INFLUENCE OF ATMOSPHERIC CONDITION ON THE POLYMER COMPOSITE BASED ON NBR RUBBER AND FUNCTIONALIZED PROTEIN WASTE

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INFLUENCE OF ATMOSPHERIC CONDITIONS ON THE POLYMER COMPOSITE BASED ON
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ABSTRACT. Technology has progressed a lot in the last 20 years, today it is possible to obtain new polymer composites that show performance properties. The ever-increasing demand for new high-performance materials has determined the appearance of new polymer structures based on elastomers and various wastes (protein, cellulosic, elastomeric, etc.) from various fields (shoes, leather goods, etc.). This paper describes the obtaining and characterization of polymer composites based on NBR rubber (butadiene-co-acrylonitrile) and protein waste from the footwear and leather goods industry, cryogenically ground to micrometric dimensions and modified with PDMS (polydimethyl siloxane). PDMS has the role of a plasticizer, but at the same time it improves the dispersion of protein waste mixed in the polymer matrix. The polymer composites were obtained by the mixing technique and tested from a physical-mechanical point of view according to the standards in force. The characterization in normal condition and accelerated aging at 70°C for 168 h (it was carried out hot, using the hot air circulation oven method) was carried out after the samples were subjected to conditioning for 24 h at ambient temperature. Also, the polymer composite samples were subjected for 365 days to atmospheric conditions (sun, rain, wind, hail, light, etc.) to see their influence on the properties of the obtained polymer composites.
KEY WORDS: NBR elastomer, polymer composite, leather waste, mechanical properties, functionalized

INFLUENȚA CONDIȚIILOR ATMOSFERICE ASUPRA COMPOZITULUI POLIMERIC PE BAZĂ DE CAUCIUC NBR ȘI DEȘEU PROTEIC FUNCȚIONALIZAT

REZUMAT. Tehnologia a progresat foarte mult în ultimii 20 de ani, astăzi fiind posibilă obținerea de noi compozite polimerice ce prezintă proprietăți performante. Cererea tot mai crescută de noi materiale performante au determinat apariția de noi structuri polimerice pe bază de elastomeri și diverse deșeuri (proteic, celulozic, elastomeric etc.) provenite din diverse domenii (încălțăminte, marochinărie, etc). Prezenta lucrare descrie obținerea și caracterizarea compozitelor polimerice pe bază de cauciuc NBR (butadien-co-acrilonitril) și deșeu proteic din industria de încălțăminte și marochinărie, măcinat criogenic la dimensiuni micrometrice și modificat cu PDMS (polidimetil siloxan). PDMS are rolul de plastifiant, dar în același timp îmbunătățește dispersia deșeului proteic amestecat în matricea polimerică. Compozitele polimerice au fost obținute prin tehnica amestecării și testate din punct de vedere fizico-mecanic conform standardelor în vigoare. Caracterizarea în stare normală și îmbătrânire accelerată la 70°C timp de 168 h (s-a realizat la cald, folosind o metodă de încălzire cu ajutorul etuvei cu aer circulant) s-a efectuat după ce epruvetele au fost supuse condiționării timp de 24 h la temperatură ambiantă. De asemenea, epruvetele de compozit polimeric au fost supuse timp de 365 zile la condiții atmosferice (soare, ploi, vânt, grindină, lumină etc.) pentru a se observa influența acestora asupra proprietăților compozitelor polimerice obținute.
CUVINTE CHEIE: elastomer NBR, compozit polimeric, deșeu de piele, proprietăți mecanice, funcționalizat

L'INFLUENCE DES CONDITIONS ATMOSPHÉRIQUES SUR LE COMPOSITE POLYMÈRE À BASE DE CAOUTCHOUC NBR ET DE DECHETS PROTÉIQUES FONCTIONNALISÉS

RÉSUMÉ. La technologie a beaucoup progressé au cours des 20 dernières années ; il est aujourd'hui possible d'obtenir de nouveaux composites polymères aux propriétés performantes. La demande toujours croissante de nouveaux matériaux performants a déterminé l'apparition de nouvelles structures polymères à base d'élastomères et de déchets divers (protéiques, cellulosiques, élastomères, etc.) issus de domaines variés (chaussure, maroquinerie, etc.). Le présent article décrit l'obtention et la caractérisation de composites polymères à base de caoutchouc NBR (butadiène-co-acrylonitrile) et de déchets protéiques issus de l'industrie de la chaussure et de la maroquinerie, broyés cryogéniquement aux dimensions micrométriques et modifiés avec du PDMS (polydiméthylsiloxane). Le PDMS a le rôle de plastifiant, mais améliore en même temps la dispersion des déchets protéiques mélangés dans la matrice polymère. Les composites polymères ont été obtenus par la technique de mélange et testés d'un point de vue physico-mécanique selon les normes en vigueur. La caractérisation en condition normale et vieillissement accéléré à 70°C pendant 168 h (effectuée à chaud, en utilisant la méthode du four à circulation d'air chaud) a été réalisée après que les échantillons aient été soumis à un conditionnement pendant 24 h à température ambiante. Aussi, les échantillons de composites polymères ont été soumis pendant 365 jours aux conditions atmosphériques (soleil, pluie, vent, grêle, lumière, etc.) pour voir leur influence sur les propriétés des composites polymères obtenus.
MOTS-CLÉS : élastomère NBR, composite polymère, déchets de cuir, propriétés mécaniques, fonctionnalisé

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INTRODUCTION

The development of new sustainable polymer composites, with predetermined properties, which are easy to recycle and ecological, with a low environmental carbon footprint, using concepts of the circular economy is a topical interest [1, 2]. The growing concern about the disposal of waste from the environment has led to the issuance of laws and regulations that take into account its management [3-6]. The main advantages of reusing waste of any type (elastomer, protein, plastic, glass, etc.) are to reduce environmental pollution, but also to protect human health. Also, through the use of new advanced and high-performance technologies, the turnover of economic agents increases. The reintroduction of a recycled material into a new composite requires certain modifications, such as grinding, putting it in contact with various precursors (modification with polydimethylsiloxane – PDMS) to improve their properties [7-9]. Grinding can be done coarsely or up to nanometric dimensions with the help of cryogenic mills, at various rotation speeds [10, 11].

Given that polymeric materials are not biodegradable, in order to obtain such composites, the current trends are to use natural fibers: protein, cellulosic fibers, eggshells, etc. [12, 13]. Natural protein waste can successfully replace inorganic fillers (silicon, carbon black, etc.) in elastomeric mixtures (vulcanized composites based on NBR). They also improve properties such as hardness, tensile modulus, etc., they do not sustain combustion, they have the ability to self-extinguish and are hygroscopic [13, 14]. We can thus say that the natural fibers (protein) added to the vulcanizates based on butadiene-co-acrylonitrile rubber bring improvements to their physical-mechanical properties [8, 9]. The NBR elastomer, due to its stability at temperatures between -40 and 108°C, is an ideal elastomer for the aeronautical industry, but it is also used in the footwear industry, and also to produce modular goods, sponges, expanded foams, floor mats, etc. NBR is an elastomer [15] (rubber) that shows resistance to oils and acids, also a superior strength, and by adding vulcanization accelerators such as tetramethylthiuram disulfide (Th), the physical and mechanical properties are improved. Antioxidants such as IPPD (N-isopropyl-N'-phenyl-p-phenylenediamine) are added to improve the aging (degradation) effect of vulcanizates under the action of atmospheric conditions: high temperatures, rain, wind, light, oxygen etc. [16, 17].

In this work, polymer composites based on NBR rubber and leather waste modified with PDMS were obtained by the mixing technique. Then they were tested rheologically and from a physical-mechanical point of view, under normal conditions at ambient temperature, accelerated aging at 70°C for 168 h, but also under atmospheric conditions (sun, rain, wind, hail, light, etc.) for 365 days to observe their influence on the properties of the obtained polymer composites [18, 19].

EXPERIMENTAL

Materials

The following materials were used in order to obtain polymer composites [18, 19]:

1) NBR rubber - butadiene-co-acrylonitrile rubber: acrylonitrile content - 34%; Mooney viscosity (100%) - 32±3; density - 0.98 g/cm^3;

2) Stearin - white flakes: moisture - 0.5% max; ash – 0.025 % max;

3) ZnO – zinc oxide microparticles: white powder, precipitate 93-95%, density – 5.5 g/cm, specific surface – 45-55 m^2/g;

4) SiO$_2$ - silicon dioxide: density: 1.9 - 4.29 g/cm^3, molar mass – 60.1 g/mol;

5) Kaolin - white powder, molecular weight 100.09;

6) PRW - protein waste: from the footwear and leather goods industry, cryogenically ground to micrometric sizes and modified with PDMS (polydimethylsiloxane);

7) PDMS - Polydimethylsiloxane fluid: has the role of plasticizer, but at the same time improves the dispersion of the protein waste mixed in the polymer matrix;

8) mineral oil;

9) IPPD 4010 – N-isopropyl-N'-phenyl-p-phenylenediamine: density – 1.1 g/cm^3, solidification point above 76.5°C, flat brown to dark purple granules;

10) S – Sulphur (vulcanization agent): fine yellow powder, insoluble in water, melting point: 115°C, faint odor;

11) Th – tetramethylthiuram disulfide (curing agent): density – 1.40g/cm^3, melting point <146°C, an ultrafast curing accelerator.

Methods

Preparation of Polymeric Composite

The stages of obtaining the polymer composites based on NBR rubber and protein waste (PRW) that were made using the mixing technique on an internal Brabender Plasti-Corder mixer are the following, Figure 1 [18, 19]:

1. collecting the protein waste (from the footwear and leather goods industry) and grinding it to a size of 0.35 mm using a cryogenic cyclone mill (Retsch ZM 200, Verder Scientific, Germany) at a speed of 12000-14000 rpm, in the presence of dry ice used as a cooling agent;

2. dosing the raw materials and obtaining the polymer composites on an internal Brabender Plasti-Corder mixer (Brabender GmbH&Co KG, Duinsburg, Germany) according to Table 1, [18] respecting the order of introducing the ingredients, Table 2, and the established working parameters;

3. obtaining a 3-4 mm thick sheet on a laboratory electric roller (Rolling mill machine, ZG-160 YRDB, Xiamen Ollital Technology Co, Ltd, Xiamen, China) after adding sulfur vulcanization activator and Th accelerators to the mixture [18] (relative to 100 parts plasticized rubber);

4. rheological testing (Monsanto R-100 Oscillating Disc Rheometer, MonTech GmbH, USA);

5. obtaining samples of standard sizes in the electric laboratory press (Fortune Press, TP/600 model, Fontijine Grotness Vlaardingen, Holland);

6. conditioning the samples for 24 hours at room temperature;

7. physical-mechanical tests on the elastomer testing equipment, according to the standards in force: under normal conditions, accelerated aging 168 h at 70°C [18] and exposure to atmospheric conditions for 365 days (then physical-mechanical tests are performed).

Table 1. Working method on the Brabender Plasti-Corder mixer [18, 19]

Order of introducing ingredients	Time (minutes)	Working speed, rpm	Working temperature, °C
NBR elastomer	1' 30" (plasticizing elastomer)	40 rpm	36°C
Ingredients according to working formulation (Table 2) (without vulcanization agents)	4'	20 rpm	40°C
Homogenization of mixture	2'	80-100 rpm	60-100°C

Figure 1. Stages of obtaining polymer composites based on NBR elastomer (butadiene-co-acrylonitrile rubber) and protein waste (PRW)

Table 2: Formulation of polymer composite based on NBR rubber and protein waste [18]

Materials	MU [g]	Bo (control)	BCPP$_0$	BCPP$_1$	BCPP$_2$	BCPP$_3$	BCPP$_4$
Butadiene-co-acrylonitrile (NBR)	g	150	150	150	150	150	150
Stearin (flakes)	g	1.8	1.8	1.8	1.8	1.8	1.8
Zinc oxide (ZnO – active powder)	g	7.5	7.5	7.5	7.5	7.5	7.5
Silicon dioxide (SiO$_2$)	g	45	-	30	20	-	-
Kaolin	g	37.5	37.5	37.5	37.5	37.5	37.5
PRW functionalized with potassium oleate	g	-	-	15	30	45	75
Non-functionalized leather waste	g	-	45	-	-	-	-
Mineral oil	g	15	15	15	15	15	15
IPPD 4010	g	4.5	4.5	4.5	4.5	4.5	4.5
Sulfur (S)	g	2.25	2.25	2.25	2.25	2.25	2.25
Tetramethylthiuram disulfide (Th)	g	0.9	1.5	0.9	0.9	0.9	0.9

Modification (Functionalization) of the Protein Waste

The PRW (protein waste) from the footwear industry was modified in the first phase by grinding to a size of 0.35 mm at a speed of 12,000-14,000 rpm, with a cryogenic mill [9, 10] continuing with the functionalization of the powder with polydimethylsiloxane (PDMS), which also acts as a plasticizer. TRW functionalization was achieved by contacting 100 g of PRW waste with 20% PDMS and then placing it in an oven with circulating air, at a temperature of 70°C, for 4-6 hours, homogenizing the mixture every 20 -30 minutes.

Characterization of the Polymer Composite

The polymer composites based on NBR elastomer and PRW were characterized according to the standards in force, in normal state, as well as in terms of behavior after accelerated aging. After the samples were conditioned at room temperature, samples were punched for each individual determination with standardized devices (punch knives), three samples for each determination. The hardness was determined according to ISO 48-4:2018 – Sh°A (for elastomers); elasticity (%) ISO 4662:2017; tensile strength, N/mm² – ISO 37-2020; accelerated aging was carried out in heat, using the hot air circulation oven method and

in atmospheric and weather conditions (rain, wind, sun, light, etc.) for 1 year according to ISO 188/2011 [9].

RESULTS AND DISCUSSIONS

Physical-Mechanical Characterization

The following physical-mechanical characteristics of the polymer composites were determined: hardness, elasticity, tensile strength, elongation at break and residual elongation after conditioning for 24 hours at room temperature, in normal state, accelerated aging at 70°C for 168 h, Table 3 [18], and atmospheric conditions and weather for 365 days, Table 4.

Following the determinations, it is observed that the hardness of the polymer composites, both in normal conditions and accelerated aging at 70°C and 168 h, increases with the amount of leather waste functionalized with PDMS added to the mixture. For the samples BCPP$_3$ and BCPP$_4$ where the active filler – SiO$_2$ – is replaced with leather waste, the hardness increases by up to 12°Sh A. The elasticity decreases by up to 5.55% in the case of the samples where the active filler is totally replaced with PRW modified with PDMS. PDMS has the role of a plasticizer, but at the same time it improves the dispersion of mixed protein waste in the polymer matrix [9, 10].

Table 3: Physical-mechanical characterization of polymer composites based on NBR, in normal state and accelerated ageing at 70°C [18]

Physical-mechanical characterization	Sample					
	BO (control)	$BCPP_0$	$BCPP_1$	$BCPP_2$	$BCPP_3$	$BCPP_4$
Normal State						
Hardness, °Sh A	61	70	66	69	71	73
Elasticity, %	18	18	21	20	19	18
Tensile strength, N/mm^2	11.3	3.44	9.4	8.1	3.97	1.7
Elongation at break, %	180	500	960	800	420	420
Residual elongation, %	80	36	56	56	28	26
Accelerated aging at 70°C and 168 h						
Hardness, °Sh A	66	73	69	72	75	75
Elasticity, %	24	22	26	24	23	22
Tensile strength, N/mm^2	14.47	3.30	9.31	6.96	2.98	1.49
Elongation at break, %	980	540	880	680	420	380
Residual elongation, %	60	28	60	40	28	26

The tear resistance values both in normal condition and accelerated aging decrease as the active layer of silicon dioxide is replaced by the leather waste. For the samples $BCPP_3$ and $BCPP_4$ containing PRW modified with PDMS tensile strength shows a decrease of 64.86 up to 84.95%, and after the accelerated aging process due to the replacement of the active filler with leather waste it decreases significantly by up to 89.7%, and presents values between 1.749 -9.31 N/mm^2.

The elongation at break in normal state for the samples that have in the mixture both leather waste and active filler ($BCPP_1$ and $BCPP_2$) increases by values between 344.4-433.3%, and for those in which the active filler is completely replaced by the leather waste modified with PDMS ($BCPP_3$ and $BCPP_4$), it also increases by up to 133.3%. After the accelerated aging process at 70°C and 168 h compared to the control BO sample, the elongation at break values decrease significantly by up to 61.22%.

For the samples that have in their composition PRW modified with PDMS, as well as SiO_2, $BCPP_1$ and $BCPP_2$, both in normal state and accelerated aging, the residual elongation decreases by 30% (normal state) and 33.33% (accelerated aging). For the samples containing only PRW modified with PDMS, $BCPP_3$ and $BCPP_4$, the values decrease significantly compared to the BO control sample by up to 67.5% in normal condition, and 56.66% after the accelerated aging process.

For all the samples, following the tests performed, according to ISO 188/2011, changes in their values can be observed, after being subjected to atmospheric conditions and weather (rain, wind, sun, light, etc.) for 365 days, Table 4.

Table 4: Physical-mechanical characterization of polymer composites based on NBR, under atmospheric conditions and weather for 365 days

Physical-mechanical characterization	Sample					
	BO (control)	$BCPP_0$	$BCPP_1$	$BCPP_2$	$BCPP_3$	$BCPP_4$
Atmospheric conditions for 365 days (sun, rain, wind, hail, light, UV radiation)						
Hardness, °Sh A	72	75	76	77	77	75
Elasticity, %	22	18	20	18	17	16
Tensile strength, N/mm^2	8.23	3.36	6.21	4.63	3.05	1.71
Elongation at break, %	700	180	500	260	140	200
Residual elongation, %	44	24	32	22	24	22

After exposure to atmospheric conditions for 365 days, the hardness increases by 5-8° Sh A, and the elasticity values decrease. For the samples containing PRW functionalized with PDMS and SiO_2, the elasticity decreases by 9.09%, and 22.72%, respectively, and in the case of the samples where the active filler was totally replaced with PRW, the values decrease by 22.72% for the $BCPP_3$ sample, and by 27.28% for the $BCPP_4$ sample, respectively.

The tensile strength has values between 1.71-6.21 N/mm^2 and decreases significantly in the case of samples in which the active filler is totally replaced with leather waste (PRW) modified with potassium oleate. Elongation at break decreases depending on the percentage of waste added to the mixture. For the samples in which SiO_2 is totally replaced by PRW modified with PDMS, $BCPP_3$ and $BCPP_4$, the values are influenced by the presence of waste and decrease significantly by up to 80%, and 71.42%, respectively. The residual elongation decreases by values between 27.27-50% for all samples subjected to atmospheric conditions for 365 days.

CONCLUSION

The ever-increasing demand for new high-performance materials has determined the emergence of new polymer structures based on elastomers and various types of waste (protein, cellulosic, elastomeric, etc.) from various fields (shoes, leather goods, etc.). By reusing waste of any type (elastomer, protein, plastic waste, glass, eggshells, etc.) and transforming it through different processing methods into new products with added value, we can reduce environmental pollution and at the same time protect people's health by reducing toxicity in the working environment.

The polymer composites based on elastomer and protein waste (PRW) were obtained by the mixing technique according to the working formulation, respecting the order of introduction of the ingredients and the established work parameters. The leather waste from the footwear and leather goods industry was cryogenically ground, and carbonic ice was used as a cooling agent in the form of 3-5 cm pellets and modified with PDMS in order to activate it. PDMS has the role of a plasticizer, but at the same time it improves the dispersion of mixed protein waste in the polymer matrix. The characterization of the polymer composites based on NBR rubber and leather waste was carried out on the specific equipment for elastomers according to the standards in force, after the samples were conditioned for 24 h at ambient temperature. After subjecting the samples to atmospheric conditions for 365 days, following the physical-mechanical characterizations, it is found that the values obtained show changes. Compared to accelerated aging at 70°C and 168 h, the values obtained for the physical-mechanical characteristics of the samples, after being subjected to atmospheric conditions for 365 days, are not very different. This fact shows that subjecting the samples to atmospheric conditions did not have a major impact on the properties of the polymer composites based on NBR elastomer/leather waste, and neither on the environment.

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