2017).

Based on the results previously presented, determining fields of application was done by including characteristics of obtained thermoplastic elastomers EPDM/HDPE in product standards. Depending on these, the following areas of application were selected: in the footwear industry (soles, heels and plates), protection equipment (boots, etc), obtaining gaskets, hoses, technical rubber products for cars etc.

Figure 1. Properties in normal state and properties after accelerated ageing for R_0 and R_2 blends

Table 3. Chemical and physico-mechanical characteristics of the composites

Characteristics	Samples Codes	
	R_0	R_2
Specific weight, g/cm ³	0.97	0.98
Abrasion Resistance, mm ³	80	91
Permanent deformation in compression, 25 %, at 23°C x 22h, %	24.7%	11.8%
Ross Flex flexions at 23°C (no. of cycles)	46000	Over 150000
Determination of the toluene action after 72h:		
-mass variation, %	115	57
-volume variation, %	178	86.3

CONCLUSIONS

By dynamic vulcanization of the elastomer, blends of ethylene-propylene terpolymer elastomer and thermoplastic polymers – polyethylene, new elasto-plastic materials with improved properties have been obtained.

The blends had a good behaviour to accelerated ageing, indicating a good lifespan of products made of these materials. This contributes to a large extent to environmental

protection, as it leads to a reduced amount of wastes. Values of resistance to abrasion are very good and allow obtaining products which can be used in extraordinary friction conditions. The specific weight of samples is low, which allows obtaining light products with low material consumption etc.

Due to their performing characteristics, the new materials can be used for the manufacturing of products like as hoses, gaskets, rubber shoes, protective equipment etc.

The potential users of the new elasto-plastic materials will be economic operators processing rubber and plastics, footwear and car component manufactures etc.

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