BIODEGRADABLE POLYMER COMPOSITE BASED ON POLYVINYL CHLORIDE AND WOOD WASTE. DEVELOPMENT AND CHARACTERIZATION

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Abstract: This work deals with the development and characterization of biodegradable polymer composites based on of polyvinyl chloride (PVC) and wood waste (WW) post-consumer waste. Wood waste resulting from wood processing into finished products is cryogenically ground to min. 500 nm, mechanically functionalized at temperature with polydimethylsiloxane (PDMS) (7%) and compounded in varying proportions (10%, 20%, 50%). The new composite is biodegradable due to the compounding with wood fibers, have low density and implicitly the products made from, a lower weight, reduced costs and recover waste. Soles for shoes will be processed by injection using these materials.

Keywords: wood waste, polymer composite, polyvinyl chloride.

1. INTRODUCTION

Currently, worldwide, researchers are developing new types of composites with optimized characteristics made from waste based on the principles of the circular economy. The new materials made from renewable resources contribute to the sustainable development of polymer composites and the fields in which they are used. The use of natural fibers as a reinforcing agent in polymer composites is significant in that it provides biodegradability properties to the new composites [1]. The global overuse of the synthetic polymer materials has brought some significant issues due to their negative impacts on the environment during the past years [2].

Most synthetic polymers made from petroleum and its allied components are not degradable after they are transformed into wastes. Today, more and more scientists shifted their attention to the eco-friendly polymeric materials [3]. The polymers used are mainly polyethylene, polypropylene, polyvinyl chloride, polyester or polycarbonate, which share the fact that most surface and/or volume modifications are necessary to achieve outstanding properties [4]. Being one of the largest polymers, polyvinyl chloride (PVC) is widely used and essential in almost all fields. The optimal ratio of properties and costs makes PVC a material capable of competing with both natural materials and other polymers in many areas of science and engineering.

Polyvinyl chloride (PVC) is one of the most used types of polymers (40% of dedicated polymeric materials) for biomedical and food applications. Although much has been done to replace PVC in medical applications, it remains the most used polymer in medical device manufacturing.

PVC applications include blood bags and tubes, intravenous containers and components, dialysis equipment, inhalation masks, examination gloves, etc. [5]. PVC-based polymeric materials are subject to continuous

* Corresponding author, email: laurentia.alexandrescu@icpi.ro https://doi.org/10.29081/jesr.v29i3.002

research for new modifications and improvements [6, 7]. Polymer based composites modified with wood fibers (also called wood plastic composites, abbreviated to WPCs) are increasingly popular since it is a feasible solution not only to the growing environmental issue, but also to the expensive cost of certain polymer-based materials [8, 9]. The use of natural fibers presents advantages compared to synthetic fibers. The advantages of using natural fibers are the following: they come from renewable sources, they provide biodegradability properties, they are not toxic, they reduce the cost of the products, they have an improved capacity as a sound and thermal insulator, and they can absorb moisture from human sweat.

The use of natural fibers in polymer composites causes the following effects: the composites have a lower density, which leads to lighter products, the wear and tear of conventional polymer processing equipment decreases, the composites can be reused for a maximum of 5 cycles without changing the properties, upon decomposition no toxic products are formed, the life time of the products after use is reduced due to the effect of biodegradation, etc. Therefore, no waste is generated at the end of the product’s life cycle after consumption.

The fillers (filling materials) have totally different properties from the polymeric material, polyvinyl chloride – PVC in this study, the properties of the composite being based on the properties of each component and on the interface reaction between the components. This can be achieved by using coupling agents that will form bonds between the polymer matrix and the other components of the composite [9]. High percentages of natural fiber fillers have been used in composites used to process commercial products to optimize properties such as: durability, mechanical resistance, manufacturing rate and reduction of moisture absorption [10-13]. There are studies on the performance of PVC-based composites with natural fibers (linen, cotton, leather), compatibilizers and coupling agents [14−19].

Wood waste is a set of products and materials whose origin is found in all wood processing stages of the industry, from forest exploitation to the manufacture of products, as well as post-consumer products (boxes, crates, pallets).

Properties such as hardness, density, tensile strength, elongation, flow index and breaking strength of polymer composites compounded with waste polyvinyl chloride (WPVC) and 10%, 20% and 50% recycled wood fiber (WF) were evaluated in comparison with the control sample made of WPVC. The influence on the performance of the physico-mechanical properties of the composites was investigated using conventional polymer processing techniques, such as twin-screw extrusion, compatibilizer addition, and fiber functionalization with a functionalization agent. The addition of 10 gr. (%) polyethylene-graft-maleic anhydride (PE-g-MA) as a compatibility agent between wood fiber and PVC improved the mechanical performance of the composite and the processing in a twin-screw extruder with corotation favored the distribution of wood fiber in the WPVC matrix.

2. EXPERIMENTAL

2.1. Materials

Polyvinyl chloride waste obtained from post-consumer shoe soles and waste from production, ground in a polymer-specific mill with knives and sieves, with 2-3 mm granulation. Wood waste (WF) from the wood processing industry, also ground and sieved, with a grain size smaller than 500 nm, polyethylene grafted with maleic anhydride (PE-g-MA) in the form of a honey-yellow granules, viscosity of 330,000 cps and an acidity index of 43.1 mg KOH/g, manufactured by Sigma Aldrich.

2.2. Functionalization of wood waste fibers

Functionalization of wood waste fibers was achieved by mixing with a stirrer with helical paddles, for 2h at a temperature of 80 °C with slow dripping of polydimethylsiloxane (PDMS) and a speed of 40 rpm. Different percentages of functionalizing agent relative to the amount of waste were experimented, but the percentage of 7% was selected, being considered optimal due to the degree of absorption, the elimination of fiber agglomeration, work method and the favorable influence on the physical-mechanical characteristics of the composite.

2.3. Procedure

Recycled polyvinyl chloride, polyethylene grafted with maleic anhydride and functionalized wood waste fibers with PDMS were mechanically mixed in a Brabender Plasti-Corder PLE-360 (Figure 1) at 10-120 rot/min, for 3 min. at 170°C to melt the plastomer, mixed for 5 min. at 175°C and 2 min. at 165°C for homogenisation. The total time was 10 minutes. Table 1 shows tested formulations.

Table 1. Control – W0 and PVC/PE-g-MA/WF polymer composite formulations with varying WF amounts. (W1-10%; W2-20%; W3-50%).

Compound	W0	W1	W2	W3
Recycled polyvinyl chloride - WPVC	270	285	270	240
Functionalized wood fibres waste (WF)	-	15	30	60
PE-g-MA	30	30	30	30
Total	300	330	330	330

Fig. 1. Malaxor Plasti-Corder Brabender Mixer 350.

The Brabender mixing diagrams, Figure 2, show the following: chamber temperature increases from 170 to 175 °C for the control sample – PVC and W0, with a maximum mixing force of 182 N/mm in 48s. When adding nanoparticles, the mixing force decreases (158 N/mm for 10-20% mixture of WF (samples W1 and W2) and 145 N/mm for 50% WF – W3 mixture).

The time need to reach maximum force, increases proportionally to the amount of WF mixture, from 48s – control sample to 52s – W1, 58s – W2, and 63s – W3. The temperature in the chamber decreases, at the maximum force, from 190 °C in the case of control W0 sample to 205 °C for W1 sample, 210 °C for W2 sample and, respectively 221 °C for W3 sample. The chamber temperature increases, at the maximum force from 190 °C – W0 control sample to 205 °C – W1, 210 °C –W2 and 221 °C – W3.

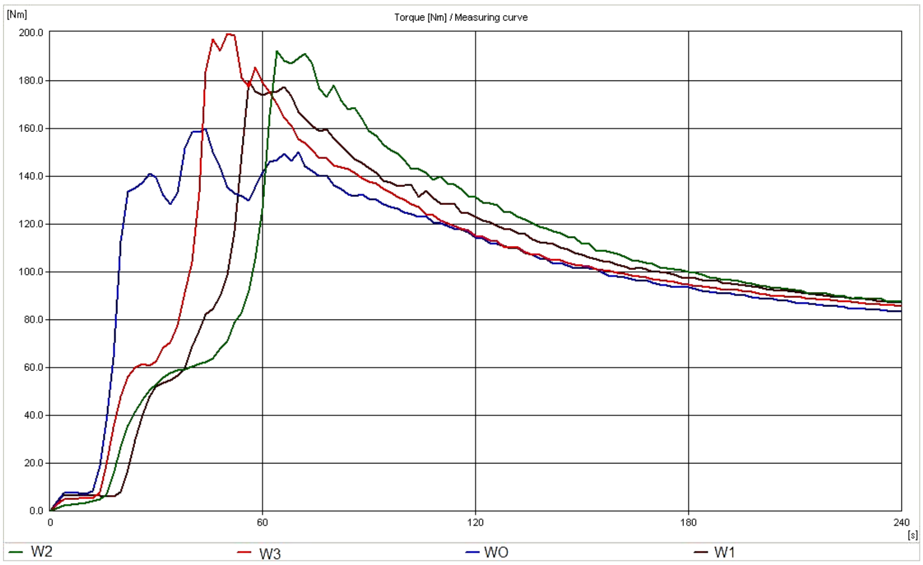

Fig. 2. The overlapping Brabender mixing diagrams of control sample and PVC/PE-g-MA/WF polymer composite formulations with varying WF amounts (W1-10%; W2-20%; W3-50%).

Industrially, the composites are made on an extruder-granulator with a capacity of 50 kg/h (Figure 3).

Fig. 3. Double screw granulator extruder with corotation TSE 35 type.

The working method on the extruder-granulator is presented in Table 2. In order, to process composites in good conditions, the initial working temperature was established at 165 °C.

Table 2. The working method on the extruder-granulator.

Order of introducing ingredients	Time [min]	Speed [rpm]	Temperature [°C]
Plasticization of plastomer waste	1’ 30”	40	160
+ fibre and vulcanized rubber waste	4’ 30”	20	165
Homogenization	2’	80	160-145
Total	8’	20-60	45-145

The obtained product is in the form of cylindrical granules with a height and diameter of 2 mm, it contains nanometric substances in its composition, and the physical-mechanical and chemical characteristics fall within the requirements set by the standards in force (Table 3).

Table 3. Technological parameters for the extruder-granulator.

No.	Name of the technological parameters	U/M	Composite type	
			W0	W1-W3
1.	Temperatures in:	°C		
	-area I		110±2	120±2
	-area II		100±2	110±2
	-area III		90±2	100±2
2.	Blade-knife speed	rpm	600-800	700-900
3.	Pellet cutter amperage	A	1-2	1.5-2.5

The compounds were then compression-molded (using an electrically heated laboratory press) to obtain a sheet of about 2 mm thick. Press parameters: preheating 3 min.; pressing 4 min.; cooling 13 min.; pressure 300 kN; temperature 170 °C. The sheet was then cooled down to room temperature under the same pressure. The specimens were die-cut from the compression molded sheet and used for testing after 24 hours of storage at room temperature.

3. RESULTS AND DISCUSSION

Table 4 shows values of physical-mechanical properties of PVC-based polymeric composites and waste wood fibres mixture functionalized with PDMS in normal state. The values of these properties after accelerated ageing only vary within the limit of 1-3% and, as a result, are not presented in the paper. Analysis of resulting physical-mechanical values indicates the following:

- Hardness increases proportionally to the amount of wood waste used for compounding, from 60 °Sh A for the WPVC control sample to 65 °Sh A for the composite with 50% functionalized wood waste.
- Elasticity decreases, also proportionally to the percentage of waste used for compounding; this is because the polymer chain is interrupted by the waste in compounding.
- For tensile strength and elongation at break, values increase proportionally to the percentage of waste used.

- Tear strength and Residual elongation decrease proportionally with the waste percentage.
- Density decreases from 1.16 g/cm^3 for the control sample W) to 1.05 g/cm^3 for the sample with 50% functionalized wood waste.
- Abrasion increases proportionally with the amount of functionalized waste but falls into the standardized range of values for PVC footwear soles, namely 250 mm^3.

Table 4. Normal physico-mechanical characterization for PVC-based polymeric composites and waste wood fibers mixture functionalized with PDMS.

Samples	W0	W1	W2	W3
Initial State				
Hardness °Sh D, SR ISO 7619-1:2011	60	62	63	65
Elasticity %, ISO 4662:2009	24	22	20	16
Tensile strength, N/mm^2, SR ISO 37:2012	23.0	24.1	24.8	25.2
Elongation at break, %, SR ISO 37:2012	260	260	300	340
Residual elongation, %, SR ISO 37:2012	84	60	40	28
Tear strength, N/mm, SR EN 12771:2003	160	142	147	149
Density, g/cm^3, SR ISO 2781:2010	1.16	1.15	1.11	1.05
Abrasion resistance, mm^3, SR ISO 4649/2010	137	144	177	211

3.1. Finished product processing

The composite granules were processed into finished products, plates, soles and seals, by injection into molds. Injection molding is a cyclical, intermittent process, in which the composite granules are heated to melting temperatures, and the melt is forced to pass through a narrowed hole, into a molding chamber, the mold. The form (mold) into which the molten material is injected, is cooled with water in the case of thermoplastic materials, until the material solidifies. The advantage of this technology is represented by the processing speed of an injected part, the period of a production cycle being 3-5 minutes, depending on the weight of the material filling the mold. The technology is clean, with no waste or burrs because the filling material of the mold is dosed automatically, and the composite materials can be recirculated in the production process at least 5 times without changing their properties.

The optimal working parameters to obtain prototype products are:
- working temperature of 170 °C.
- injection with the pressure of 300 KN.
- injection time (depending on the size of the mold) - 32 min.
- cooling time - 4 min.

The finished products which are most frequently requested by beneficiaries and processed in the micro production section are presented in Figure 4.

		
Plate from PVC mixed with 1% ground wood of 0.35 mm granulation	Soles from PVC mixed with 1% ground wood of 0.35 mm granulation	Plate and soles from PVC mixed with 1% ground wood of 0.35 mm granulation

		
Plate from PVC mixed with 10 % ground wood of 0.35 mm granulation	Soles from PVC mixed with 10 % ground wood of 0.35 mm granulation	Plate and soles from PVC mixed with 10 % ground wood of 0.35 mm granulation

Fig. 4. The finished products which are most frequently requested by beneficiaries and processed in the micro production section.

4. CONCLUSIONS

The composites experimented in this work, based on post-consumer PVC waste (transparent PVC medical products) and wood waste functionalized with PDMS compounded with a compatibilizing agent – PE-g-MA processed on a twin-screw granulator extruder, have values of physical-mechanical properties that fall within the product standards specific to PVC-based footwear soles.

The new materials respect the principles of the circular economy, both by the fact that recycled materials are used in the composition, and by the fact that these materials can be reused five times without changing their physical-mechanical characteristics.

ACKNOWLEDGMENTS

This project has been funded with the support of the Ministry of Research and Innovation, by Program 1 – Development of the national system for R&D, Subprogram 1.2 – Institutional performance – projects for funding excellence in R&D&I, contract no.4PFE/30.12.2021.

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