

DETERMINATION OF THE IMMERSION RESISTANCE OF POLYMERIC BIOCOMPOSITES BASED ON TPU (THERMOPLASTIC POLYURETHANE) / RECYCLED TPU / PROTEIN AND ELASTOMERIC WASTE MIXTURE

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DETERMINATION OF THE IMMERSION RESISTANCE OF POLYMERIC BIOCOMPOSITES BASED ON TPU (THERMOPLASTIC POLYURETHANE) / RECYCLED TPU / PROTEIN AND ELASTOMERIC WASTE MIXTURE

ABSTRACT. Collection and recycling of waste from the footwear industry (elastomeric waste) and leather goods (protein waste), as well as other related fields, in order to use it to obtain new products, also easy to recycle and environmentally friendly, is increasingly emphasized. Both elastomeric and protein waste mixed with current elastomers, thanks to new technologies, lead to obtaining new polymer structures / composites (biocomposites) with high-performance properties. This article describes the obtaining of polymeric biocomposites based on thermoplastic polyurethane/recycled thermoplastic polyurethane/mixed protein and elastomeric waste, and also the determination of their immersion resistance in different immersion environments. Recycled thermoplastic polyurethane waste, but also mixed protein and elastomeric waste (SBR rubber) were modified in the first phase by cryogenic grinding. Subsequently only the mixed leather and SBR rubber waste was modified with 5% polydimethylsiloxane (PDMS). The polymer biocomposite specimens were characterized from the point of view of immersion in liquids in various immersion environments, after being conditioned at room temperature for 22-24 hours. The characterization is done according to the ISO 1817:2015 standard, following the variation in volume (ΔV) and mass (ΔM). The immersion was carried out in brown and tightly closed containers. The immersion time was 22 hours, at ambient temperature.

KEY WORDS: resistance to immersion, polymeric biocomposites, TPU, protein and elastomeric waste, recycled TPU

DETERMINAREA REZISTENȚEI LA IMERSIE A BIOCOMPOZITELOR POLIMERICE PE BAZĂ DE TPU (POLIURETAN TERMOPLASTIC) / TPU RECICLAT / DEȘEU PROTEIC ȘI ELASTOMERIC ÎN AMESTEC

REZUMAT. Colectarea și reciclarea deșeurilor provenite din industria de încălțăminte (deșeu elastomeric) și din domeniul marochinării (deșeu proteic), dar și alte domenii conexe, în vederea utilizării acestora pentru a obține noi produse și, de asemenea, ușor de reciclat și prietenoase cu mediul, este din ce în ce mai accentuată. Atât deșeurile elastomerice, cât și cele proteice în amestec cu elastomeri actuali, datorită noilor tehnologii, duc la obținerea de noi structuri / compozite polimerice (biocompozite) cu proprietăți performante. Prezenta lucrare descrie obținerea, dar și determinarea rezistenței la imersie în diferite medii de imersare a biocompozitelor polimerice pe bază de poliuretan termoplastic/poliuretan termoplastic reciclat/deșeu proteic și elastomeric în amestec. Deșeurile de poliuretan termoplastic reciclat, dar și deșeul proteic și elastomeric (cauciuc SBR) în amestec au fost modificate în primă fază prin măcinare criogenică. Ulterior doar deșeul de piele și cauciuc SBR în amestec a fost modificat cu 5% polidimetilsiloxan (PDMS). Epruvetele de biocompozite polimerice au fost caracterizate din punctul de vedere al imersării în lichide în medii de imersare diverse, după ce au fost condiționate la temperatura camerei timp de 22-24 de ore. Caracterizarea se face conform standard ISO 1817:2015 urmărind variația de volum (ΔV) și de masă (ΔM). Imersarea s-a realizat în recipiente de culoare brună și închise etanș. Timpul de imersie a fost de 22 de ore, la temperatură ambiantă.

CUVINTE CHEIE: rezistență la imersie, biocompozite polimerice, TPU, deșeu proteic și elastomeric, TPU reciclat

DÉTERMINATION DE LA RÉSISTANCE À L'IMMERSION DE BIOCOMPOSITES POLYMÈRES À BASE DE TPU (POLYURÉTHANE THERMOPLASTIQUE) / TPU RECYCLÉ / DÉCHETS PROTÉIQUES ET ÉLASTOMÈRES EN MÉLANGE

RÉSUMÉ. La collecte et le recyclage des déchets de l'industrie de la chaussure (déchets élastomères) et de la maroquinerie (déchets protéiques), ainsi que d'autres domaines connexes, afin de les utiliser pour obtenir de nouveaux produits, également faciles à recycler et respectueux de l'environnement, sont de plus en plus soulignés. Les déchets élastomères et protéiques mélangés aux élastomères actuels, grâce aux nouvelles technologies, conduisent à l'obtention de nouvelles structures polymères/composites (biocomposites) aux propriétés performantes. Le présent article décrit l'obtention, ainsi que la détermination de la résistance à l'immersion dans différents milieux d'immersion, de biocomposites polymères à base de polyuréthane thermoplastique/polyuréthane thermoplastique recyclé/déchets de protéines et d'élastomères en mélange. Les déchets de polyuréthane thermoplastique recyclé, mais également les déchets protéiques et élastomères (caoutchouc SBR) présents dans le mélange ont été modifiés dans une première phase par broyage cryogénique. Par la suite, seuls les déchets de cuir et de caoutchouc SBR présents dans le mélange ont été modifiés avec 5 % de polydiméthylsiloxane (PDMS). Les échantillons de biocomposites polymères ont été caractérisés du point de vue de l'immersion dans des liquides dans divers environnements d'immersion, après avoir été conditionnés à température ambiante pendant 22 à 24 heures. La caractérisation se fait selon la norme ISO 1817 : 2015 suivant la variation de volume (ΔV) et de masse (ΔM). L'immersion a été réalisée dans des récipients marron et bien fermés. La durée d'immersion est de 22 heures, à température ambiante.

MOTS-CLÉS : résistance à l'immersion, biocomposites polymères, TPU, déchets protéiques et élastomères, TPU recyclé

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INTRODUCTION

Thanks to advances in science and production, the development of new innovative materials, as well as techniques capable of eliminating waste and at the same time recycling and reintroducing it into the production process, are of topical interest. The increasing concern about the elimination of waste from the environment has led to the issuance of laws and regulations in this regard [1-4]. Innovative, high-performance materials have determined the emergence of new polymer structures based on elastomers (thermoplastics) and different types of wastes. Waste can come from various fields – footwear, leather goods, textiles, agriculture, etc. – and it can be: elastomeric, protein-based, textile fibers, and so on [5, 6]. By recycling and reusing it, we can also reduce the environmental impact and, of course, protect human health, through a less toxic working environment.

The reintroduction of a waste into a new composite requires certain modifications such as grinding, putting it in contact with various precursors [7, 8]. These precursors can be silanes (polydimethylsiloxane – PDMS) and are used to improve the properties of new composites [9-11]. In mixtures based on thermoplastic elastomers (TPU) [12, 13] and not only, natural protein, cellulosic and other types of waste can successfully replace inorganic fillers such as silicon or carbon black, etc., also leading to formation of biocomposites [8-11]. Thermoplastic polyurethane is resistant to abrasion, low temperatures, aggressive working environments, it has adhesion to the surface and is resistant to slipping, it returns to its original shape when it is deformed, and the working temperature is low: 80°C. However, these properties can be improved by adding compatibilizers such as PE-g-MA [7, 8, 14, 15].

In this work, polymer biocomposites based on TPU, TPUW (recycled), protein and elastomeric waste (SBR) in a modified/unmodified mixture with PDMS (5%) and PP-g-MA (compatibilizer) were obtained using the mixing technique on a Plasti-Corder

Brabender mixer with a capacity of 350 cm³, according to the working recipe [16-20]. Polymeric biocomposites were tested in terms of solvent behavior by appropriate techniques. The solutions used for immersion were oil, HCl 30%, NaOH 10% [21].

EXPERIMENTAL

Materials

The following materials were used in making the polymer biocomposites [11]:

➤ TPU – Thermoplastic Polyurethane: specific gravity - 1.03 g/cc, hardness – 65-85 Sh°A, tensile strength - >20 N/mm², colour – black, melt temperature of 170°-190°C, from MD Graphene SL, Spain;

➤ PP-g-AM – polypropylene-graft-maleic anhydride: density – 0.91 g/cm³, hardness – 45 Sh°D, melting point – 117°C, MFI – 2 g/10 min (190°C/2.16 kg), viscosity 330000 cps, colour – honey yellow, from PolyRam Group;

➤ TPUW – recycled thermoplastic polyurethane waste, from the footwear industry, cryogenically ground to sizes of approximately 0.3-0.5 mm;

➤ Mixed leather and butadiene-styrene rubber (SBR) waste: from the footwear industry, cryogenically ground to micrometric sizes of 0.35 mm;

➤ PDMS – Polydimethylsiloxane fluid, from Sigma-Aldrich, Inc., USA.

Preparation of Polymeric Composite

Polymeric biocomposites based on TPU/recycled TPUW/mixed protein and elastomeric waste/PP-g-MA were obtained on a Brabender mixer (Brabender GmbH&Co KG, Duinsburg, Germany). Stages for obtaining polymeric biocomposites are the following [11], Figure 1: collection of recycled TPU waste, but also of mixed leather and SBR rubber waste; cryogenic grinding of waste to sizes of 0.3-0.5 mm using a cryogenic mill at 12.000 rpm (Retsch ZM 200, Verder Scientific, Germany), and using dry ice as a cooling agent, in the form of 3-6 cm pellets; waste modification; dosage of raw materials that are

used to obtain polymer biocomposites – Table 1; obtaining polymeric biocomposites through the mixing technique using the Plasti-Corder Brabender mixer; obtaining dumbbell-type specimens to standard size on an electric

laboratory press (Fortune Press, TP/600 model, Fontijne Grotness Vlaardingen, the Netherlands); tests according to the standards in force.

Table 1: Formulation of biopolymeric composite based on TPU, TPUW waste, mixed leather and SBR rubber waste and PE-g-MA [11]

Ingredients	UM %	MM	T20	T60	T80	TBB1	Sample			
							TBB2	TBB11	TBB12	TBB13
TPU	%	100	80	40	20	80	80	80	80	80
Recycled TPU	%	0	20	60	80	-	-	20	-	-
Leather and SBR rubber waste	%	-	-	-	-	20	-	-	20	-
Leather and SBR rubber waste modified with 5% PDMS	%	-	-	-	-	-	20	-	-	20
PE-g-MA 5%	%	-	-	-	-	-	-	5	5	5



Figure 1. The stages of obtaining polymer biocomposites based on TPU/recycled TPUW/elastomer and protein waste in mixture/PE-g-MA

The working method and parameters for obtaining polymer biocomposites based on TPU/recycled TPUW/mixed protein and

elastomeric waste/PE-g-MA is shown in Table 2 [11].

Table 2: Working method using the Brabender Plasti-Corder mixer [11]

The order of introducing the ingredients	Time (minutes)	Working speed, rpm	Working temperature, °C
TPU	2' (TPU plasticization)	30 rpm	160°C
Recycled TPUW (in the proportion of 20, 60, 80%) - and ingredients according to the working recipe	4'	30 rpm	160°C
Leather and SBR rubber waste in mixture, modified with PDMS - and ingredients according to the working recipe	4'	30 rpm	160°C
Mixture homogenization	5'	80 rpm	160°C

The specimens for testing were obtained in the laboratory-scale electric press by pressing between its plates, in forming

molds, by the compression method according to the following parameters, Table 3.

Table 3: Vulcanization parameters for making specimens in the electric press for mixtures based on TPR/TPUW/mixed leather and SBR rubber waste/PE-g-MA [11]

Vulcanization parameters (All the samples were carried out at the same parameters)	
Vulcanization temperature	160°C
Pressing force	300 kN
Preheating time	3'
Press time	3'
Cooling time	10'
Cooling temperature	45°C
The samples are conditioned for 24 h at ambient temperature and then subjected to testing	

The waste was modified by cryogenic grinding, a process in which the chemical bonds of the polymer chains of the vulcanized elastomer, and those of the leather waste, respectively, were broken under the action of mechanical forces. The process of modifying this waste continued by adding 5% PDMS under temperature conditions (70°C) and mixing every 15-20 minutes for 3-4 hours, with the aim of forming intermolecular or even chemical bonds between the waste and PDMS, to eliminate the tendency of waste particles to agglomerate. At the same time, this procedure ensures an improved dispersion of the waste particles in the polymer matrix. PDMS has the role of a plasticizer, but at the same time it improves the dispersion of mixed protein and rubber waste in the polymer matrix.

Characterization of Polymer Biocomposites

Polymer biocomposites were characterized in terms of immersion in various liquid environments. The characterization was performed according to the ISO 1817:2015 standard [21, 22], following the volume and mass variation. The two methods used according to the mentioned standard are: volumetric method and gravimetric method. Immersion is done in a liquid medium, in dark and sealed vessels, for 22 hours. The immersion mediums were oil, sodium hydroxide 10% and sulfuric acid 30%. For each sample, three discs were used. The specimens that are subjected to the immersion have a thickness of 2 ± 0.2 mm and a volume of $1-3$ cm³. After the 22 h period, the specimens are removed from the test liquids, the excess

liquid is removed by gently dabbing with a filter paper. Then the samples are weighed, and the calculated results are expressed as the percentage difference compared to the initial value.

The calculation for determining immersion in liquids is done according to equation 1 for mass variation and equation 2 for volume variation from the standard [22]:

$$\Delta m_{100} = \frac{m_1 - m_0}{m_0} \times 100 \quad (1)$$

where:

m_0 = initial mass of the specimen,

m_1 = mass of the specimen after immersion,

and the result is expressed as the average value for the three weighed samples.

$$\Delta v_{100} = \left[\left(\frac{m_i - m_{i,w} + m_{s,w}}{m_0 - m_{0,w} + m_{s,w}} - 1 \right) \times 100 \right] \quad (2)$$

where:

m_0 = initial mass of the specimen,

m_i = mass of the specimen after immersion,

$m_{0,w}$ = initial mass of the specimen in water,

$m_{i,w}$ = mass of the specimen after immersion in water,

$m_{s,w}$ = mass of sinker, if used, in water.

The final result is expressed as the average value for the three tested specimens.

RESULTS AND DISCUSSIONS

Characteristics of Plastograms (Obtained from Brabender Plasti-Corder)

The polymer biocomposites were made using the mixing technique on a Brabender mixer with a capacity of 350 cm³, which records the variation of torque and temperature versus time. For each mixture, the variation of torque and temperature was recorded as a function of time, and the diagrams obtained are shown in Figures 2-6.

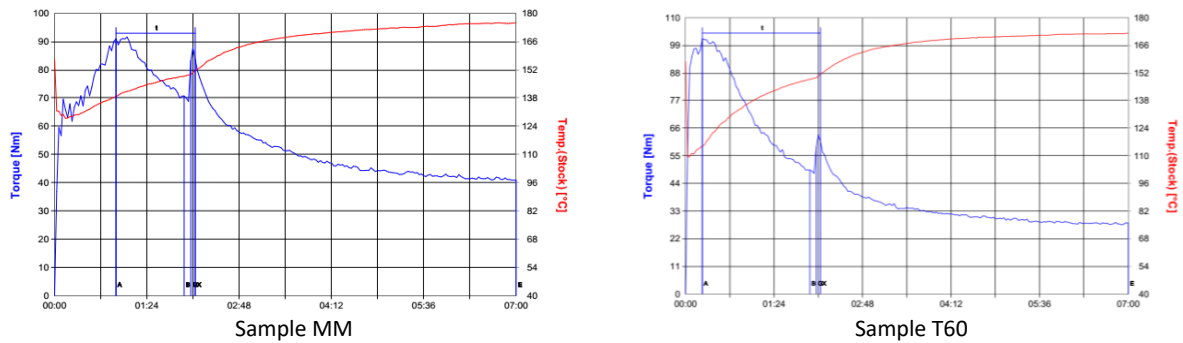


Figure 2. The torque and temperature variation as a function of time recorded on the Brabender Plasti-Corder mixer when obtaining the MM (control) and T60 samples

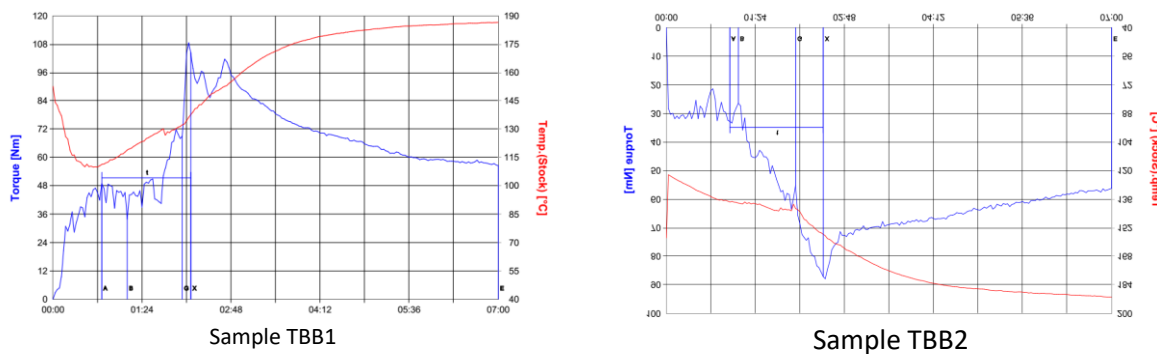


Figure 3. The torque and temperature variation as a function of time recorded on the Brabender Plasti-Corder mixer when obtaining samples (TBB1 and TBB2)

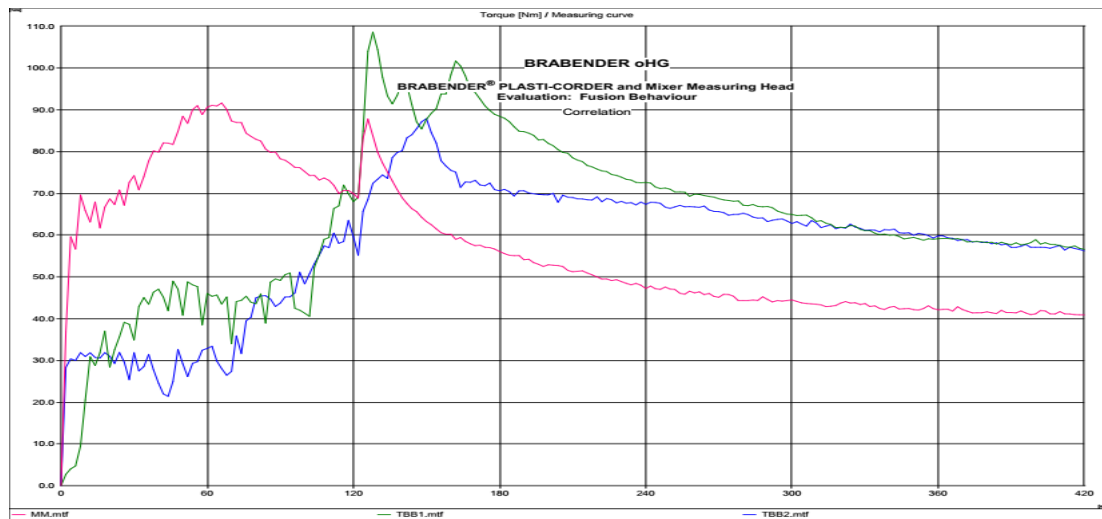


Figure 4. The torque variation as a function of time recorded on the Brabender Plasti-Corder mixer when obtaining the polymer biocomposite mixtures, samples MM (control), TBB1 and TBB2

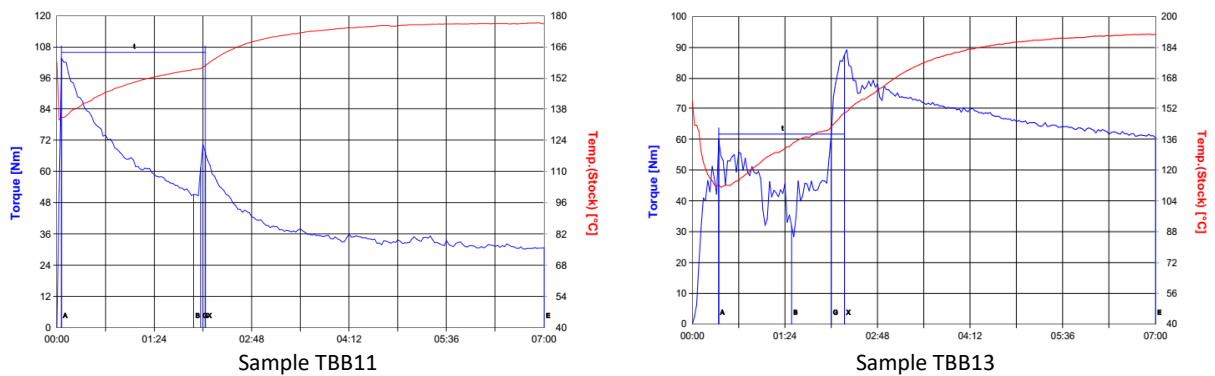


Figure 5. The torque and temperature variation as a function of time recorded on the Brabender Plasti-Corder mixer when obtaining samples TBB11 and TBB13

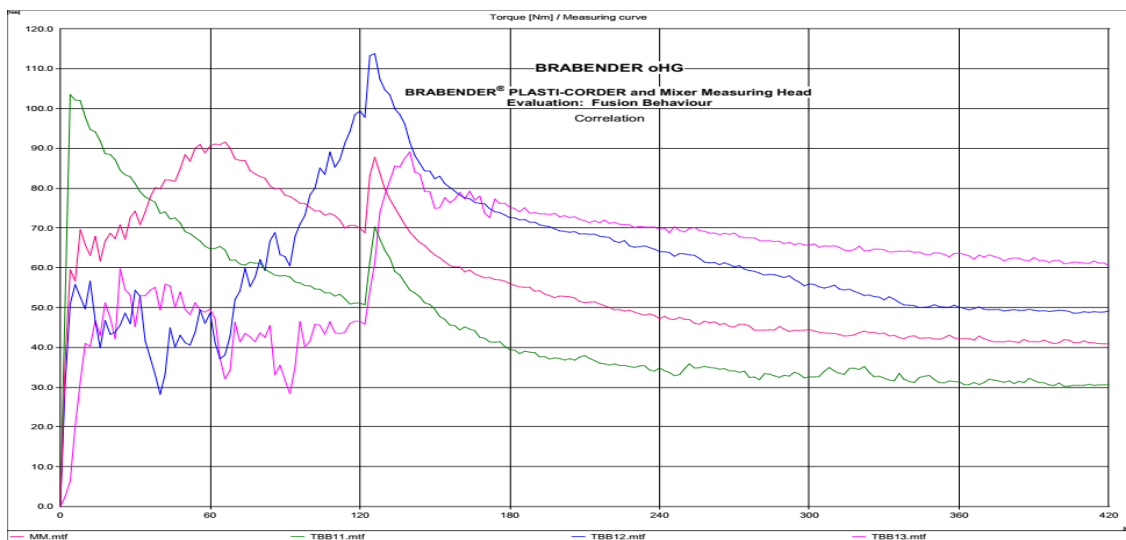


Figure 6. The torque variation as a function of time recorded on the Brabender Plasti-Corder mixer when obtaining the polymeric biocomposite mixtures, samples MM (control) and the TBB11-TBB13 series

From the torque and temperature variation as a function of time recorded on the Brabender Plasti-Corder mixer during the preparation of the recipes (MM, T20, T60, T80, TBB1, TBB2 and TBB11-TBB13 series), presented in Figures 2-6, it can be noted that for each series of tests carried out, the working method is respected according to the established work parameters. In A-B part, which represents the plasticization of the thermoplastic polyurethane for 2 minutes at 30 rpm, the torque increases. As the torque increases, the temperature in the working chamber (mixing chamber) also increases due to the friction of the screws of the Brabender mixer. As the thermoplastic polyurethane plasticizes and its homogenization takes place, the torque decreases in the A-B part. After the TPU plasticizes, the rest of the ingredients are introduced, following the order specified in the

working recipe (see Table 1) in 4', at 30 rpm, during which the mixer is open, so that the torque shows variations between points B and X. Mixing continues for 5' at 80 rpm, at a temperature of 160°C, until homogenization, so that the torque, due to the homogenization of the mixture, has a maximum value.

Determination of Resistance to Immersion

Immersion was carried out in dark-brown containers (tightly closed). The immersion time was 22 hours, at ambient temperature. The mixtures were analyzed from the point of view of behavior after immersion in the established liquids (oil, NaOH 10%, HCl 30%), and the values calculated according to the standard for mass and volume variation are shown in Table 4 [10, 23-26].

Table 4: Immersions of polymer biocomposites based on TPR/TPUW/mixed leather and SBR rubber waste/PP-g-MA

Sample		Immersion environment		
		Oil (ASTM)	Hydrochloric acid 30%	Sodium hydroxide 10%
MM	ΔM	1.22	0.36	-0.22
	ΔV	1.36	0.77	-0.40
T20	ΔM	0.54	1.036	-0.24
	ΔV	1.04	1.28	-0.51
T60	ΔM	-0.28	0.60	0.18
	ΔV	-0.74	1.07	0.51
T80	ΔM	0.34	0.40	0.04
	ΔV	0.77	0.76	0.24
TBB1	ΔM	1.01	0.66	0.42
	ΔV	1.08	0.71	0.65
TBB2	ΔM	1.47	1.7	-3.02
	ΔV	1.72	2.08	-3.60
TBB11	ΔM	0.51	0.73	-0.28
	ΔV	0.72	0.85	-0.57
TBB12	ΔM	1.61	1.17	-0.57
	ΔV	1.82	1.36	-0.66
TBB13	ΔM	1.68	1.10	-4.72
	ΔV	1.18	1.30	-5.34

Following the immersion in ASTM oil solutions, sodium hydroxide 10% and hydrochloric acid 30%, as well as the values calculated for the mass variation (ΔM) and the volumetric variation (ΔV), the following are found:

- For polymer composites based on TPU/TPUW (recycled thermoplastic

polyurethane), the mass and volumetric variations depend on the concentration of TPUW introduced into the mixture, concentration between 20 and 80% (samples T20-20%, T60-60%, T80-80%);

- For polymer biocomposites based on TPU/recycled TPU, mixed leather and SBR rubber waste, unmodified or

modified with 5% PDMS and compatibilized with PE-g-MA, both mass and volumetric variation are influenced by the compatibilizer used and the modification of leather and SBR waste mixed with 5% PDMS. The values are approximately close, which demonstrates a good compatibility, as well as a good homogenization of the waste in the polymer biocomposite mass;

- After immersing the samples in the relevant solutions, they do not undergo changes in the appearance of the surface through color change or swelling through liquid absorption. This indicates that both the working (processing) parameters, the established production technologies, and the waste modification method are the optimal ones, demonstrating at the same time a good mixing of the ingredients.

CONCLUSION

The polymer biocomposites based on TPU, TPUW, protein and elastomeric waste in a mixture modified/unmodified with PDMS and compatibilized with PP-g-MA were obtained by the mixing technique on a Plasti-Corder Brabender mixer with a capacity of 350 cm³, according to the working recipe. Using the mixer, the variation of torque and temperature versus time is recorded for each mixture, and it can be observed that for each series of tests carried out, the working method is respected according to the established working parameters.

The thermoplastic polyurethane waste and protein and SBR rubber waste used in the mixture underwent changes both by cryogenic grinding and by the use of PDMS, which has the role of a plasticizer, but at the same time it improves the dispersion of mixed protein and rubber waste in the polymer matrix.

Determination of the resistance to immersion of polymer biocomposites was tested by immersion in different environments (ASTM oil, NaOH 10%, HCl 30%) and the mass and volume variation was calculated according

to the standard. After immersion in the solutions, it is found that the samples do not undergo changes in the appearance of the surface due to color change or swelling due to liquid absorption, thus demonstrating a good homogenization of the ingredients (a good compatibility, as well as a good homogenization of the waste in the polymer biocomposite mass).

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REFERENCES

1. Nations Environment Programme, Global Waste Management Outlook, **2015**, available at: <https://www.unenvironment.org/resources/report/global-waste-management-outlook>.
2. Regulation (EC) No. 1013/2006 of the European Parliament and of the Council of 14 June 2006 on shipments of waste, **2006**.
3. Plastic Recyclers Europe, Increased EU Plastics Recycling Targets: Environmental, Economic and Social Impact Assessment – Final Report, Deloitte, **2015**, available at: <https://www.plasticsrecyclers.eu/plastics-recyclers-publications>.
4. Plastics, The Facts, "An Analysis of European Plastics Production, Demand and Waste Data. Plastics Europe", **2017**, available online: [the_facts_2017_FINAL_for_website_one_page.pdf](https://www.plasticseurope.org/application/files/5715/1717/4180/Plastics) (accessed on 5 December 2018), <https://www.plasticseurope.org/application/files/5715/1717/4180/Plastics>
5. Lee, B.H., Kim, H.J., Yu, W.R., Fabrication of Long and Discontinuous Natural Fiber Reinforced Polypropylene Biocomposites and Their Mechanical Properties, *Fibers Polym*, **2009**, 10, 1, 83–90, <https://doi.org/10.1007/s12221-009-0083-z>.
6. Mohammed, L., Ansari, M.N.M., Pua, G., Jawaid, M., Islam, M.S., A Review on Natural Fiber Reinforced Polymer Composite and Its

- Applications, *Int J Polym Sci*, **2015**, 243947, <https://doi.org/10.1155/2015/243947>.
7. Stelescu, M.D., Sonmez, M., Alexandrescu, L., Nituica, M., Gurau, D.F., Georgescu, M., Structure and Properties of Blends Based on Vulcanized Rubber Waste and Styrene–Butadiene–Styrene Thermoplastic Elastomer, *J Rubber Res*, **2022**, 25, 4, 421-434, <https://doi.org/10.1007/s42464-022-00187-y>.
 8. Alexandrescu, L., Georgescu, M., Sonmez, M., Nituica, M., Biodegradable Polymeric Composite Based on Recycled Polyurethane and Rubber Wastes: Material for Green Shoe Manufacturing, *Leather and Footwear Journal*, **2020**, 20, 3, 323-331, <https://doi.org/10.24264/lfj.20.3.10>.
 9. Alexandrescu, L., Deselnicu, V., Sonmez, M., Georgescu, M., Nituica, M., Deselnicu, D.C., Pang, X., Biodegradable Polymer Composite Based on Recycled Polyurethane and Finished Leather Waste, *IOP Conf Ser: Earth Environ Sci*, **2019**, 401, 012006, <https://doi.org/10.1088/1755-1315/401/1/012006>.
 10. Stelescu, M.D., Airinei, A., Bargan, A., Fifere, N., Georgescu, M., Sonmez, M., Nituica, M., Alexandrescu, L., Stefan, A., Mechanical Properties and Equilibrium Swelling Characteristics of Some Polymer Composite Based on Ethylene Propylene Diene Terpolymer (EPDM) Reinforced with Hemp Fibers, *Materials*, **2022**, 15, 19, 6838, <https://doi.org/10.3390/ma15196838>.
 11. Nituica, M., Oprea, O., Stelescu, M.D., Sonmez, M., Georgescu, M., Alexandrescu, L., Motelica, L., Polymeric Biocomposite Based on Thermoplastic Polyurethane (TPU) and Protein and Elastomeric Waste Mixture, *Materials*, **2023**, 16, 15, 5279, <https://doi.org/10.3390/ma16155279>.
 12. Sonnenschein, M.F., Polyurethane, Science, Technology, Markets, and Trends, John Wiley & Sons, Inc., Hoboken, New Jersey, **2015**, pp. 127-157, 160-206, 294-335.
 13. Vilsan (Nituica), M., Fikai, M., Georgescu, M., Panturu, L., Chelaru, C., Dragomir, T., Application of Advanced Polymers in the Footwear Industry, *Leather and Footwear Journal*, **2009**, 9, 1, 33-41.
 14. Wang, Y., Li, Z., Cao, Y., Design of an Environmentally Friendly Leather-like Fabric Based on Thermoplastic Polyurethane Covered Yarn, *J Phys: Conf Ser*, **2022**, 2256, 012032, <https://doi.org/10.1088/1742-6596/2256/1/012032>.
 15. Rogulska, M., Polycarbonate-based Thermoplastic Polyurethane Elastomers Modified by MMPA, *Polym Bull*, **2019**, 76, 4719-4733, <https://doi.org/10.1007/s00289-018-2632-3>.
 16. Nituica, M., Alexandrescu, L., Georgescu, M., Sonmez, M., Stelescu, M.D., Gurau, D.F., Curutiu, C., Stoleriu, S., Biodegradable Polymeric Composites Based on EPDM Rubber and Functionalized Elastomeric Waste, *Proceedings of the 8th International Conference on Advanced Materials and Systems (ICAMS 2020)*, 1-3 October **2020**, Bucharest, Romania, 417-422, <https://doi.org/10.24264/icams-2020.IV.13>.
 17. Yang, W., Dong, Q., Liu, S., Xie, H., Liu, L., Li, J., Recycling and Disposal Methods for Polyurethane Foam Waste, *Procedia Environ Sci*, **2012**, 16, 167-175, <https://doi.org/10.1016/j.proenv.2012.10.023>.
 18. Radzi, A.M., Sapuan, S.M., Jawaid, M., Mansor, M.R., Influence of Fibre Contents on Mechanical and Thermal Properties of Roselle Fibre Reinforced Polyurethane Composites, *Fibers Polym*, **2017**, 18, 7, 1353-1358, <https://doi.org/10.1007/s12221-017-7311-8>.
 19. Elmrabet, N., Siegkas, P., Dimensional Consideration on the Mechanical Properties of 3D Printed Polymers Parts, *Polym Test*, **2020**, 90, 7, 106656, <https://doi.org/10.1016/j.polymertesting.2020.106656>.
 20. Calvo-Correas, T., Benitez, M., Larraza, I., Ugarte, L., Pena-Rodriguez, C, Eceiza, A., Advances and Traditional Processing of Thermoplastic Polyurethane Waste, *Polym Degrad Stab*, **2022**, 198, 109880, <https://doi.org/10.1016/j.polymdegradstab.2022.109880>.
 21. ISO 1817:2015 Rubber, vulcanized or thermoplastic – Determination of the effect of liquids.
 22. Vilsan (Nituica), M., Hybrid Polymer Nanocomposites Based on Rubber and Chemically Modified Clays for Footwear Industry, Doctoral Thesis, Politehnica University of Bucharest, Romania, **2016**.
 23. Vilsan (Nițuică), M., Meghea, A., Sonmez, M., Gurău, D., Georgescu, M., Polyolefin Polymer Composites Reinforced with Chemically Modified Layered Clay, *Rev Rom Mater*, **2015**, 45, 4, 377-383, WOS: 000367029800011.
 24. Vilsan, M., Meghea, A., Sonmez, M., Georgescu, M., Dynamically Cured Hybrid Polymer Nanocomposite Based on Polypropylene and EPDM Rubber, *UPB Sci Bull B: Chem Mater Sci*, **2015**, 77, 3, 165-174, ISSN: 1454-2331.
 25. Nituica, M., Sonmez, M., Georgescu, M., Stelescu, M.D., Alexandrescu, L., Gurau, D., Biodegradable Polymer Composites Based on NBR Rubber and Protein Waste, *Leather and Footwear Journal*, **2021**, 21, 4, 229-236, <https://doi.org/10.24264/lfj.21.4.3>.

26. Nituica, M., Sonmez, M., Georgescu, M., Stelescu, M.D., Alexandrescu, L., Gurau, D., Pantazi-Bajenaru, M., Polymer Composite Based on NBR Rubber Compounded with Rubber Waste Functionalized with Potassium Oleate,

Leather and Footwear Journal, **2022**, 22, 1, 45,
<https://doi.org/10.24264/lfj.22.1.5>.

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