DEVELOPMENT AND CHARACTERIZATION OF BIODEGRADABLE COMPOUND BASED ON EPDM AND WOOD 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*

In the European Union, the potential for recycling technological and post-consumer polymeric waste is untapped. Their recycling and reuse are very low, compared to other types of waste such as glass, paper, etc., and the rates of storage, even of incineration, is very high in terms of percentage. Therefore, by reusing them, but also making use of new advanced technologies, we can contribute to improving the quality of products, and to environmental protection by recycling waste, protecting human health by eliminating toxins during their incineration, but also increasing turnover for global economic agents. Thus, this paper presents the obtaining and characterization of an antibacterial compound based on EPDM elastomer and wood waste (sawdust). The antibacterial compound is characterized from a physical-mechanical and structural point of view (FT-IR), all according to standards in force.

Keywords: polymeric materials, wood waste, characterization, EPDM

INTRODUCTION

Worldwide, and in Europe especially, millions of tons of waste are generated every year from the textile industry, from the wood processing industry and not only. Reuse and recycling of waste are real options to reduce the amount of waste and thus their impact on the environment, as provided by Directive 2008/98/EC (Plastics, The Facts, 2017). About 30% of this waste, even less, is collected for recycling. A large part of this is stored in improper conditions, and incineration has seen an alarming increase in the last decade. Thus, it has been globally estimated that by generating and burning only plastic waste and those from the wood industry, approximately 600 million tons of CO_2 are generated (Plastics, The Facts, 2017). Wood waste is classified by European standards as common waste, not hazardous or toxic to the environment. The transformation of waste (cryogenically ground and functionalized) into new value-added products will lead to remarkable improvements in the life cycle of raw materials and sustainable use of this waste, contributing to increasing sustainability, improving eco-efficiency and economic efficiency and reducing the "pressure" of environmental waste (Alexandrescu *et al*., 2019; Zhu *et al*., 2017; Fan *et al*., 2019).

The compounding of elastomers and wastes, in the presence of vulcanization systems, led to biodegradable mixtures with good properties for the footwear industry and for elastomeric parts without special characteristics (Nituica *et al*., 2018). Vulcanization of compounds has a major impact on the final properties of products, representing an important property, and in order to obtain biodegradable composites, current trends are the use of natural materials (wood, protein fibers, etc.) and vulcanized rubber as a reinforcing material (Roucoules *et al*., 2007; Stelescu, 2011; Stelescu *et al*., 2020).

https://doi.org/10.24264/icams-2020.IV.14

EXPERIMENTAL PROCEDURE

Materials

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

Procedure

The biodegradable compounds based on EPDM elastomer, wood waste (sawdust), $CaCO_3$, SiO_2, ZnO, antioxidants, sulfur, Th, M and plasticizers were made on a Plasti-Corder Brabender Mixer, in strict compliance with the order of introduction of the ingredients, Table 2. After the mixing process, the recipes were completed with accelerators on a laboratory roller, 1 kg capacity, water cooling. The making of the mixtures on the Plasti-Corder Brabender mixer is presented in Table 1.

Table 1. Working method using Brabender mixer

The order of introduction of the ingredients	Mixing time (minutes)	Mixing speed	Temperature, °C
EPDM rubber	1’ 30”	40 rpm	45°C
Ingredients (without vulcanizing agents)	4’ 30”	20 rpm	
Homogenization time	2’	60 rpm	60-145°C
TOTAL	8’	20-60 rpm	45°C-145°C

Vulcanizing agents are added on the laboratory electric roller, at temperatures of 23-30°C, 50 rpm, and the working method is as follows: dosing of raw materials; the mixture is plasticized between the rollers; the vulcanizing agents are introduced according to the recipe, Table 1; addition and mixing time 5-10 minutes; after adding the vulcanization accelerators, mixing is continued for 1-2 minutes for a good homogenization. The mixture is then removed in the form of a 2-3 mm thick sheet.

https://doi.org/10.24264/icams-2020.IV.14

For the characterization the obtained polymer composite is added in the molds, using the electrically heated press, TP 600, by means of compression method, between its platters, at a temperature of 165°C and 300 KN pressure for 6 to 13 minutes actual forming in the press and 10 minutes cooling with water.

Table 2. Formulation of biodegradable compounds based on EPDM rubber and wood waste

Symbol	MU	S0	SL_1	SL_2	SL_3	SL_4
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	0	0
$CaCO_3$	g	76	47.5	47.5	47.5	9.5
Wood 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
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

Characterization of Biodegradable Compounds

The testing of biodegradable polymeric compounds based on EPDM rubber and wood waste was performed in terms of physical-mechanical and structural characterization (FT-IR) by appropriate techniques.

The biodegradable compounds were tested in compliance with the physical-mechanical standards in effect: °ShA hardness – 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; Abrasion, mm^3, SR ISO 4649/2010, normal condition.

FT-IR spectral determinations were performed with a double beam IR molecular absorption spectrometer, in the range 4000-400 cm^{-1}, using the FT-IR Thermo Nicolet iS 50, equipped with ATR with diamond crystal.

RESULTS AND DISCUSSION

The obtained biodegradable compounds were physically-mechanically and structurally characterized according to the standards in force.

Physical-Mechanical Characterization of Biodegradable Compounds

After stabilization at room temperature for 24 hours, the biodegradable compound specimens based on EPDM rubber and sawdust (wood waste) are subjected to physical-mechanical determinations, Table 3.

https://doi.org/10.24264/icams-2020.IV.14

Table 3. Physical-mechanical characterization of biodegradable compounds based on EPDM rubber and wood waste

Symbol	S0	SL_1	SL_2	SL_3	SL_4
Physical-mechanical characterization: normal condition					
Hardness, °Sh A	50	61	62	63	61
Elasticity, %	32	34	36	34	32
Modulus 100, %	0.89	1.2	1.03	0.89	0,75
Modulus 300, %	1.47	1.8	-	-	-
Tensile strength, N/mm^2	2.06	2.62	1.5	1.04	0.90
Elongation at break, %	420	440	300	180	240
Tear strength, N/mm^2	10.37	18.05	12.76	7.76	12
Abrasion resistance, mm^3	121.14	144.78	282.13	395.4	431.38

As the amount of SiO_2 in the mixtures is replaced, it is observed that the hardness of the compounds increases from 61-63°ShA. The increase is determined by the hardness of the sawdust, as well as by the bonds that are formed during processing between the EPDM elastomer and the filler. Elasticity presents a small and non-uniform variation. The values of tensile strength, tear strength, elongation at break and modulus increase as the active filler is replaced with wood waste, reach a maximum point for the SL_1 sample, and then decrease; this phenomenon may be due to larger particle sizes of wood and powder, respectively, compared to those of the active filler of silicon dioxide. The abrasion resistance in the case of these mixtures made with wood waste increases by approximately 9%.

Comparing the 2 specimens that do not contain silicon dioxide, SL_3 and SL_4, it is observed that by replacing 20 phr (parts) of calcium carbonate (inactive filler) with wood waste, there is a decrease of hardness by approximately 2°ShA; also the values of tensile strength increase by 13% and of course in the case of the abrasion resistance an increase of 9% is observed. Elongation at break and tear strength also increase. The changes in characteristics are not significant, compared to the changes observed by replacing the silicon dioxide active filler.

FT-IR Spectrometric Analysis

The spectra for biodegradable compounds based on EPDM elastomer and wood waste are shown in Figures 1 and 2. The bands related to the stretching vibrations are a function of those obtained in the reference spectra for EPDM rubber and those of simple wood waste treated with potassium oleate. The vibration attributes obtained for the non-vulcanized EPDM elastomer are shown in Table 4.

Table 4. Vibration assignments and IR frequencies of unvulcanized EPDM

Sample code	Frequency	Intensity	Vibration assignment
EPDM	1463,71	0,1755108	(CH_2) CH_3 asymmetric
	1375,96	0,0827913	CH_3 symmetric
	721,247	0,0512599	(CH_2) crystallinity

The FTIR spectrum of untreated wood waste (Figure 1) shows the adsorption bands in the region 3339.55, 2901.48 and 1735.06 cm^{-1} due to the stretching vibrations of the O-H, C-H and C=O bonds. These adsorption bands are due to the hydroxyl groups in cellulose, the carbonyl group of acetyl ester in hemicellulose and the -CHO groups in lignin. The bands from 1601.17 cm^{-1} and 1508.58 cm^{-1} are due to C=C bonds in the

https://doi.org/10.24264/icams-2020.IV.14

aromatic skeleton of lignin. The band corresponding to the peak at 1422.04 cm^{-1} is due to the deformation of lignin C-H bonds and the band from 1263.31 cm^{-1} represents the stretching vibration of C-O bonds from lignin, while the one from 1027.01 cm^{-1} is due to the stretching of C-O and C-C bonds of the ring from cellulose and hemicellulose.

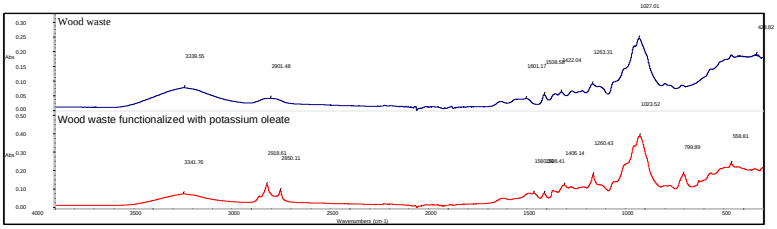

Figure 1. FTIR spectra of untreated wood waste and wood waste treated with potassium oleate

In the case of wood waste treated with potassium oleate, Figure 1, the band associated with -OH groups moved to the value of 3341.76 cm^{-1}, and the band corresponding to C-H groups moved to 2918.61 cm^{-1} compared to the values obtained for the untreated wood waste. Moreover, the peak corresponding to the carbonyl groups C=O moved to the value of 1722.9 cm^{-1} in the case of treated wood waste, because the ester bonds in hemicellulose were broken following the chemical treatment. The band from 1560.39 cm^{-1} comes from the -COO- group from oleate, which demonstrates that the process of modifying wood waste has taken place.

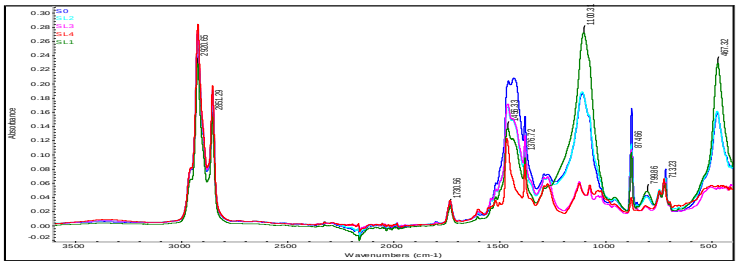

Figure 2. FTIR spectra of biodegradable compounds based on EPDM rubber and wood waste treated with potassium oleate, S0, SL_1, SL_2, SL_3, SL_4

In the case of EPDM potassium oleate-treated wood waste samples, Figure 2, the bands from silica, calcium carbonate, wood waste (sawdust) and EPDM rubber can be identified; their relative intensities vary depending on the percentage existing in mixtures. Thus, for a better identification of the presence of wood, the three spectra related to SO mixtures (control sample with the highest percentage of $CaCO_3$ - 40%, 10% SiO_2, but without treated wood waste), the SL_2 mixture containing 20% SiO_2, 20% treated wood waste and 25% $CaCO_3$, and SL_4 mixture containing 50% treated wood waste, 5% $CaCO_3$ and 0% SiO_2 were overlapped. Thus, in SL_2 one can easily see the SiO_2 peak centered at about 1107 cm^{-1}, and calcium carbonate at about 1427, 874 and 713 cm^{-1}. For the SL_4 sample, the 1107 cm^{-1} band characteristic of silica disappears, and the band characteristic of calcium carbonate decreases significantly, due to the considerable reduction of the percentage of $CaCO_3$. The wood waste, due to the low intensity peaks can be highlighted at about 1030 cm^{-1} as peaks

https://doi.org/10.24264/icams-2020.IV.14

superimposed over the peaks characteristic of the basic compositions. The band from approximately 1730 cm^{-1} can be assigned to C=O groups from the plasticizer used and DOF, its relative intensity being similar in all mixtures, because the amount introduced in all mixtures remained constant at 10%.

CONCLUSIONS

The testing of biodegradable polymeric compounds based on EPDM rubber and wood waste was performed in terms of physical-mechanical and FT-IR characterization according to the standards in force after stabilization of room temperature for 24h.

From the comparison of the specimens that do not contain silicon dioxide, SL_3 and SL_4, it is observed that by replacing 20 phr of calcium carbonate with wood waste, there is a decrease of hardness and an increase in tensile strength and abrasion. The changes in characteristics are not significant, compared to the changes observed by replacing the silicon dioxide active filler.

From the FT-IR spectra of the EPDM/potassium oleate-treated wood waste samples, the bands from silica, calcium carbonate, wood waste and EPDM rubber can be identified, their relative intensities varying depending on the percentage present in the mixtures.

The biodegradable compounds obtained are used in the processing of general-purpose footwear and elastomeric parts without special characteristics.

Acknowledgements

This research was financed by ANCSI through PN 19- 17 01 03/2019 project: "Biodegradable composites from technological and post-consumption polymeric wastes by designing and applying 4R eco-innovative technologies (4R-ECO-MAT)", and 6PFE/2018 – PERFORM-TEX-PEL.

REFERENCES

Alexandrescu, L., Deselnicu, V., Sonmez, M., Georgescu, M., Nituica, M., Zainescu, G., Deselnicu, D.C. and Pang, X. (2019), "Biodegradable polymer composite based on recycled polyurethane and finished leather waste", *IOP Conf. Series: Earth and Environmental Science*, 401, https://doi.org/10.1088/1755-1315/401/1/012006.

Fan, Q., Ma, J. and Xu, Q. (2019), "Insights into functional polymer-based organic-inorganic nanocomposites as leather finishes", *Journal of Leather Science and Engineering*, 1(3), https://doi.org/10.1186/s42825-019-0005-9.

Nițuică (Vîlsan), M., Meghea, A., Gurău, D. and Stelescu, M.D. (2018), "PP/EPDM Polymeric Compound Dynamically Cured Compatibilized and Reinforced with Nanoclay", *Plastic Materials*, 53(3), 335-339, https://doi.org/10.37358/MP.18.3.5024.

Plastics, The Facts (2017), "An Analysis of European Plastics Production, Demand and Waste Data. Plastics Europe", available online: the_facts_2017_FINAL_for_website_one_page.pdf (accessed on 5 December 2018), https://www.plasticseurope.org/application/files/5715/1717/4180/Plastics

Roucoules, V., Siffer, F., Ponche, A., Egurrola, U. and Vallat, M.F. (2007), "Strengthening the Junction Between EPDM and Aluminium Substrate via Plasma Polymerisation", *The Journal of Adhesion*, 83(10), 875-895, https://doi.org/10.1080/00218460701699732.

Stelescu, M.D. (2011), *Thermoplastic elastomers based on ethylene-propylene rubber (EPDM), which can be used in the footwear industry* (in Romanian), Performantica Press, Iasi, ISBN: 978-973-730-809-2.

Stelescu, M.D., Manaila, E., Nituica, M. and Georgescu, M. (2020), "New materials based on Ethylene Propylene Diene Terpolymerand Hemp Fibres Obtained by Green Reactive Processing", *Materials*, 13, 2067, https://doi.org/10.3390/ma13092067.

Zhu, G., Xing, X., Wang, J. and Zhang, X. (2017), "Effect of acid and hydrothermal treatments on the dye adsorption properties of biomass-derived activated carbon", *J Mater Sci*, 52, 7664–7676, https://doi.org/10.1007/s10853-017-1055-0.

https://doi.org/10.24264/icams-2020.IV.14