BIODEGRADABLE POLYMERIC COMPOSITES BASED ON EPDM RUBBER AND FUNCTIONALIZED ELASTOMERIC WASTE

MIHAELA (VILSAN) NITUICA[1], LAURENTIA ALEXANDRESCU[1], MIHAI GEORGESCU[1], MARIA SONMEZ[1], MARIA DANIELA STELESCU[1], DANA GURAU[1], CARMEN CURUTIU[2], STEFANIA STOLERIU[3]

[1]*INCDTP - Division Leather and Footwear Research Institute, 93 Ion Minulescu St., district 3, Bucharest, icpi@icpi.ro, mihaela.nituica@icpi.ro*

[2]*University of Bucharest, Faculty of Biology, 1-3 Portocalelor St., 6th district, 060101, Bucharest, Romania*

[3]*University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 1 Polizu Str., 011061, Bucharest, Romania*

Elastomeric and plastic materials are used in different sectors of the European Union, and their recycling and reuse is still at a low level, compared to other types of waste (paper, glass, etc.). By approaching an efficient global strategy related to waste management, it is possible to make the transition to a circular economy with low CO2 emissions, offering the population a cleaner and safer environment. Due to the transformation of waste by various methods into new value-added products, we can say that their life cycle contributes to the efficiency of the economy and to the reduction of the negative impact on the environment. Research can make a difference in preventing the generation of technological and post-consumer polymeric waste by making biodegradable polymer composites that are harmless to the environment and ecosystem. The biodegradable polymer composites based on EPDM elastomer and rubber waste (rubber powder) were made on equipment specific to elastomers and characterized rheologically and physically-mechanically according to the standards in force.

Keywords: polymeric materials, elastomeric waste, characterization, EPDM

INTRODUCTION

An important part of the source of pollution with CO_2 and other harmful elements originates from the industries producing and processing elastomers and plastics. The direct and indirect harmful effects due to these industries, as well as the materials used as raw materials and finished products can be mitigated by developing reusable technologies and environmentally friendly materials (optimized by their longer lifespan, through a much longer cycle large, compared to the current one - up to 4 cycles of reuse in production) (Plastic Recyclers Europe, 2015; United Nations Environment Programme, 2015).

By making biodegradable polymer composites based on elastomers compounded with technological and post-consumer polymeric waste using appropriate technologies, without them having a negative impact on the ecosystem for a long time, the products obtained will be viable both in terms of high performance, economic and ecological properties (Nituica *et al*., 2018; Plastics, The Facts, 2017; Regulation (EC) No. 1013/2006; Fan *et al*., 2019).

The development of new biodegradable polymeric materials based on EPDM rubber compounded with elastomeric waste (rubber powder) through various vulcanization systems, lead to the greening of processing technology by eliminating pollutants released during the vulcanization operation and of course waste elimination, by the possibility of reintroducing it into the production process, without negatively influencing the quality of products to protect the human factor and natural resources, increasing the sustainability of both the current population and future generations

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(Stelescu, 2011; Roucoules *et al*., 2007; Stelescu *et al*., 2020). All these meet the current quality and aesthetic requirements, for obtaining components designed for footwear and elastomeric parts without special characteristics by injection, as well as by mold pressing. This paper describes their development and testing by methods of obtaining and characterization using equipment specific to elastomers (Alexandrescu *et al*., 2019).

EXPERIMENTAL PROCEDURE

Materials

Materials used to obtained the antibacterial composites were: **(1) EPDM,** ethylene-propylene-diene terpolymer rubber, specific gravity – 0.872, Mooney viscosity – 60 MU, ethylene content – 67.5 wt%, ethylidene norbornene (EBN) contents – 5.0 wt%; **(2) ST**, stearin, granules, white color, molecular weight 284,48 g/mol, dynamic viscosity 9,87 mPa.s at 70°C, volumetric weight approx. 400 - 500 kg/m^3; **(3) ZnO**, zinc oxide, microparticles: white powder, precipitate 93-95%, density – 5.5 g/cm, specific surface – 45-55 m^2/g; **(4) SiO_2 -** silicon dioxide, molecular mass 60,08 g/mol, white color, volumetric weight approx. 200 - 1.430 kg/m^3, particle size < 0,5 mm; **(5) $CaCO_3$**, chalk precipitate white powder, molecular weight 100.09; **(6) elastomeric waste**, obtained by cryogenic grinding at 10000 rpm for 15 s and screened through a 1 mm mesh screen; **(7) PEG 4000**, polyethylene glycol, slightly yellow or white flakes, pH: 5-7 (1% APA), density: 1.080 g/cm^3, dynamic viscosity: 310 mPa.s; **(8) DOF**, dioctylphthalate, colorless liquid, density: 0.982 g/cm^3; **(9) IPPD,** N-Isopropyl-N'-phenyl-1,4-phenylenediamine, brown flat granules, molar mass: 226,317 g/mol, density: 1.04 g/cm^3; **(10) S**, sulphur, vulcanization agent (fine yellow powder, insoluble in water, melting point: 115°C, faint odor); **(11) TH**, tetramethylthiuram disulfide– curing agent (density 1.40 g/cm, melting point <146°C, an ultrafast curing accelerator); **(12) M**, 2 – mercaptobenzothiazole, curing agent (slow curing accelerator, molar mass: 167.25 g/mol, assay 97%, density 1.19 g/cm).

Preparation and Characterization of Biodegradable Polymer Composites

Biodegradable polymeric composites based on EPDM rubber and functionalized elastomeric waste were made by mixing technique on a Plasti-Corder Brabender Mixer (Table 1), with the possibility of adjusting the temperature and mixing speed, by strictly observing the order of introduction of the ingredients according to the recipe in Table 1. Vulcanization accelerators were added on a laboratory roller, of 1 kg mixing capacity, according to the working method in Table 1.

The obtained biodegradable polymer composite recipes are then rheologically tested on a Monsanto 100S Rheometer, to establish the optimal vulcanization time and processing in the electric press (at the preset pressure and temperature parameters). The sample is closed tightly in a cavity of the device, at a controlled temperature, which surrounds a rotor with oscillations at a frequency of 1.67Hz (100 cpm), so the output data correlates with the degree of vulcanization depending on the vulcanization time. To determine vulcanization characteristics for Monsanto rheometer, the working temperature was 165°C and time of 24’.

To characterize the biodegradable polymer composites, plates were pressed in the electric laboratory press, TP 600, at specific parameters, by means of compression

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method, between its platters, Table 2. After conditioning the plates for 24 hours at ambient temperature they are subjected to determinations.

Biodegradable polymeric composites based on EPDM and elastomeric waste were characterized in terms of rheological and physical-mechanical characteristics by appropriate techniques.

The biodegradable polymeric composites were tested in compliance with the rheological and physical-mechanical standards in effect: determination of vulcanization characteristics – SR ISO 3417; hardness °ShA – ISO 48-4:2018; elasticity %, ISO 4662:2017; tensile strength, modulus, N/mm^2 – SR ISO 37-2020; tear strength, N/mm – ISO 34-1:2015; elongation at break, N/mm^2 – SR ISO 37-2020; density, g/cm^3 – ISO 2781:2018, normal condition.

Table 1. Formulation of biodegradable compounds based on EPDM rubber and wood waste

Symbol	MU	S0	SC_1	SC_2	SC_3	SC_4
Processing on Plasti-Corder Brabender Mixer, capacity 350 g, following the order in Table 1, plasticizing EPDM for 1'30'', 40 rpm, at 45°C; all ingredients (without vulcanizing agents), mixing time – 4'30'', 20 rpm, at 45°C; homogenization time – 2', 60 rpm, at 60°-145°C; total mixing time – 8'.						
EPDM	g	190	190	190	190	190
Stearin	g	2.85	2.85	2.85	2.85	2.85
ZnO	g	9.5	9.5	9.5	9.5	9.5
SiO_2	g	19	38	19	-	-
$CaCO_3$	g	76	47.5	47.5	47.5	9.5
Elastomeric waste	g	-	19	38	57	95
PEG4000	g	7.6	7.6	7.6	7.6	7.6
DOF	g	19	19	19	19	19
IPPD	g	5.7	5.7	5.7	5.7	5.7
Processing on laboratory electric roller, water cooling; mixing at 20°-30°C temperature, 50 rpm, addition and mixing time between 4' to 8', continuing mixing for maximum 2', the mixture obtained is in the form of a 3 mm thick sheet.						
Sulphur	g	1.9	1.9	1.9	1.9	1.9
M	g	2.28	2.28	2.28	2.28	2.28
Th	g	1.14	1.14	1.14	1.14	1.14

Table 2. Vulcanization parameters on electric press, TP 600, for biodegradable polymeric composites, S0, SC_1–SC_4

Vulcanization parameters	Symbol				
	S0	SC_1	SC_2	SC_3	SC_4
Vulcanization temperature	165°C	165°C	165°C	165°C	165°C
Vulcanization time	6'	6'	6'	6'	6'
Cooling time	10'	10'	10'	10'	10'
Pressing force	300 kN	300 kN	300 kN	300 kN	300 kN
Cooling temperature	45°C	45°C	45°C	45°C	45°C

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RESULTS AND DISCUSSION

The biodegradable polymeric composites based on EPDM rubber and elastomeric waste (rubber powder) were characterized from a rheological and physical-mechanical point of view.

Rheological Characterization of Biodegradable Polymeric Composites

The rheological characteristics (Table 3) for the biodegradable polymeric composites based on EPDM rubber and rubber powder (elastomeric waste) were determined using the Monsanto rheometer, at T=165°C. By replacing the amount of active batch, SiO_2 with elastomeric waste functionalized with potassium oleate, from the interpretation of the interregistered rheological characteristics the following are observed:

- minimum torque - ML, increases by a maximum of 28%, and the maximum torque (MH) decreases by a maximum of 48%, so that the variation of the torque (ΔM) decreases by a maximum of 54% as the amount of elastomeric waste increases, to the detriment of the amount of SiO_2, indicating a slight increase in the rigidity of the mixtures in the unvulcanized state and a decrease in the rigidity of the rubber mixtures in the vulcanized state;
- because the vulcanization system used in the mixing process is based on sulphur and semi-efficient vulcanization accelerators, for all samples there is NO reversal phenomenon, which is specific to vulcanized mixtures by the classical method (Figure 1), indicating a good behavior of mixtures at high temperatures or accelerated aging;
- scorching time (ts_2) decreases as the amount of rubber powder increases and the amount of active charge decreases, and the optimal vulcanization time shows a slight increase by replacing SiO_2 with elastomeric waste functionalized with potassium oleate (rubber powder);
- comparing sample SC_3 with sample SC_4, it is observed that by replacing 20 phr of calcium carbonate, which is inactive batch, with rubber powder, there is a decrease of MH and ΔM, by 11, respectively 20% and increases of 4%, 14%, 12% and 5% of ML, ts_2, t_{50} and t_{90}, respectively.

Table 3. Rheological characteristics for biodegradable polymeric composites, S0, SC_1–SC_4

Rheological characteristics, T = 165°C	Symbol S0	SC_1	SC_2	SC_3	SC_4
ML: minimum torque (dNm)	11.1		14.2	14.1	14.7
MH: maximum torque (dNm)	66.4		51.16	38.4	34.1
ΔM = MH-ML (dNm)	53.3		36.9	24.3	19.4
ts_2: scorching time (min)	0.8		0.77	1.17	1.33
t_{50}: (min)	1.52		1.49	2.22	2.48
t_{90}: optimal vulcanization time (min)	4.7		7.42	8.09	8.52

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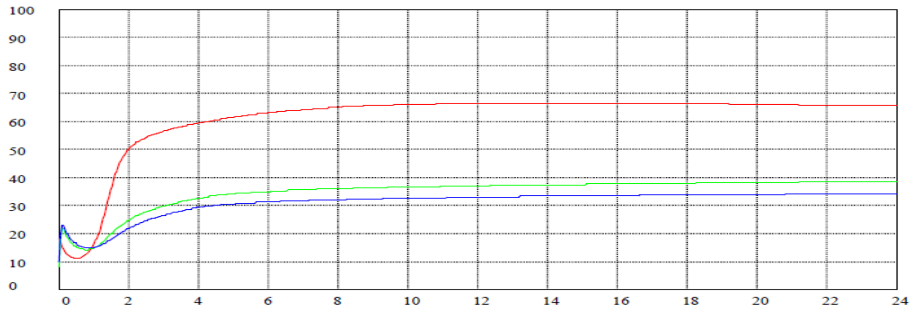

Figure 1. Rheogram recorded on Monsanto Rheometer for samples – S0 (red), SC_2 (green), SC_3 (blue)

Physical-Mechanical Characterization of Biodegradable Polymeric Composites

The biodegradable polymeric composites based on EPDM rubber and functionalized elastomeric waste (rubber waste) are subjected to physical-mechanical determinations. After stabilization at room temperature for 24 hours the following were recorded, Table 4:

Table 4. Physical-mechanical characterisation of biodegradable polymeric composites based on EPDM rubber and functionalized elastomeric waste

Symbol	S0	SC_1	SC_2	SC_3	SC_4
Physical-mechanical characterization: normal condition					
Hardness, °Sh A	50	54	49	47	46
Elasticity, %	32	34	28	32	30
Modulus 100, %	0.89	0.91	0.75	0.83	0.68
Modulus 300, %	1.47	1.3	1.04	0.85	0.81
Tensile strength, N/mm^2	2.06	3.51	1.4	0.99	0.81
Elongation at break, %	420	580	500	500	560
Tear strength, N/mm^2	10.37	16.6	11.03	8.6	7.53
Density, g/cm^3	1.14	1.12	1.1	1.07	1.0

From the data recorded for biodegradable polymeric composites based on ethylene-propylene-terpolymer rubber (EPDM) and rubber powder (elastomeric waste functionalized with potassium oleate), it is observed that by replacing the amount of active filler – SiO_2 with functionalized elastomeric waste, the physical-mechanical characteristics of the sample are modified as follows:

- the hardness varies with ±5°ShA, and the elasticity presents a non-uniform variation of ±13%;
- the values of tensile strength, tear strength, elongation at break and modulus increase as the active filler is replaced with the elastomeric waste functionalized with potassium oleate, presenting a maximum point for the SC_1 sample;
- the density of the samples decreases as the amount of powder increases.

Comparing sample SC_3 with SC_4, it is observed that by replacing 20 phr of calcium carbonate with rubber powder there is a decrease in hardness, modulus, tear strength, and an increase in elongation at break. The results obtained are due primarily to the composition and morphology of the mixture obtained.

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CONCLUSIONS

The biodegradable polymeric composites based on EPDM rubber and functionalized elastomeric waste (rubber waste) are tested in compliance to rheological and physical-mechanical determinations, on equipment specific to elastomer determinations (normal condition).

The rheological characteristics for the biodegradable polymeric composites based on EPDM rubber and rubber powder were performed to establish the optimal vulcanization and processing times in the electric press.

Comparing sample SC_3 with SC_4, it is observed that by replacing 20 phr of calcium carbonate with rubber powder there is a decrease in hardness, modulus, tear strength, and an increase in elongation at break. The results obtained are due primarily to the composition and morphology of the mixture obtained.

The obtained biodegradable polymeric composites based on elastomeric rubber (EPDM rubber) and elastomeric waste (rubber powder) are used in the processing of general-purpose footwear and elastomeric parts without special characteristics.

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