Biodegradable Polymer Composite based on Recycled Polyurethane and Finished Leather Waste

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Abstract. The issue of polluting waste has been addressed over the years by means of several methods: depollution, recovery by reuse and/or energy recycling and/or mechanical and/or chemical recycling. In the integrated plastic waste management concept, along with these methods are included the possibilities of reducing the quantities by using biodegradable polymeric materials. The goal paper is to recover footwear waste after use: polymer and finished leather by making new biodegradable polymeric composites. The waste is ground to 1-5 mm and compounded by melt extrusion-granulation, processable by injection into new products (footwear soles) with pre-established advanced features. Biodegradable polymer composite based on post-consumption thermoplastic polyurethane (WTPU) waste compounded with post-consumption finished leather waste, ground and functionalized. This composite will be made into a low-density product, with low cost, recovery and reuse of waste, containing both polymer and protein, 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 carried out on a corotating twin-screw extruder-granulator with the possibility of adapting the length of the screw depending on the material (L/D-35). Waste transformation (ground and functionalized) in 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.

1. Introduction

The issue of polluting waste has been addressed over the years by means of several methods: depollution, recovery by reuse and/or energy recycling and/or mechanical and/or chemical recycling. In the integrated plastic waste management concept, along with these methods are included the possibilities of reducing the quantities by using biodegradable polymeric materials [1];[2]. The use of natural fibers as reinforcing agent in polymeric composites industry is getting a new impulse nowadays, though the manufacturing techniques are yet incipient and poorly productive. Some advantages are attributed to the use of natural fibers in many industrial applications as compared to...
synthetic fibers like glass fibers [3]. The natural fiber comes from renewable sources; it is biodegradable, non-toxic, shows low cost and improved capacity as sound and thermal insulator. Besides natural fibers have the advantage of being recyclable and they decompose without toxic compounds production or can be consumed by biodegradation [4];[5];[6]. The leather industry is a traditional industry. As a finished product of tanneries, the leather represents the raw material for other industries such as: footwear industry (approx. 62%), clothing (approx. 24%), leather goods (approx. 12%), and upholstery (approx. 2%). Leather processing generates at the same time by-products applicable in other fields of activity: sources of protein for food, chemicals, cosmetics or medical purposes, skin and artificial sole. These products being intensely used generate large quantities of post-consumer waste, which are managed improperly and treated improperly compared to industrial ones. Thus, Qianqian Fan et al., presented a research paper on the recycling of chromed leather waste (chromed shavings) used in the manufacture of shoe soles and insoles [7]. Tanned leather fibers have been used as filling material by mixing the rubber and nanoparticles of synthetic polymers. K. Patchai Murugana et al., 2016 uses tanned leather fibers mixed with dust from sanding the skins in a bitumen matrix resulting in a bio-composite used in the surface asphalt layer for pavement. Also in this paper is presented pyrolysis, in an oxygen controlled atmosphere, of tanned leather fibers [8].

Consequently, there is no waste generation at the end of the product life cycle. According to the latest report published by Plastic Europe-the Facts 2017 [9], the demand for plastic in Europe in 2016 was 49.9 MTn, 3.1% higher as regards to 2014. Of this demand, 7.5% is polyurethane. Of the 3.78 MTn, approximately 70% is in the form of foam, 30% being that of polyurethane elastomers and other products. The sectors according to demand are: Construction and building (24.5%); automotive (19.5%), refrigeration (21.3%) and other sectors within the shoes and textile industry, usage in technology, etc. (34.7%). Thermoplastic polyurethane (TPU) is a preferred choice of polymer to produce engineering products because it has good physical and chemical characteristics, TPU can be processed with extrusion, injection, blow and compression molding equipment. Besides that, TPU is well suited for a wide variety of fabrication processes [10]. There are previous studies reporting on TPU composites used with several different fibres, for instance TPU reinforced with synthetic fibres such as glass [11] and carbon fibre [12], with other natural fibres such as curaua fibre [13], kenaf fibre [14] and rossele fibres [15]. It is in the literature that no study has been carried out on post-consumption thermoplastic polyurethane (WTPU) /post-consumption finished leather waste composites. The aim of this paper is to study the properties of WL reinforced WTPU composites with differential fibre contents (10, 20, and 50 wt%). Tensile strength, tear strength, elasticity, hardness, elongation of break, attrition, melt flow index and morphological study (FT-IR) of WTPU/WL composites were examined.

2. Experimental

2.1 Materials.
All composites contain post-consumption thermoplastic polyurethane waste (WTPU) compounded with post-consumption finished leather waste (WL), cryogenically milled at 10000 rpm for 15 sec. and sieved through a 1mm mesh sieve.

2.2 Preparation of various types of biodegradable polymer composite
WTPU and WL were mechanically mixed in Brabender Plasti-Corder PLE 360 at 175°C and 80 rot/min for 3 minutes, to melt the plastomer, and 2 min. at 170°C for homogenisation. The total time was 7 min. Table 1 shows tested formulations. From the Brabender mixing diagrams, figure 1.

It can be seen that the temperature in the mixing chamber raises, depending on the percentage of protein fiber waste (starting from 175°C decreases to 60-90 °C having a maximum 90°C – CH1, 120°C for CH2, and 240°C for CH3, sample with a percentage of 50% protein waste). The mixing forces for samples CH1 (10% WL), and CH2 (20% WL) start at a temperature of 175°C and reach a maximum of 60 Nmm at temp. 90°C and 120°C, respectively, the maximum force is reached when
WTPU is plasticizing and WL disperse. For the sample with 50% WL the maximum mixing force has the same value of 60 Nmm, but at temp. 240°C.

Table 1. Control – polyurethane and PE-g-MA, WTPU/PE-g-MA/WF polymer composite formulations with varying WF amounts CH\(_1\)-10%; CH\(_2\)-20%; CH\(_3\)-50%;

| Compound                                    | W\(_0\) | CH\(_1\) | CH\(_2\) | CH\(_3\) |
|---------------------------------------------|---------|----------|----------|----------|
| Post-consumption waste thermoplastic polyurethane (WTPU) | 270     | 270      | 240      | 150      |
| Waste leather fibres (WF)                   | -       | 30       | 60       | 150      |
| PE-g-MA                                     | 30      | 30       | 30       | 30       |
| Total                                       | 300     | 330      | 330      | 330      |

Figure 1. Brabender mixing diagram for composites CH 1-3

Table 2. The characteristics, presented in the Brabender processing diagrams, for WTPU/PE-g-MA/WF polymer composites

| Compound/ Characteristics | CH\(_1\) (10% WL) | CH\(_2\) (20% WL) | CH\(_3\) (50% WL) |
|---------------------------|-------------------|-------------------|-------------------|
| Loading peak temperature, °C | 119               | 122               | 131               |
| Inflection point temperature, °C | 193               | 144               | 228               |
| Maximum temperature, °C | 193               | 202               | 228               |
| Loading peak energy, Nm  | 167.7             | 178.5             | 168.3             |
| Maximum energy, kNm     | 128.7             | 148.6             | 180.7             |
| Gelation area energy, J | 0.1               | 2.3               | 0.1               |
| Specific energy (W/Sample mass), kJ | 1.1               | 1.5               | 1.6               |
| Gelation speed, Nm/min. | 9.1               | 17.9              | 26.71             |

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 175°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.
2.3 Mechanical Testing

Tensile tests, elasticity, elongation at break, residual elongation, tear strength 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 $500 \pm 5$ mm/min.

Hardness of the samples was measured by Shore “A” Durometer according to SR ISO 7619-1:2011. Abrasion test is carried out with the roll abrader, in compliance with SR ISO 4649/2010.

Melt flow index. Samples were tested using a Melt Flow Index device – Haake that displays values for the melt volume rate (MVR – cm³/10min) as well as melt flow rate (MFR- g/10min). Working temperature (chamber temperature up to 350°C), 2 heating areas, operating according to ISO 1133 standard.

FT-IR spectroscopy was done using the FT-IR 4200 JASCO, Herschel series instrument, equipped with ATR having diamond crystal and sapphire head within the spectrometric range 2000-530 cm⁻¹.

3. Results and discussion

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, and melt flow index. (See tables 3 and 4).

The hardness, for normal state, is 27°Sh A and increase to 51°Sh for CH₃ sample, proportional to the leather fiber content. Thermo-oxidative aging increase the hardness value to 52°Sh A, which demonstrates that the curing process continues during processing. Fiber content does not influence hardness for accelerated aging.

| Symbols | Physical-mechanical characterization - normal state |
|---------|-----------------------------------------------------|
| Hardness 0Sh A, SR ISO 7619-1:2011 | 27 32 41 51 |
| Elasticity %, ISO 4662:2009 | 28 30 30 22 |
| Tensile strength, N /mm², SR ISO 37:2012 | 5.8 5.6 7.6 9.8 |
| Elongation at break, %, SR ISO 37:2012 | 260 160 70 |
| Residual elongation, %, SR ISO 37:2012 | 25 24 16 |
| Tear strength, N/mm, SR EN 12771:2003 | 70 55 45 26 |
| Density, g/cm³, SR ISO 2781:2010 | 1.19 1.21 1.23 1.29 |
| Abrasion, mm³, SR ISO 4649/2010 | 39 29 33 32 |
| Melt flow index, 180°C pressure of 5 Kg, g/10min | 71 155 205 265 |

The tensile strength falls in the range from 5.8 - 9.8 N/mm², for normal state and 6.6 - 10.3 N/mm² after aging. The values are comparable to those of virgin polyurethane and increase proportionally with the WL content introduced into the composite. Compared to the normal state, accelerated aging modifies the tensile strength values only by 1-2%. Elasticity values increase by two percent compared to the control sample at low concentrations of leather fibers and decrease at high concentrations (50%) below the value of the control sample. The values fall within the specific standards. At accelerated aging, the values are lower than those characteristic of the control sample. Tear strength is an index with performance values, maintaining the same values (55-26 N/mm) due to tested elastic-plastic nanocomposites morphology (Tables 2, 3) and decreases proportionally with the amount of composite leather fiber waste compared to the control sample value of 70 N / mm. Density increases compared to the control sample (1.19 g /cm³) up to 1.29 g/cm³ - value for the composite sample with the highest amount of leather fiber waste (50%). The abrasion shows low values and increases proportionally with the leather fibers waste content (29-32 mm³), having poorer values than the control sample - 39 mm³.
In order to establish the technological parameters for processing WTPU/PE-g-MA/WF polymer composites in finished products, tests were carried out to determine the melt flow index at a temperatures of 180°C and a pressure of 5 kg. The analysis of the obtained values (Table 3) show an increased flow compared to control sample Wo (71g/10min) for the samples CH1-CH3: 155-265 g/10min. The values increase proportionally with the amount of leather fibers waste, which leads to higher injection parameters, respectively pressure and temperature.

Table 4. Physical-mechanical characterization after thermo-oxidative aging for 168h at 70°C

| Symbols | Wo | CH1 | CH2 | CH3 |
|---------|----|-----|-----|-----|
| Hardness 0Sh A, SR ISO 7619-1:2011 | 31 | 32 | 38 | 52 |
| Elasticity %, ISO 4662:2009 | 32 | 28 | 24 | 21 |
| Tensile strength, N /mm², SR ISO 37:2012 | 6.6 | 6.0 | 7.0 | 10.3 |
| Elongation at break, %, SR ISO 37:2012 | 340 | 220 | 100 | - |
| Residual elongation, %, SR ISO 37:2012 | 30 | 24 | 24 | - |
| Tear strength, N/mm, SR EN 12771:2003 | 63 | 66 | 41 | 33 |

FT-IT spectroscopy. The FTIR spectra of the analyzed materials are presented in Figure 2. These figures clearly show the interaction between urethane groups and WF. The FTIR analysis confirmed the presence of functional groups characteristic for the PU. The urethane moieties of WTPUs are confirmed by the presence of the main characteristic absorption bands. They are well represented by the characteristic ν(C=O) vibration region (1700–1770 cm⁻¹) [29,30], ν(N-H) stretching vibration region (3200–3400 cm⁻¹) [16] and δ(N-H) bending vibration absorption peak at 1590 cm⁻¹ [17]. It should be pointing out that with increasing content of WL in the reaction mixture the carbonyl peak at 1700-1770 cm⁻¹ decreases.

Figure 2. FTIR spectra for WTPU/PE-g-MA/WF polymer composites

This phenomena can be connected with the fact that some amount of isocyanate is consumed in the reaction with amine groups, which are incorporated with WL, leading to the formation of urea and carbon dioxide. Because of this, a decreased number of urethane links in the modified WTPUs can be observed. The influence of WL active groups on the chemical structure of polyurethane is confirmed with the shift from 1220 cm⁻¹ to 1230 cm⁻¹. This signal is associated to ν(C=N) amide III of urethane and WL protein [18]. With increasing content of WL in the reaction mixture the intensity of the signal increases. Regarding WL, the signal from 3400 cm⁻¹ and 1400 cm⁻¹ recorded for the spectrum of the raw material decreases consistently for WTPU / PE-g-MA / WL composites. The presence of PE-g-MA specific groups does not appear in the spectra due to the small amount of material.
4. Conclusion

Post-consumption thermoplastic polyurethane waste (WTPU) compounded with post-consumption finished leather waste (WL) cryogenically milled, polymer composites composite processed in a double-screw extruder using 1% by weight of polyethylene graft with maleic anhydride and 10, 20, % by weight of fiber content showed the best mechanical performance among the composites manufactured in this work. Properties like elongation at break and elasticity showed a slight reduction with respect to WTPU, however hardness increased remarkably, indicating that the composite is becoming more rigid. The tear strength of the composite decreased more than twice in relation to WTPU. Thus, the WTPU/PE-G-MA/WL composite has a great potential for use in the shoe industry as shoe soles. Thus, the use of post-consumption leather waste in polymeric composites could contribute to sustainable development in a close future.

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