

BIODEGRADABLE POLYMER COMPOSITE BASED ON POLYVINYL CHLORIDE AND POLY (ETHYLENE-VINYL ACETATE) WASTE

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BIODEGRADABLE POLYMER COMPOSITE BASED ON POLYVINYL CHLORIDE AND POLY (ETHYLENE-VINYL ACETATE) WASTE

ABSTRACT. This paper presents experiments on developing and characterizing biodegradable polymer composites based on polyvinyl chloride and expanded poly(ethylene vinyl acetate) (EVA) post-consumer waste. This type of waste is a thermoplastic material collected from the footwear industry, residues from the production of outer and intermediate soles and used footwear. It is used due to its shock absorption properties and low density (0.6-0.8 g/cm³). To make these products, EVA is injected into molds, a process that generates waste that cannot be reused. In this paper, a method of EVA waste recovery is presented and the possibility of developing a recycled product is investigated. Expanded EVA waste is cryogenically ground to sizes of min. 500 nm, functionalized by a mechanical process at temperature with polydimethylsiloxane (PDMS) and mixed in the composite in various proportions (10, 20, 50%). This composite will be made into a low-density product, with low cost, recovery and reuse of waste, and last but not least, biodegradable. The methodology for making the new materials involves the following steps: sorting waste, grinding, functionalization and compounding. These operations are easy to manage and do not involve new equipment. Compounding, the most important operation, will be performed on an extruder-granulator. The experimented biodegradable composites were physico-mechanically characterized. Waste transformation (ground and functionalized) into new value-added products will lead to remarkable improvements in the life cycle of raw materials and the sustainable use of this waste, contributing to sustainability, improving eco-efficiency and economic efficiency and reducing the "pressure" of waste on the environment.

KEY WORDS: expanded EVA waste, polymer composite, biodegradability

COMPOZIT POLIMERIC BIODEGRADABIL PE BAZĂ DE POLICLORURĂ DE VINIL ȘI DEȘEURI DE POLI(ETILENVINIL ACETAT)

REZUMAT. Prezentă lucrare experimentează realizare și caracterizare de compozite polimerice biodegradabile pe bază de policlorură de vinil și deșeuri post-consum de poli(etilenvinil acetat) (EVA) expandat. Acest tip de deșeu este un material termoplastic colectat din industria de încălțăminte, din resturi din producția de tălpi exterioare și intermediare și încălțăminte utilizată. El este utilizat datorită proprietăților de absorbție a șocurilor și densitate mică (0,6-0,8 g/cm³). Pentru realizarea acestor produse, EVA este injectat în matrițe, proces care generează deșeuri ce nu pot fi reutilizate. În această lucrare se prezintă o metodă de recuperare a deșeurilor EVA și se investighează posibilitatea dezvoltării unui produs reciclat. Deșeurile de EVA expandate sunt măcinate criogenic la dimensiuni de min. 500 nm, funcționalitate prin procedeu mecanic la temperatură cu polidimetilsiloxan (PDMS) și amestecate în compozit în proporții variate (10, 20, 50%). Acest compozit va fi transformat într-un produs cu densitate scăzută, cu costuri reduse, valorificare și reutilizare a deșeurilor și, nu în ultimul rând, biodegradabil. Metodologia de realizare a noilor materiale implică următoarele etape: sortarea deșeurilor, măcinarea, funcționalizarea și amestecarea. Aceste operațiuni sunt ușor de gestionat și nu implică echipamente noi. Compundarea, cea mai importantă operațiune, se realizează pe un extruder-granulator. Compozitele biodegradabile experimentate au fost caracterizate fizico-mecanic. Transformarea deșeurilor (măcinate și funcționalizate) în noi produse cu valoare adăugată va duce la îmbunătățiri remarcabile ale ciclului de viață al materiilor prime și la utilizarea durabilă a acestor deșeuri, contribuind la sustenabilitate, îmbunătățirea eco-eficienței și a eficienței economice, precum și la reducerea „presiunii” deșeurilor asupra mediului.

CUVINTE CHEIE: deșeu de EVA expandat, compozit polimeric, biodegradabilitate

COMPOSITE POLYMÈRE BIODÉGRADABLE À BASE DE CHLORURE DE POLYVINYLE ET DE DÉCHETS DE POLY(ÉTHYLÈNE-ACÉTATE DE VINYLE)

RÉSUMÉ. Le présent article expérimente la création et la caractérisation de composites polymères biodégradables à base de chlorure de polyvinyle et de déchets post-consommation de poly(éthylène-acétate de vinyle) (EVA) expansé. Ce type de déchet est un matériau thermoplastique collecté dans l'industrie de la chaussure, à partir de résidus de production de semelles extérieures et intermédiaires et de chaussures usées. Il est utilisé en raison de ses propriétés d'absorption des chocs et de sa faible densité (0.6-0.8 g/cm³). Pour fabriquer ces produits, l'EVA est injecté dans des moules, un processus qui génère des déchets non réutilisables. Dans cet article, une méthode de valorisation des déchets EVA est présentée et la possibilité de développer un produit recyclé est étudiée. Les déchets EVA expansés sont broyés cryogéniquement jusqu'à des tailles de min. 500 nm, fonctionnalisés par un procédé mécanique en température avec du polydiméthylsiloxane (PDMS) et mélangé au composite dans diverses proportions (10, 20, 50%). Ce composite sera transformé en un produit à faible densité, à faible coût, en récupérant et en réutilisant des déchets et, enfin et surtout, biodégradable. La méthodologie de fabrication de nouveaux matériaux comprend les étapes suivantes : tri des déchets, broyage, fonctionnalisation et mélange. Ces opérations sont faciles à gérer et ne nécessitent pas de nouveaux équipements. Le mélange, l'opération la plus importante, est réalisé sur une extrudeuse-granulatrice. Les composites biodégradables testés ont été caractérisés physico-mécaniquement. La transformation des déchets (broyés et fonctionnalisés) en nouveaux produits à valeur ajoutée entraînera des améliorations remarquables dans le cycle de vie

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des matières premières et l'utilisation durable de ces déchets, contribuant à la durabilité, améliorant l'éco-efficacité et l'efficacité économique, ainsi que réduire la « pression » des déchets sur l'environnement.

MOTS CLÉS : déchet EVA expansé, composite polymère, biodégradabilité

INTRODUCTION

Methods of eliminating waste that pollute the environment have been approached through several technologies: depollution (deposition on the ground, burial, composting, burning), valorization through reuse and/or energetic recycling (incineration) and/or mechanical and/or chemical (pyrolysis, gasification, hydrolysis, etc.). In the integrated concept of polymer waste management, along with these methods, the possibilities of reducing quantities by reusing them into new biodegradable polymer composites are also included. If the re-introduction of these materials into the production circuit is carried out without taking into account the influences of the content of non-polymeric impurities and those resulting from specific destruction processes, then the materials resulting from simple mechanical recycling have mechanical properties that are all the lower the more the content of non-polymeric impurities is higher. For this reason, these polymers can be used for peripheral, low-performing applications [1-2]. It has been demonstrated that the residual properties can be brought to useful values by modification with a primary polymer and necessarily by subsequent homogenization from the melt, i.e., by mechanical recycling, the method of diluting defects.

Composites represent a versatile and very valuable family of materials, which can solve a series of existing problems in various applications/industries, because they facilitate the introduction of new properties in materials. The development of environmentally friendly "green" materials is due to the biodegradability of these polymeric materials (from various sources), low weight, low cost, high availability, high specific resistance, as well as due to the possibility of adapting existing equipment to processors in the field, to mass production [2-4].

Ethylene vinyl acetate (EVA) is a thermoplastic elastomer widely used in the production of footwear. Due to its outstanding flexibility, abrasion resistance and

low density (below 1g/cm^3), EVA is used to make outsoles and midsoles for sneakers and other types of shoes. Unlike other materials, such as thermoplastic polyurethane (TPU) and polyvinyl chloride (PVC), EVA is easier to process and allows the production of higher performing running shoes with greater shock absorption capabilities [5]. EVA midsoles and outsoles are usually made by injection molding at temperature; EVA expands into a foam [6]. This process is automated and allows for high production due to the short processing time (usually in minutes) [7]. Currently, a real recycling process for EVA has not yet been validated industrially and the residues generated in the injection process are used as fillers [8, 9] or thrown in the landfill [10]. With an estimated annual production of 24 billion shoes [11] (most of which contain EVA soles), it is easy to understand the importance of reuse [12]. Lopes *et al.* [13] used EVA waste as a filler for natural rubber, styrene-butadiene rubber, and acrylonitrile-butadiene rubber in vulcanization/pressing sole manufacturing processes. Two percentages of waste were tested (10 phr and 20 phr) and the produced shoe soles showed good mechanical properties. Pavia Junior *et al.* [10] evaluated the recovery of EVA waste in micronized form and added to virgin material. These studies confirmed the possibility of successfully using these wastes for the production of footwear components with mechanical performance comparable to virgin ones.

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 [14]. 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 [15]. 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. [16]. PVC-based polymeric materials are subject to continuous research for new modifications and improvements [17, 18]. Polymer based composites modified with EVA waste (WEVA/PVC) 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 [19, 20].

Properties such as hardness, density, tensile strength, elongation, flow index and tear strength of polymer composites compounded with waste polyvinyl chloride (WPVC) and 10, 20 and 50% waste EVA (WEVA) were evaluated, compared with the blank sample composed of WPVC. The influence of conventional polymer processing techniques, such as twin-screw extrusion, addition of compatibilizer and functionalization of the fiber using a functionalization agent, on the performance of the physico-mechanical properties of the experimental composites was investigated. The addition of 10 g (%) polyethylene-graft-maleic anhydride (PE-g-MA) as a compatibility agent between EVA waste and PVC improved the mechanical performance of the composite, while processing in a corotating double screw extruder favored the distribution of the cryogenically ground EVA waste powder in the WPVC matrix.

EXPERIMENTAL

Materials and Methods

Materials

Polyvinyl chloride waste (WPVC) obtained from post-consumer shoe soles and expanded poly(ethylene vinyl acetate) waste (WEVA) obtained from manufacturing soles for footwear by cutting out from expanded EVA plates, ground in a polymer-specific mill with knives and sieves, with 2-3 mm granulation, also ground and sieved, with a grain size smaller than 500 nm, polyethylene-graft-maleic anhydride (PE-g-MA) in the form of yellow granules, viscosity of 240000 cps and an acidity index of 43.1 mg KOH/g and polydimethylsiloxane (PDMS), clear, colourless liquid, viscosity of $1.00 \cdot 10^{-4} \text{ m}^2\text{s}^{-1}$ at 25°C and density of 0.977g/cm³, the last two manufactured by Sigma Aldrich.

Functionalization of ethylene vinyl acetate waste particles 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 5% was selected, being considered optimal due to the degree of absorption, the elimination of expanded particles agglomeration, work method and the favorable influence on the physical-mechanical characteristics of the composite.

Preparation of Various Types of Biodegradable Polymer Composite

Recycled polyvinyl chloride, polyethylene-graft-maleic anhydride and waste WEVA particles were mechanically mixed in a Brabender Plasti-Corder PLE-360 at 10-120 rotations/min, for 3 min. at 155°C to melt the plastomer, mixed for 5 min. at 165°C and 2 min. at 160°C for homogenisation. The total time was 10 minutes. Table 1 shows tested formulations.

Table 1: Control – A0 and WPVC/PE-g-MA/WEVA polymer composite formulations with varying WEVA amounts (A1-10%; A2-20%; A3-50%)

Compound	A0	A1	A2	A3
	WPVC	10%WEVA	20%WEVA	30%WEVA
Recycled polyvinyl chloride	270	285	270	225
Waste EVA functionalized with PDMS	-	15	30	75
PE-g-MA	30	30	30	30
Total	300	330	330	330



Figure 1. Brabender Plasti-Corder Mixer 350

The Brabender mixing diagrams, Figure 2, show the following: chamber temperature increases from 155 to 160°C for the control sample – PVC waste and A0, with a maximum mixing force of 182 N/mm in 48s. When adding particles, the mixing force decreases (158 N/mm for 10-20% mixture of WEVA (samples A1 and A2) and 145 N/mm for 50%

WEVA – A3 mixture). The time needed to reach maximum force, increases proportionally to the amount of WEVA mixture, from 40s – control sample to 45s – A1, 48s – A2, and 53s – A3. The temperature in the chamber decreases, at the maximum force, from 180°C – A0 control sample to 195°C – A1, 205°C – A2 and 211°C – A3.

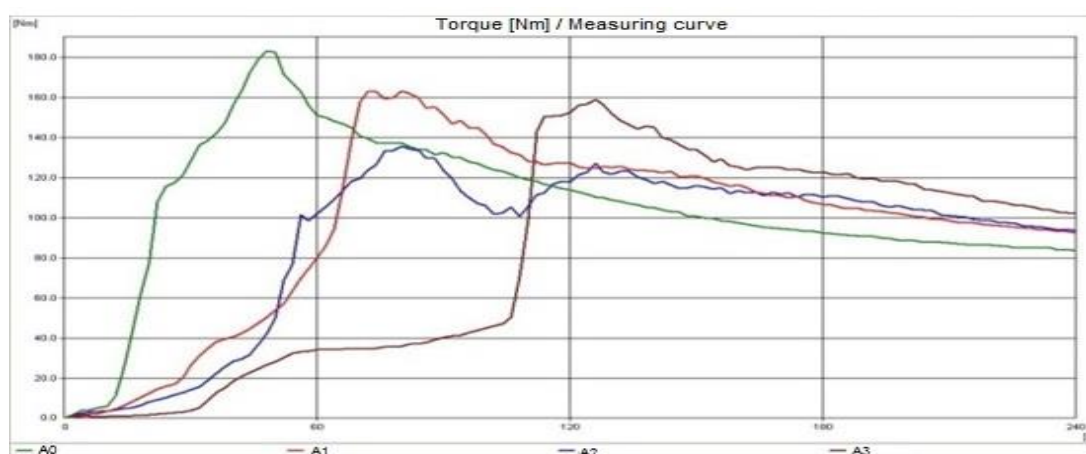


Figure 2. The overlapping Brabender mixing diagrams of control sample and PVC/PE-g-MA/WEVA polymer composite formulations with varying WEVA amounts (A1-10%; A2-20%; A3-30%)

According to the diagrams (Fig. 2-3), the following can be observed: in the first portion (A-B), the elastomer is introduced into the mixer and the torque increases. The first loading peak, A, corresponds to the

plasticization of PVC waste, PE-g-MA and EVA waste. As the torque increases, so does the temperature due to friction. The torque starts to decrease until it reaches B, mainly due to the homogenization and plasticization of the

ingredients, as well as due to the increase in temperature as a result of the shear forces, which indicates the homogenization of the mixture. As a result, a maximum torque value is obtained due to the compaction and homogenization of plastic waste. This is

generally followed by a decrease in the value of the torque, which indicates both the homogenization of the mixture and the increase in the temperature of the mixture due to friction at a higher rotational speed (60 rpm) with the mixer closed.

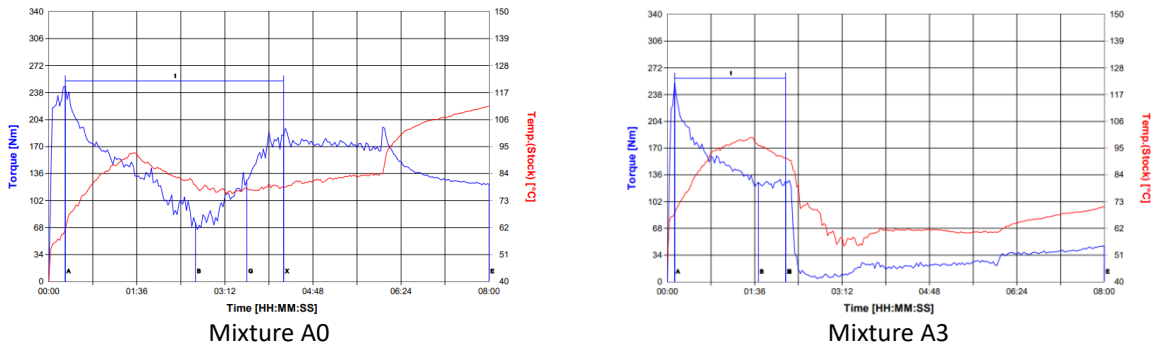


Figure 3. Torque and temperature variation depending on time, recorded using the Brabender Plasticorder while obtaining samples N0 and NP4

From the diagrams shown in Figure 3, it can be seen that the temperature in the mixing chamber increases, depending on the percentage of protein waste introduced into the polymer composite (starting from 90-96°C, it decreases to 80°C – in the control sample, then it increases to 110°C – at the end of mixing. In the case of biocomposites, the temperature in the mixing chamber increases, depending on the percentage of protein waste introduced into the polymer composite

(starting from 90-96°C, it decreases to approximately 55°C – in the sample with the highest EVA concentration – A3, then increases to 72°C – at the end of mixing. This decrease is due to the elastic behavior of the composite. Table 2 shows the processing characteristics presented in the Brabender diagrams, for each processed composite. Industrially, the composites are made on an extruder-granulator with a capacity of 50Kg/h.

Table 2: Characteristics presented in Brabender processing diagrams for polymer biocomposites with EVA waste

Characteristics	Sample code			
	A0	A1	A2	A3
Temperature at loading peak, °C	94	94	96	97
Temperature at the inflection point, °C	78	70	67	61
Maximum temperature, °C	110	99	82	73
Energy at loading peak, Nm	246.0	255.9	230.0	243.6
Maximum energy, Nm	183.5	171.4	169.6	159.1
Energy in gelation zone, kNm	10.3	33.7	33.1	94.7
Specific energy, kNm/g	0.7	0.8	0.6	0.6
Gelation rate, Nm/min.	142.5	171.2	22.0	26.3



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

The working method on the extruder-granulator is presented in Table 3. In order to process composites in good conditions, the

initial working temperature was established at 165°C.

Table 3: The working method on the extruder-granulator

Order of introducing ingredients	Time (minutes)	Speed	Temperature, °C
Plasticization of plastomer	1' 30"	40 rpm	160°C
+ EVA waste	4' 30"	20 rpm	165°C
Homogenization	2'	80 rpm	160-145°C
TOTAL	8'	20-60 rpm	45°C-145°C

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 4: Technological parameters for the extruder-granulator

No.	Name of the technological parameters	U/M	Composite type	
			A0	A1-A3
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.

Testing Methods

Tensile tests of the samples were carried out according to SR ISO 37:2012 using a Schopper Tensile Testing machine 1445, at a constant crosshead speed of 500 ± 5 mm/min.

Hardness of the samples was measured by Shore "A" Durometer according to SR ISO 7619-1:2011.

Abrasion resistance 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 having granulation of 212–80 mm (PE 80). The samples used were obtained from rolled blends and pressed into sheets, then cutting with a rotating die and have cylindrical shape, with a diameter of 16 mm and height of min. 6 mm.

Repeated flexing – Ross Flex – SR ISO 132/2018 is the test that determines the resistance of the specimens to the appearance and propagation of cracks when they are subjected to repeated flexing at an angle of 90 degrees, on a mandrel with a diameter of 10

mm, up to 150,000 cycles or until the crack appears or the material breaks.

RESULTS AND DISCUSSIONS

Physical-mechanical tests were carried out in the Investigation laboratory from INCDTP – Division ICPI, accredited by RENAR, and materialized in the determination of hardness, elasticity, tensile and tear strength, attrition, residual elongation and elongation at break for thermo-oxidative aging (168h x 100°C) and normal state. (See Table 5).

Table 5: Physical-mechanical characteristics of mixtures – NC series

Physical-mechanical characteristics	Sample code			
	A0	A1	A2	A3
Hardness, °Sh A	44	65	68	72
Elasticity, %	32	20	21	22
100% modulus, N/mm ²	1.0	1.96	1.65	1.70
300% modulus, N/mm ²	2.0	-	0.84	-
Tensile strength, N/mm ²	14.23	3.75	3.05	2.14
Elongation at break, %	740	300	280	220
Residual elongation, %	28	28	26	26
Tear strength, N/mm	24.39	21.42	16.9	17.29
Specific gravity, g/cm ³	1.2	1.15	1.11	1.12
Resistance to abrasion, mm ³	123.45	203.79	224.26	246.46
Rosflex repeated flexions SR ISO 132/2018	Resist up to 150.000 cycles			90.000 cycles crack appear, resist up to 109.000 cycles

- The hardness increases proportionally with the amount of EVA waste used in compounding, from 44°Sh A for the control sample A0 to 72 °Sh A for the composite with a percentage of 30% functionalized EVA waste;
- The elasticity decreases, it also decreases compared to the control (this is due to the fact that the polymer chain is interrupted by the waste during compounding), but it increases insignificantly in proportion to the amount of waste due to the plasticity of the waste;
- Tensile strength and Elongation at break values decrease proportionally with the percentage of waste used;
- Tear strength and Residual elongation decrease proportionally with the percentage of waste
- Density decreases from 1.16 g/cm³ in the control sample W) to 1.05 g/cm³

- in the sample with 50% percentage of functionalized wood waste;
- Abrasion increases proportionally with the amount of functionalized waste, but falls within the standardized value for PVC shoe soles, namely 250 mm³.
- Repeated flexions – Ross Flex – The footwear standards in force specify values of 150,000 cycles when determining repeated flexions for PVC shoe soles. From the values presented in Table 5, it appears that only composites A1 and A2 with EVA waste content of 10-20% fall within the limits imposed by the standard, and 50% do not fall within this value (at 90,000 cycles cracks appear, resist up to 109,000 cycles). The others have values higher than 150,000 cycles, higher than the values imposed by the standard.

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, it does not result in waste or burrs due to the fact that 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 make 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.

Below are the finished products made, the ones most frequently requested by beneficiaries and processed in the microproduction section.



Plate from PVC mixed with 10% ground EVA of 0.35 mm granulation



Soles from PVC mixed with 10% ground EVA of 0.35 mm granulation



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

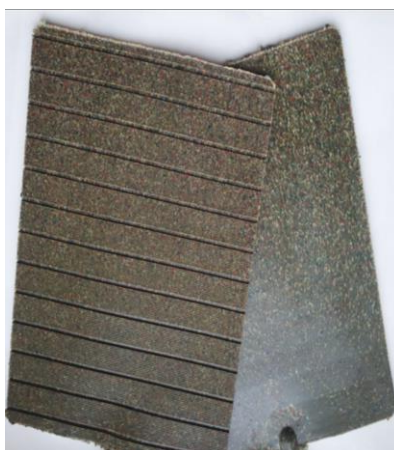


Plate from PVC mixed with 10% ground EVA of 0.5 mm granulation



Soles from PVC mixed with 10% ground EVA of 0.5 mm granulation



Plate and soles from PVC mixed with 10% ground EVA of 0.5 mm granulation

Figure 4. Finished products processed in the microproduction section

CONCLUSIONS

The composites experimented in this work based on post-consumer PVC waste (transparent PVC medical products) and EVA 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 shoe soles. The materials experimented respect the principles of the circular economy, by using recycled materials in the composition, PVC and EVA waste, and they can be reused up to five times without their properties changing.

Thus, the WPVC/WEVA biocomposite has a great potential for use in the shoe industry as shoe soles, boots and sandal strips. Production of new recycled footwear components (e.g., soles) based on medical wastes PVC and EVA wastes will definitely contribute to lower environmental footprint and sustainable development in this industrial sector.

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