DEVELOPMENT OF ELASTO-PLASTIC ECO-NANO-MATERIALS FOR FOOTWEAR INDUSTRY

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The paper refers to the obtaining of new types of eco-nano elasto-plastic materials with high-performance characteristics based on ethylene-propylene-terpolymer rubber (EPDM), high-density polyethylene (HDPE), plasticized starch and organically modified montmorillonite (OMMT). The new materials were obtained by the technique of dynamic vulcanization and melt intercalation in a Plasti-Corder Brabender internal mixer, at 80 rpm and a temperature of 170°C. The influence of using the OMMT type nanofiller and the plasticized starch filler on the characteristics was observed. The new materials have a melt flow index of over 12g/10 min at 180°C for a force of 10 kg, which allows injection processing - an ecological method of processing polymeric materials. The samples show very good physical-mechanical characteristics both in the normal state and after accelerated aging at 168 hours at 170°C (tensile strength over 16 N/mm², tear strength over 102 N/mm, hardness 55-59°ShD, elasticity over 30%, etc.). The materials show high values of abrasion resistance (below 30 mm³), and very good results for mass and volume variation after 22 hours at 23°C in: water, acids and concentrated bases. These characteristics are due both to the composition of the new materials and to the obtaining technology. For evaluating the structural modification, analysis of the FT-IR spectral of the samples was carried out. The new materials can be used in different fields such as: in the footwear industry (soles, heels and plates), safety equipment (boots, etc), obtaining gaskets, hoses, technical rubber products for cars etc.

Keywords: eco-nano-materials, EPDM, OMMT, plastified starch.

INTRODUCTION

In recent years, much research has been done on the development of starch-based products, as an ecological alternative to the use of polymeric materials obtained by petroleum synthesis (Carvalho *et al.*, 2003). Based on these, we set out to create new eco-materials for the footwear industry, made by incorporating starch into the synthetic polymer matrix. Because starch cannot be processed in the melt as it is, because it degrades before melting, it was plasticized with glycerin to lower the melting temperature below the degradation temperature (Nafchi *et al.*, 2013). In order to improve some chemical characteristics (such as: resistance to water, to chemical agents, etc.) and physical-mechanical (tensile and tear strength, etc.), the aim was to obtain nanocomposites by introducing in the mixture a layered clay - organically modified montmorillonite (OMMT). Obtaining these nanocomposites was carried out by the "melt intercalation" method, which is an ecological method of obtaining a nanocomposite, and leads to significant improvements of the properties (Steleescu, 2011). At the same time, the dynamic vulcanization technique was used - the crosslinking of the elastomer in the melt of a thermoplastic polymer in dynamic conditions when dynamically vulcanized thermoplastic elastomers (TPV) are obtained (Mirici, 2005). Dynamic crosslinking was performed with small amounts of vulcanizing agents such as alkylphenolic resins. In this way, the new materials can be processed by the method of injection or extrusion, eliminating the classic vulcanization operation with sulfur and organic accelerators, which is highly consuming electricity and which

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releases toxic gases (nitrosamines - carcinogens). At the same time, the technological flow is simplified and the total processing time corresponding to obtaining the finished products is significantly reduced.

MATERIALS AND METHODS

Materials

The materials used to obtain eco-nano materials were: (a) ethylene-propylene-terpolymer rubber (EPDM) Nordel rubber 3745P (ethylene content 70%, density 0.88 g/cm³), from Dow Chemical Company; (b) thermoplastic polymer – high density polyethylene (HDPE) Hostalen GC 7260 (density 0.962 g/cm³) from Lyondell Basell Industries Holdings; (c) compatibility agent chlor-butyl rubber Butyl (IIR-Cl) CB 1240 DISP IIR-Cl (1.25 % Chlorine, density 0.92 g/cm³) produced by Lanxess; (d) soluble starch obtained from potatoes produced by Lach-Ner; (e) starch plasticizer - glycerin (free acidity 0.02%, density 1.26 g/cm³), produced by S.C. Chimreactiv S.R.L.; (f) organic modified montmorillonite (OMMT) - Nanoclay I 31.PS (chemically modified montmorillonite layered clay with 0.5 - 5% propyl-amino-trietoxysilane and 15–35% octadecylamine, particle size below 20 microns), from Sigma Aldrich; (g) antioxidant pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate Irganox 1010 (98 % active ingredient), (h) vulcanize agent - heat-reactive resin SP-1055 - based on octylphenol-formaldehyde containing methylol groups (bromine content 4%, methylol content 11%, density 1.05 g/cm³), (i) zinc oxide I grade quality (99% purity).

Obtaining Mixtures and Plates for Characteristic Analysis

The mixtures were obtained according to the formulations presented in Table 1, using an internal Brabender mixer, at 175°C and max 80 rpm. The ingredients order was: HDPE - melts about 2', and then EPDM and IIR-Cl elastomers are added in approx. 2', add and incorporate the resin in 1', and then add the other ingredients. Homogenize for 2' and remove from the mixer. Prior to use, the starch was dried at 100°C for 8 hours and then plasticized with glycerin in a 2:1 mass ratio with continuous stirring at 70°C until a homogeneous mixture was obtained.

Table 1. Blend formulations

Ingredients, g	Sample Codes				
	1	2	3	4	5
EPDM Nordel 3745D	75	75	70	70	70
HDPE Hostalen GC7260	175	175	175	175	175
IIR-Cl	0	0	5	5	5
Zinc oxide	3.75	3.75	3.75	3.75	3.75
Irganox 1010	2.5	2.5	2.5	2.5	2.5
Resin SP 1055	-	7.5	7.5	7.5	7.5
OMMT I 31	-	-	-	7.5	7.5
Starch plasticized with glycerine	-	-	-	-	30

The semi-finished products obtained in the form of rubber mixtures, are modeled in plates for determining the characteristics using molds and vulcanizing presses. The processing parameters for the press were: ♦ preheating time 2' at a temperature of

170°C; ♦ molding time 5' at 170°C, and 300 kN pressing force; ♦ cooling time 8' until reach 45°C and 300 kN pressing force.

Specimen Characterization

After conditioning for 24 hours at room temperature, the plates were subjected to physical-mechanical determinations. *Tensile strength* and *tearing strength* tests were carried out with a Schopper1445 strength tester with testing speed 500 mm/min, using dumb-bell shaped specimens according to ISO 37/2020 and angular test pieces (Type II) according to EN 12771/2003, respectively. *Hardness* was measured by using a hardness tester according to ISO 48-4/2018 using 6-mm thick samples. *Elasticity* was evaluated with a Schob test machine using 6-mm thick samples, according to ISO 4662/2017.

Accelerated ageing evaluation was carried out according to ISO 188/2001 using the hot air oven method. Test duration was of 168 h and temperature of 70±1°C.

Melt flow index (MFI) of the thermoplastic materials was measured by means of an extrusion plastometer (capillary rheometer - Melt Flow Index – Haake), at 180°C and a 10 kg force was employed according to ISO 1133/2003.

The densities of elastomer samples were measured according to ISO 2781/2011.

Determining abrasion resistance was carried out according to ISO 4649/2017 the cylinder method, using a force of 10 N. Abrasion resistance was expressed by relative volume loss in relation to calibrated abrasive paper. The samples used were obtained from rolled mixtures and pressed, by cutting with a rotating die and have cylindrical shape, with a diameter of 16 mm and height of min. 6 mm.

In order to *determine the action of various mediums*, volume and mass variation was monitored using the volumetric and gravimetric methods according to ISO 1817/2015. Immersion time was 22±0.25 h. The samples used had a volume of 1-3 cm³ and a uniform thickness of 2±0.2 mm.

Fourier Transform Infrared Spectroscopy (FTIR) spectra of all the samples were obtained using Nicolet iS50 FT-IR spectrophotometer in the wave number ranging from 400 cm⁻¹ to 4000 cm⁻¹.

RESULTS AND DISCUSSIONS

Melt Flow Index (MFI)

All samples show very good values of the MFI (Table 2), showing a good process ability by the injection method. Compared to the control sample (sample 1), the MFI value decreases by introducing the crosslinking agent (resin) - see sample 2, as a result of the crosslinking of the elastomer in the plastomer melt. The decrease is even greater with the addition of the chlor-butyl rubber (II-Cl) compatibilizer (see sample 3), showing that it has significantly improved the yield of elastomer crosslinking reactions in the presence of phenolic resin, due to improved phase compatibility. The melt flow index increases by the addition of nanofiller (see sample 4), indicating the change in the morphology of the mixture in the molten state due to the formation of the nanocomposite. The MFI value improves at sample 5 compared to sample 4, because it also contains plasticizer from plasticized starch.

The Density of the Mixtures

The density of the mixtures (Table 2) increases from the control sample (sample 1) to the samples with phenolic resin (samples 2-5) and the samples with nanofiller (samples 4-5), indicating both the modification of the morphology with the formation of the micro / nanocomposite, and the introduction of dense ingredients (such as glycerin, resin or OMMT).

Abrasion Resistance

Abrasion resistance has high performance values, below 30 mm³ for all samples due to the very good wear values of HDPE - the polymer matrix of these (nano) composites (Table 2).

Table 2. Characteristics of blends

Characteristics	Sample Codes				
	1	2	3	4	5
<i>MFI 180°C and 10 kg force, g/10'</i>	21.6	16.6	5.59	12.5	19.5
<i>Density, g/cm³</i>	0.95	0.96	0.96	0.97	1.00
<i>Abrasion resistance, mm³</i>	27.03	20.71	20.81	26.54	28.88
<i>Medium action analysis, 22hx23°C</i>					
Immersion in distilled water					
• Mass variation, %	+0.22	+1.61	+0.03	+0.12	+0.43
• Volume variation, %	+0.50	+1.98	+0.03	+0.53	+0.60
Immersion in sol. H ₂ SO ₄ , 70%					
• Mass variation, %	+0.47	-0.07	+0.01	-0.09	+0.18
• Volume variation, %	+0.62	-0.16	+0.29	+0.18	-8.32
Immersion in sol. NaOH 50%					
• Mass variation, %	+1.06	+0.3	+0.28	+0.01	-0.03
• Volume variation, %	-7.43	-0.16	+0.03	+0.13	+1.12
Immersion in toluene					
• Mass variation, %	+29.00	+25.04	+26.04	+29.47	+30.90
• Volume variation, %	+33.56	+26.50	+27.61	+33.82	+38.83
<i>Physical-mechanical properties - normal state</i>					
○ Hardness, °ShA	99	99	99	98	99
○ Hardness, °ShD	57	57	58	58	59
○ Elasticity, %	52	53	52	48	30
○ Tensile strength, N/mm ²	18.20	17.67	16.04	16.76	16.85
○ Elongation at break, %	80	80	120	100	80
○ Residual elongation, %	4	8	28	20	40
○ Tear strength, N/mm	107	119	130	121	102
<i>Physical-mechanical properties after accelerated ageing 168h at 170°C</i>					
○ Hardness, °ShA	99	99	99	99	99
○ Hardness, °ShD	58	57	56	56	55
○ Elasticity, %	42	50	53	52	36
○ Tensile strength, N/mm ²	21.62	18.32	16.49	16.39	16.82
○ Elongation at break, %	80	100	100	100	80
○ Residual elongation, %	4	36	36	36	20
○ Tear strength, N/mm	106	115	141	127	105

Medium Action Analysis

Medium action analysis, 22 h x 23°C – the samples show small variations of mass and volume after immersion in distilled water, sulfuric acid 70%, sodium hydroxide 50% because EPDM rubber materials with and without HDPE have a very good stability to the action of chemical agents. Because EPDM rubber is not resistant to toluene, the samples are inflated after immersion for 22 hours in toluene and increase its mass and volume. According to Table 2, there is an improvement in this feature by crosslinking the rubber and a slight increase in the addition of charge, behavior observed by other researchers (Steleescu, 2011).

Physical-Mechanical Properties in Normal State and After Accelerated Aging (168h at 70°C)

The analysis of the physical-mechanical properties in normal state and after accelerated aging (Table 2) shows the following: • *hardness* has high values (98-99°ShA, respectively 55-59°ShD) and varies with $\max \pm 1^\circ\text{ShA}$, respectively with $\pm 4^\circ\text{ShD}$ after accelerated aging; • *the elasticity* shows high values for samples 1-4 (42-53%) and shows a decrease to the value of 30-36% by introducing the plasticized starch in the mixture; • both *hardness and elasticity* are surface properties and are strongly influenced by the characteristics of the thermoplastic matrix, namely HDPE, respectively HDPE and plasticized starch; • the values of *tensile strength* are high, over 16 N/mm^2 for all samples, and show variations between +18.8% and -2.4% after accelerated aging; • elongation at break has small values, of 80-120%, and the remanent elongation has values of 4-40%; • the phenomenon of forming a neck specific to plastics was observed; • tear resistance is very good (102-141 N/mm), with small variations after accelerated aging (between + 8.5% and -3.4%); • there is an increase in tear strength and elongation at break due to dynamic crosslinking with resin, respectively as a result of the introduction of OMMT; • the addition of plasticized starch did not lead to a decrease in characteristics.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Figures 1-6 present the infrared spectra obtained in the range of $450\text{-}3000 \text{ cm}^{-1}$ of the control blend (sample 1), plasticized starch and sample 5. Control sample spectrum (sample 1) includes C–H stretching vibration ($2914,53 \text{ cm}^{-1}$ and $2847,59 \text{ cm}^{-1}$), CH_2 bending and rocking vibrations (1472 cm^{-1} , 1462 cm^{-1} and $719\text{-}730 \text{ cm}^{-1}$), specific bands of EPDM and HDPE (Craciun *et al.*, 2020).

Figure 1. FTIR spectra of Sample 1 (Control) for $3000\text{-}3650 \text{ cm}^{-1}$ and $1150\text{-}750 \text{ cm}^{-1}$

Figure 2. FTIR spectra of plasticized starch for 3000-3650 cm^{-1} and 1150-1750 cm^{-1} Figure 3. FTIR spectra of Sample 5 for 3000-3650 cm^{-1} (left) and 1150-1750 cm^{-1} (right)

The FTIR spectra of starch typically shows bands at 2870–2950 cm^{-1} (C-H stretching), 1100–1150 cm^{-1} (C-O, C-C and C-O-H stretching) and 1100–900 cm^{-1} (C-O-H bending). Overlapping are, the plasticizer-glycerin specific bands, such as the absorption bands from 3000–3700 cm^{-1} specific for hydrogen bonds, the absorption bands from the region 1200–1000 cm^{-1} due to C-O, C-C, C-OH stretching and C-OH bending (Warren *et al.*, 2016). In the spectrum of sample 5, in addition to the control sample, new bands appear due to the plasticized starch, the addition of OMMT and dynamic crosslinking using phenolic resin. Thus, it can observe the absorption bands of the stretching vibration of -OH from the phenolic resin at 3600 cm^{-1} and the hydrogen bonds formed by dynamic crosslinking at 3340–3380 cm^{-1} (Van Duin and Souphanthong, 1995). The band observed at 3600–3640 cm^{-1} can also be attributed to the structural water of OMMT crystal lattices, and the bands from 1027.83 cm^{-1} , 803.41 cm^{-1} and 464.64 cm^{-1} to the vibration absorptions of Si-O-Si and Si-O-Al groups in OMMT crystal lattice (Lü *et al.*, 2006).

Figure 4. FTIR spectra of Sample 1 for 400-1150 cm^{-1} Figure 5. FTIR spectra of plasticized starch for 400-1150 cm^{-1}

Figure 6. FTIR spectra of Sample 5 for 400-1150 cm⁻¹

CONCLUSIONS

The new types of elastic-plastic materials for the footwear industry based on EPDM rubber and HDPE, reinforced with plasticized starch and OMMT, were obtained using the latest technologies in the field, namely: the dynamic vulcanization technique and the melt interleaving method. Due to the composition and the processing technology, materials with very good properties were obtained (very good resistance to concentrated acids and bases, very good values of abrasion resistance, tensile and tear strength, etc.). The materials have MFI values over 3 g/10' and can be processed by injection method.

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