

BIODEGRADABLE POLYMERIC COMPOSITES BASED ON NATURAL RUBBER AND FUNCTIONALIZED POST-CONSUMER LEATHER WASTE

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Received: 26.05.2022

Accepted: 27.09.2022

<https://doi.org/10.24264/lfj.22.3.8>

BIODEGRADABLE POLYMERIC COMPOSITES BASED ON NATURAL RUBBER AND FUNCTIONALIZED POST-CONSUMER LEATHER WASTE

ABSTRACT. This work presents the development and characterization of biodegradable polymeric composites based on natural rubber and protein waste from finished post-consumer leather. Protein waste is cryogenically ground to min. 500 nm, functionalized by a mechanical process at temperature with potassium oleate (5%) and mixed in the composite in various proportions (5, 10, 20, 30, 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 carried out on a roller and the mixtures will be processed into finished products by compression in an electric press. The tested biodegradable composites were structurally and 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: protein waste, polymer composite, biodegradability

COMPOZITE POLIMERICE BIODEGRADABILE PE BAZĂ DE CAUCIUC NATURAL ȘI DEȘEURI DE PIELE POST-CONSUM FUNCȚIONALIZATE

REZUMAT. Această lucrare prezintă realizarea și caracterizarea unor compozite polimerice biodegradabile pe bază de cauciuc natural și deșeuri proteice de piele finită post-consum. Deșeurile proteice sunt măcinate criogenic la dimensiuni de min. 500 nm, funcționalitate prin procedeu mecanic la temperatură cu oleat de potasiu (5%) și amestecate în compozit în proporții variate (5, 10, 20, 30, 50%). Acest compozit va fi transformat într-un produs cu densitate scăzută, cu costuri reduse, valorificând și reutilizând deșeurile 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, va fi realizată pe un valț și amestecurile vor fi procesate în produse finite prin compresie într-o presă electrică. Compozitele biodegradabile experimentate au fost caracterizate structural și 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 proteic, compozit polimeric, biodegradabilitate

COMPOSITES POLYMÈRES BIODÉGRADABLES À BASE DE CAOUTCHOUC NATUREL ET DE DÉCHETS DE CUIR POST-CONSOMMATION FONCTIONNALISÉS

RÉSUMÉ. Cet article présente la réalisation et la caractérisation de composites polymères biodégradables à base de caoutchouc naturel et de déchets protéiques provenant de cuirs finis post-consommation. Les déchets protéiques sont cryogéniquement broyés à min. 500 nm, fonctionnalisés par un procédé mécanique à température avec de l'oléate de potassium (5%) et mélangé au composite en différentes proportions (5, 10, 20, 30, 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 des nouveaux matériaux comprend les étapes suivantes : tri des déchets, broyage, fonctionnalisation et compoundage. Ces opérations sont faciles à gérer et n'impliquent pas de nouveaux équipements. Le compoundage, opération la plus importante, sera réalisé sur rouleau et les mélanges seront transformés en produits finis par compression dans une presse électrique. Les composites biodégradables testés ont été caractérisés structurellement et physico-mécaniquement. La transformation des déchets (broyés et fonctionnalisés) en nouveaux produits à valeur ajoutée conduira à des améliorations remarquables du cycle de vie des matières premières et à l'utilisation durable de ces déchets, contribuant à la durabilité, améliorant l'éco-efficacité et l'efficacité économique et réduisant la « pression » des déchets sur l'environnement.

MOTS CLÉS : déchets protéiques, composite polymère, biodégradabilité

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INTRODUCTION

The problem of waste polluting the environment has been addressed over the years through several methods: depollution (deposition on the ground, burial, composting, burning), recovery through reuse and/or energetic recycling (incineration) and/or mechanical and/or chemical recycling (pyrolysis, gasification, hydrolysis, etc.). In the integrated concept of waste management of natural fibers, vulcanized rubber and plastic materials, along with these methods, there is also the possibility of reducing quantities through the use of biodegradable polymer materials. If the re-introduction of these materials into the productive 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 the 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-performance 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.

Composites represent a versatile and very valuable family of materials, which can solve a number of existing problems in various applications/industries, because they provide materials with new properties. Recycling and the use of renewable natural resources offer a new dimension in the discovery of new materials. Recently, special attention has been paid to the development of composites with polymer matrix reinforced with natural fibers instead of conventional composites reinforced with inorganic fibers (glass, carbon, etc.). The development of environmentally friendly "green" materials is due to the biodegradability of these natural materials (from various sources), low

weight, low cost, high availability, high specific resistance compared to glass or carbon fibers, as well as due to the possibility of adapting existing equipment to processors from the field, to mass production [2-4]. Composites reinforced with natural fibers are used in a variety of structural applications such as aerospace, automotive components/parts, sports or recreational equipment, boats and office products, equipment, etc. The most common types of waste from renewable resources used for reinforcing polymer matrices are natural fibers from plants or ligno-cellulosic (flax, hemp, cotton), natural fibers from animals (leather fibers, wool, etc.), wood fibers – wood flour, sawdust (having as the majority component cellulose and lignocellulose, etc.) [5-7]. Leather is a natural polymer, derived from amino acid monomers, with the original fibrous structure more or less intact, tanned or treated to limit putrefaction. Leather is made up of millions of short fibers, having an average length, treated with numerous chemicals during the tanning process. It is known that the leather industry is one of the most polluting sectors on the environment, because it generates both organic and inorganic pollutants, which strongly affect the surroundings and the "bionetwork". The environment is under continuous pressure due to the solid and liquid waste that is generated by this industry. The footwear sector "consumes" most (60%) of the amount of leather produced worldwide. Logically, this industry also produces the largest amount of finished leather waste (~ 60% w). Tanned leather waste contains chromium (III) as a result of the tanning process. Chromium can exist in different oxidation states and its compounds behave differently. Chromium (VI) compounds are extremely toxic and are classified as MAK III A 2 carcinogens. Neutralization of hide waste particles (blocking the transformation of trivalent beneficial Cr into hexavalent harmful element) can be done by treatment with ammonia solution and formic acid [8]. Therefore, chromium-containing leather waste is considered toxic to

the environment and humans, and this has been an important environmental problem for the footwear industry in recent decades. Although in the past, a number of other procedures for using these wastes have been developed, only a few of them are applied in practice due to low financial viability [9-11]. Today, protein powder is either incinerated or bio-gasified [12]. The cost of incineration has increased in recent years by 300-400%. Eco-technologies are a result of multi-disciplinary and integrated research with huge potential for improving competitiveness and sustainable development in a wide range of industrial sectors. The benefits of using leather waste to obtain bio-composites with applications in construction are the following:

- Leather waste is a source of renewable natural materials;
- They are easy to recycle, eco-friendly;
- Leather fibers are self-extinguishing, do not sustain combustion and burn at high temperatures;
 - in a relaxed state, they do not change their volume and do not lose their elasticity;
 - they are very hygroscopic, up to 35% [8, 13].

Currently, there are several conventional methods for the management of solid waste generated from the leather processing industry, which include codification, thermal incineration and anaerobic digestion. These methods of elimination / treatment generally have several deficiencies, such as environmental pollution mainly due to being thrown in the landfill, risks to the health of people who handle this waste due to unhygienic conditions, as well as the possibility of conversion / transformation of trivalent chromium (non-toxic) to hexavalent chromium (toxic) during incineration. Trivalent chromium in the environment will have its own toxic effects when it comes into contact with living organisms [14]. Environmental pollution is a common problem in the vast majority of countries in the world, and unfortunately in some countries, this problem of solid waste is neglected, and thrown

without any restriction into rivers, in open places, etc. Incineration of solid waste is one of the most welcome methods in many fields. There is no sorting of solid waste based on their properties and mixed solid waste is dumped in landfills, which confirms a negligible attention to waste at the moment. In the leather goods industry and the footwear manufacturing industry, enormous amounts of leather are thrown away as waste, and it is essential to pay more attention to this waste, because it currently represents a resource not fully exploited. The nature of the tanning industry and the negative effect of the waste, as well as the minimal attention paid to the practice of using and/or disposing of waste at this time require advanced scientific research [15]. In this regard, experiments regarding composites based on natural rubber with vulcanized rubber waste [16] and wood waste were conducted.

The aim of this paper is to study the properties of natural rubber reinforced composites with differential leather waste contents (10, 20, 30 and 50 wt%). Tensile strength, tear strength, elasticity, hardness, elongation of break, attrition and morphological study (FT-IR) of natural rubber/leather waste composites were examined.

EXPERIMENTAL

Materials and Methods

Materials

Materials used were: (1) natural rubber (NR rubber): purity 99%; Mooney viscosity (100%) – 32 ± 3 ; density – 0.96 g/cm^3 ; (2) stearin: white flakes; moisture – 0.5% max.; (3) zinc oxide microparticles (ZnO): yellow powder, precipitate 93-95%, density – 5.5 g/cm^3 , specific surface – $45\text{-}55 \text{ m}^2/\text{g}$; (4) silicon dioxide (SiO_2): density – $1.9\text{-}4.29 \text{ g/cm}^3$, molar mass – 60.1 g/mol ; (5) precipitated chalk: white powder, purity 99.09%; (6) leather waste – leather fibres functionalized with potassium oleate; (7) mineral oil; (8)

N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD 4010): density – 1.1 g/cm³, solidification point over 76.5°C, flat granules coloured brown to dark purple); (9) sulphur (S): vulcanization agent, fine yellow powder, insoluble in water, melting point: 115°C, faint odor; (10) N-cyclohexylbenzothiazole-2-sulphenamide (Cz): curing agent, density – 1.26 g/cm³, melting point 93-100°C; (11) diphenyl guanidine (D): curing agent, density – 1.34g/cm³; (12) PEG – Polyethylene glycol: plasticizer, white pellets.

The functionalization of protein waste fibers (finished leather) was achieved by mixing with a stirrer with helical paddles, for 2 hours at a temperature of 80°C with slow dripping of potassium oleate and a speed of 40 rpm. Different percentages of functionalizing agent related to the amount of waste were experimented, but the percentage of 7% was selected, considered optimal due to the degree of absorption, the

elimination of fiber agglomeration, the working method and the favorable influence on the physical-mechanical characteristics of the composite.

Preparation of Various Types of Biodegradable Polymer Composite

Table 1 presents the recipes for polymer composites based on natural rubber, with semi-active white mineral charge – ZnO and precipitated chalk, recipes based on the formulation for processing caps for antibiotic bottles for zootechnical use. In order to obtain polymer composites based on natural rubber and protein waste from finished post-consumer leather, the basic recipe was modified by adding protein waste functionalized with potassium oleate in different proportions, respectively 10, 20, 30, 50% waste relative to the amount of elastomer.

Table 1: Polymeric composites based on natural rubber compounded with protein waste functionalized with potassium oleate

Material	UM	NO	NP1	NP2	NP3	NP4
<i>Processing on Brabender mixer</i>						
Natural rubber	g	190	190	190	190	190
Stearic acid	g	3.8	3.8	3.8	3.8	3.8
Zinc oxide	g	9.5	9.5	9.5	9.5	9.5
Precipitated chalk	g	95	76	57	38	0
Protein waste	g	-	19	38	57	95
Mineral oil	g	4.5	5.7	5.7	5.7	5.7
IPPD antioxidant	g	4.5	5.7	5.7	5.7	5.7
PEG 4000	g	1.14	1.14	1.14	1.14	1.14
<i>Processing on roller</i>						
Sulfur	g	4.85	4.85	4.85	4.85	4.85
Cz accelerator	g	2.28	2.28	2.28	2.28	2.28
D accelerator	g	0.29	0.285	0.285	0.285	0.285

NO, NP1-NP4 composites were mechanically mixed in Brabender Plasti-Corder PLE 360 at 45°C and 80 rpm for 3 minutes and 2 min. at 23°C for homogenisation. The total time was 5 min.

According to the diagrams (Fig. 1-2), 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 introduction of elastomers. As the torque increases, so does the temperature due to friction. The torque starts to decrease until B, mainly due to the homogenization and plasticization of the elastomer, as well as due to the increase in temperature as a result of the shear forces. The other ingredients are introduced and the rotation speed is reduced to 20 rpm, and the mixer is kept open. Between point B and

point X, the torque starts to increase due to the inclusion of the ingredients. After incorporating the fillers and the other ingredients, the second loading peak, X, is observed, when a maximum torque appears. The torque begins to decrease, indicating the homogenization of the mixture. As a result, a maximum torque value is obtained

due to the compaction and homogenization of the rubber mixture. This is generally followed by a decrease in the torque value, 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.

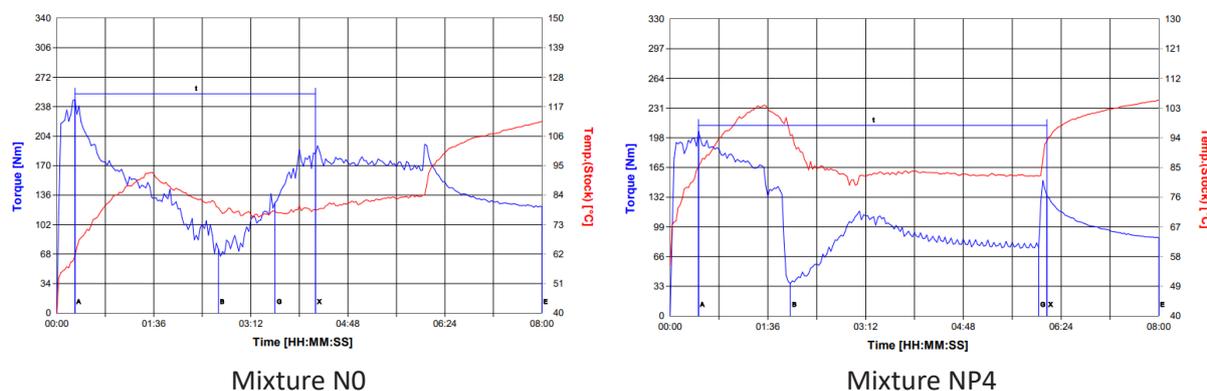


Figure 1. Torque and temperature variation over time recorded on the Brabender Plasticorder while obtaining samples NO and NP4

From the diagrams shown in Figure 1 it can be seen that the temperature in the mixing chamber increases, depending on the percentage of post-consumer protein waste introduced into the polymer composite (starting from 84°C to 105°C, it decreases approximately to 85°C, then increases to 107°C). Also, the mixing forces increase proportionally with the percentage of protein waste in the composite, starting at a temperature of 185°C and reaching a maximum at 30 seconds of mixing of 246 Nm for sample NO and decreasing proportionally to 198 Nm for sample NP4. The maximum torque is reached when the natural rubber plasticizes, mixes with the ingredients (plasticizer, fillers, antioxidants,

protein waste) and begins to disperse the waste particles. After reaching the maximum torque, it decreases uniformly (195 Nm), in the last minute decreasing uniformly to 66 Nm, which indicates the homogenization of the mixture. This decrease is due to the elastic behavior of the protein waste functionalized with potassium oleate, which also acts as a plasticizer. Table 2 shows the processing characteristics presented in the Brabender diagrams, for each processed composite. The data obtained from the Brabender diagrams are similar to those obtained when making composites based on natural rubber with elastomeric and functionalized wood waste, previously experimented [16].

Table 2: Characteristics presented in Brabender processing diagrams for polymeric composites – NP series

Characteristics	Sample code				
	NO	NP1	NP2	NP3	NP4
Temperature at peak load, °C	61	63	67	68	71
Temperature at the inflection point, °C	78	82	84	89	91
Maximum temperature, °C	112	109	112	108	97
Energy at the peak load, Nm	2.0	255.9	263.0	271.6	263.1
Maximum energy, Nm	183.5	171.4	169.6	159.1	128.2
Gelation zone energy, kNM	10.3	33.7	33.1	34.7	35.2
Specific energy, kNm/g	0.7	0.8	0.6	0.6	0.5
Gelation rate, Nm/min.	142.5	171.2	22.0	26.3	52.5

The mixtures made on the Brabender were added on the roll with the vulcanizing agents. The working method on the laboratory-scale electric roller for adding vulcanizing agents to the mixtures is as follows, mentioning the fact that the mixture is processed on the roller at a temperature of 23-30°C, roller friction 1:2 and with 50 revolutions/min:

- the composite is plasticized;
- the vulcanization agents are introduced and mixed for approximately 5-10 minutes;
- the mixture is homogenized on the roller for 1-2 minutes and taken out in the form of a 1-2 mm thick sheet.

The Monsanto 100S Rheometer was used to determine the vulcanization parameters of the tested composites, which describes their vulcanization and processing parameters. The analysis is carried out as follows: a sample is sealed in a cavity of the device, at a controlled and constant temperature (in the case of this work a temperature of 165°C was used), which surrounds a rotor with oscillations at a frequency of 1.67 Hz (100 cpm). The output correlates with the degree of vulcanization depending on vulcanization time.

From the experimental data (Table 3) it can be seen that by replacing the amount of precipitated chalk inactive filler with functionalized elastomeric waste, the rheological characteristics of the mixtures are changed as follows:

- the minimum torque (ML) decreases, the maximum torque (MH) has a value of about 4 dNm, and the torque variation ($\Delta M = MH - ML$) increases as the amount of rubber powder increases compared to quantities of silicon dioxide; this indicates a stiffness of the mixtures in the unvulcanized state which may be due to the agglomeration of the rubber powder or its larger dimensions compared to the sizes of the silicon dioxide particles, but in the vulcanized state, the mixtures show a similar stiffness.
- the scorching time (t_{s2}) shows very good values, over 2', and the optimal vulcanization time (t_{90}) is over 20' and increases with the replacement of the silicon dioxide active filler with the elastomeric filler (indicating a decrease in crosslinking density as a result of reducing the amount of active reinforcing filler).

Table 3: Rheological characteristics of mixtures – NP series

Rheological characteristics at 165°C	Sample code				
	N0	NP1	NP2	NP3	NP4
ML (dNm)	8	16.5	19.3	16.5	18.5
MH (dNm)	54.3	74	74	74.1	74.2
$\Delta M = MH - ML$ (dNm)	46.3	57.5	54.7	57.6	55.7
Mf - Reversion (dNm)	47	2.47	2	2.4	2.86
t_{s2} (min)	1.2	10.01	9.28	11.15	6.91
t_{50} (min)	1.67	25.76	25.16	28.03	11.05
t_{90} (min)	2.54	16.5	19.3	16.5	18.5

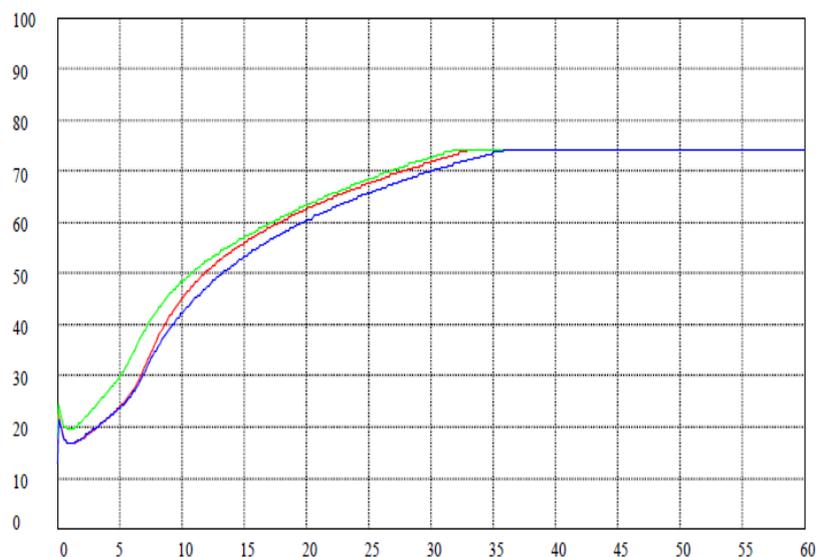


Figure 2. Torque variation expressed in dNm (OY axis) depending on time expressed in minutes (OX axis) for mixtures based on natural rubber: NP1 (red), NP2 (green) and NP3 (blue)

The vulcanization parameters presented in Table 4 were set according to the data from the rheograms.

The compounds were then compression-molded (using an electrically heated laboratory press) to obtain a sheet of about 2 mm thick.

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.

Table 4: Vulcanization parameters for making samples by vulcanization in the press for mixtures based on natural rubber and elastomeric waste – NP series

Vulcanization parameters	Sample code				
	N0	NP1	NP2	NP3	NP4
Vulcanization temperature	165°C	165°C	165°C	165°C	165°C
Vulcanization time - T_{90}	4 min	4 min	4 min	4 min	4 min
Pressing force	300 kN	300 kN	300 kN	300 kN	300 kN
Cooling temperature	45°C	45°C	45°C	45°C	45°C
Cooling time	10'	10'	10'	10'	10'
Pressing force	300 kN	300 kN	300 kN	300 kN	300 kN

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 flexions – 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 flexions at an angle of 90°C, on a mandrel with a diameter of 10mm, up to 30,000 cycles or until the crack appears or the material breaks.

FT-IR spectroscopy was performed 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.

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 (Table 5).

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

Physical-mechanical characteristics	Sample code				
	NO	NP1	NP2	NP3	NP4
<i>Normal state</i>					
Hardness, °Sh A	44	45	42	38	34
Elasticity, %	32	24	26	28	24
100% modulus, N/mm ²	1.0	0.51	0.05	0.046	0.046
300% modulus, N/mm ²	2.0	1.04	0.64	0,87	1.11
500% modulus, N/mm ²	4.52	3.21	1,76	1.97	2.88
Tensile strength, N/mm ²	14.23	10.46	6.2	3.17	5.31
Elongation at break, %	740	820	740	700	560
Residual elongation, %	28	38	32	28	22
Tear strength, N/mm	24.39	19.23	16.9	15	13
Specific weight, g/cm ³	1.2	1.12	1.10	1.08	1.06
Attrition, mm ³	123.45	320	280	265.36	231.71
Rossflex repeated flexions SR ISO 132/2018	Resist up to 150.000 cycles			100.000 cycles crack appear, resist up to 128.000 cycles	
<i>After accelerated ageing for 168 hours at 70°C</i>					
Hardness, °Sh A	51	40	39	37	38
Elasticity, %	34	38	32	34	28
100% modulus, N/mm ²	1.22	1.0	0.84	0.06	0.06
300% modulus, N/mm ²	2.8	1.5	1.0	1.3	1.28
Tensile strength, N/mm ²	11.3	6.6	5.4	4.7	4.3
Elongation at break, %	620	660	780	580	620
Residual elongation, %	32	28	30	24	20
Tear strength, N/mm	29.2	25.6	21.4	20.7	16.1

The hardness decreases by 9-14 °ShA, from 45 °ShA in the control sample to 34 °ShA in the composite based on natural rubber with functionalized post-consumer finished leather waste in a proportion of 30-50%. The decrease in hardness is due to the increase in plasticizer from the rubber waste functionalization process and its low density. After accelerated aging, the hardness increases due to the loss of plasticizer

when the samples are kept at a temperature of 70°C for 168 h.

- Elasticity decreases by 25-38%, but the variations are uneven.

- The modulus, tensile strength and tear strength values decrease as the precipitated chalk inactive filler is replaced by the elastomeric waste. When the precipitated chalk is completely replaced with rubber powder, an increase in

these characteristics is observed, but without exceeding the values of the control sample.

- Elongation at break shows good values, over 620%.
- Attrition increases in samples with elastomeric waste.
- The density of the mixtures decreases as the amount of powder increases and the amount of precipitated chalk decreases, because the density of elastomeric waste is lower than that of chalk.
- Repeated flexions – Ross Flex – The footwear standards in force specify values of 100,000 cycles for vulcanized rubber shoe soles when determining repeated flexions. The values presented in Table 5 show that only the NP3 and NP4 composites with rubber waste content of 30%, and 50%, respectively, do not fall within this value (after 90,000 cycles crack appears, resist up to 128,000 cycles). The others have values higher than 150,000 cycles, higher than the values imposed by the standard.
- IR spectrum represents the radiant energy absorption curve in the IR domain by the sample molecule, depending on the wave length or radiation frequency. The infrared domain of the electromagnetic radiation is between 0.8 and 200 μm . IR domain for usual organic chemistry is between 2.5 and 25 μm . The structural determinations were carried out on an IR molecular absorption

spectrometer with double beam, in the range of 4000-600 cm^{-1} , using 4200 FT-IR equipped with ATR diamond crystal and sapphire head. The solid-state samples were set in the ATR and the equipment recorded the transmittance spectra of the sample and then compared it with the background spectra previously recorded. The recorded spectra of the samples were compared with the natural rubber and rubber waste elastomeric spectrum. The FTIR spectra of the analyzed materials are presented in Figure 5. In the spectrum recorded for the unvulcanized natural rubber, the most important bands that allow its qualitative and quantitative identification can be highlighted. The band at 2960.79 and 2851.81 cm^{-1} can be attributed to asymmetric (ν_{as}) and symmetric (ν_{s}) stretching of $-\text{CH}_3$ bond, and the one at 1375.58 cm^{-1} represents the in-plane deformation vibration, namely the shear (δ^{s}) of $-\text{CH}_3$ bond, the band at 841.97 cm^{-1} represents the out-of-plane deformation vibration (γ) of $-\text{CH}-\text{CH}$ bond originating from cis-1,4 units. The band at 1444.82 cm^{-1} is associated with deformation bonds of CH_2 groups, the band at 1375.58 cm^{-1} comes from the shear vibration of $-\text{CH}_3$ bonds and the one at 1663.01 cm^{-1} represents the stretching vibration of $\text{C}=\text{C}$ bond [15].

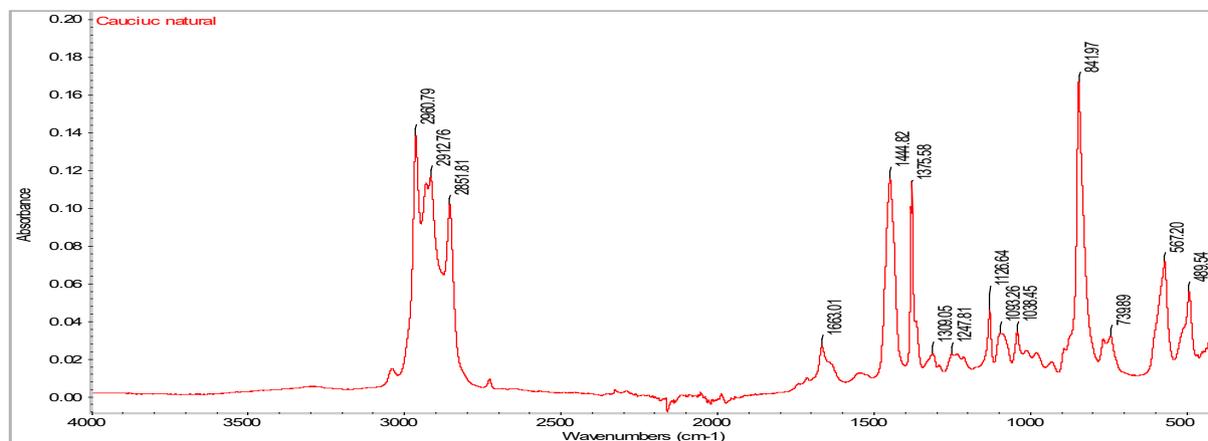


Figure 3. FTIR spectrum of unvulcanized natural rubber

In the case of the elastomeric waste used as filler in the tested composites, both the bands characteristic of SBR rubber and bands originating from other specific processing additives can be identified. Thus, in the spectrum recorded for the unmodified elastomeric waste, the bands characteristic of the functional groups in SBR can be highlighted. Thus, the band at 962.41 cm^{-1} is attributed to 1,4 groups from trans-butadiene and the one at 907.46 cm^{-1} is attributed to 1,2 units from butadiene. The

bands at 2914.39 and 2847.55 cm^{-1} correspond to CH bond deformations originating from the aromatic styrenic ring.

In the case of the elastomeric waste modified on the surface with potassium oleate, the appearance of peaks at 1560.84 and at 1413.25 cm^{-1} are characteristic of the mode of asymmetric and symmetric stretching of COO^- bond. The band at 1463.59 cm^{-1} comes from the CH_2 bond vibration. The band at 719.08 cm^{-1} is due to $-(\text{CH}_2)_n-$ bond deformations.

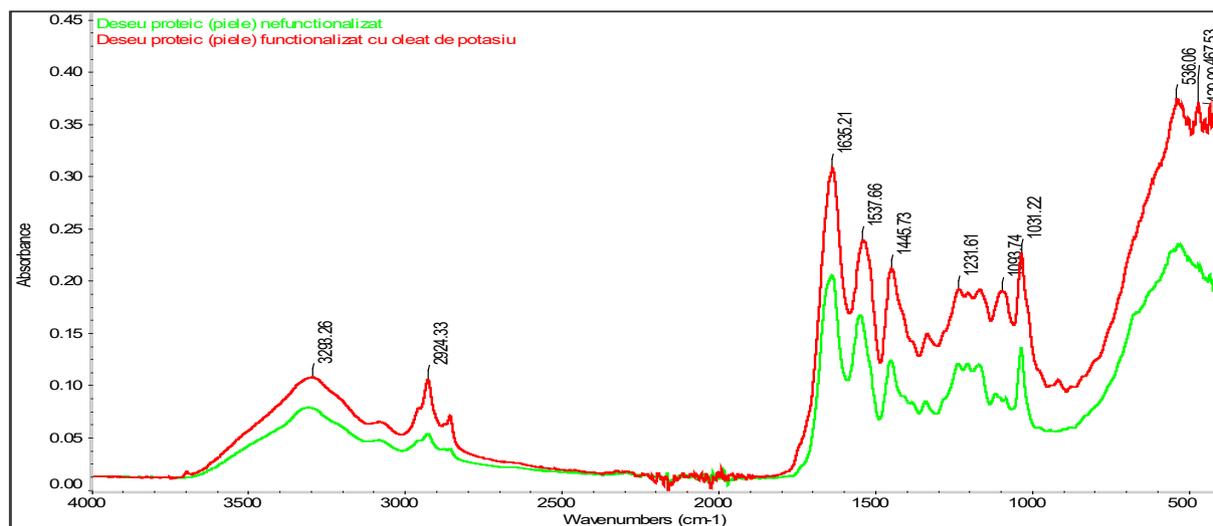


Figure 4. FTIR spectra of protein waste non-functionalized (green) / functionalized with potassium oleate (red)

The spectra obtained for the protein waste non-functionalized/functionalized with potassium oleate highlight the characteristic bands originating from leather, namely: the band at 3293.26 cm^{-1} can be associated with N-H stretching bonds, the band at 1635.21 cm^{-1} (Amide I – associated with the stretching vibration of C=O bond originating from the protein structure). The band at 1537.66 cm^{-1} , known as Amide II, can be associated with the bending vibration of N-H bond and the stretching

vibration of C-H bond. The band at 1231.61 cm^{-1} – Amide III – represents the stretching vibration of C-N bond, respectively the in-plane bending vibration of N-H bond from the amide bond, the vibration of CH_2 groups originating from glycine and proline (cyclic secondary amine), respectively. The presence of potassium oleate could not be visualized in the spectrum, most likely due to the fact that it was adsorbed inside the leather fibers.

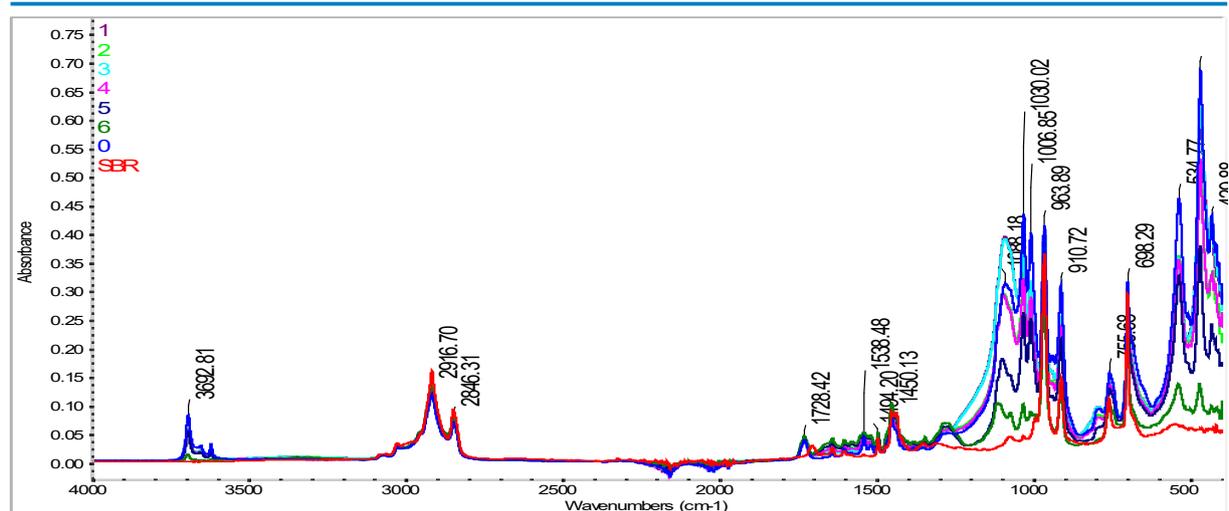


Figure 5. FTIR spectra of mixtures based on natural rubber reinforced with varying percentages of protein waste modified with potassium oleate

In the case of the N0 mixture (control sample without elastomeric waste), besides the bands characteristic of natural rubber, the presence of very intense bands due to the groups originating from calcium carbonate at 1424.82, 873.75 and 712.6 cm^{-1} can be highlighted. The intensity of these bands is directly proportional to the amount of calcium carbonate introduced into the mixtures. Thus, the control mixture N0 contains the highest amount of calcium carbonate, following that in the mixtures NP1-NP3 the amount of carbonate is gradually replaced by the elastomeric waste modified with oleate. Instead, in the case of the NP4 mixture, the calcium carbonate was completely replaced by the protein waste, which led to the disappearance of the bands associated with CaCO_3 . The characteristic bands of the protein residue modified with oleate, and in particular the band at $\sim 1537 \text{ cm}^{-1}$ (due to the bending vibration of N-H bond and the stretching vibration of C-H bond) and 1621 cm^{-1} (the stretching vibration of C=O bond from oleate) can be visualized in all processed mixtures NP1-NP4, the greater the amount of rubber waste modified with oleate, the greater their intensity. In the case of vulcanized mixtures, it can be observed that the band at 1663.01 cm^{-1} associated with the stretching vibration of C=C bond (clearly detectable in the spectrum

obtained on the unvulcanized natural rubber) is consumed during the sulfur vulcanization process, its relative intensity decreasing.

CONCLUSIONS

The recipe based on natural rubber used in the processing of stoppers for bottles of antibiotics for zootechnical use was modified by replacing the inactive filler (precipitated calcium carbonate) with cryogenically ground post-consumer protein waste with a particle size of 500 nm and functionalized with potassium oleate. These polymeric composites were processed on a Brabender mixer and laboratory roller using elastomeric waste with different proportions (10, 20, 30 and 50%). The polymeric composite samples with percentages of 10 and 20% post-consumer protein waste presented the best physical-mechanical performance compared to those with higher percentages of elastomeric waste (30 and 50%), characteristics that fall within the specific values for the control sample without waste. Properties such as elongation at break and elasticity showed a slight reduction compared to the control sample – N0, and the hardness decreased by 9-14 units. The tensile strength of the composition decreased to about half that of N0. Although the values are lower, the NP1-NP3 composites, with a percentage of

10-30% functionalized elastomeric waste, fall within the standardized physical-mechanical values. The physical-mechanical values obtained after accelerated aging are slightly modified, corresponding to the standardized ones. The experimental data in the case of composites based on natural rubber and protein waste are similar to those obtained when making composites based on natural rubber with functionalized elastomeric and wood waste, previously experimented [16].

Acknowledgements

This paper is funded by the LIFE program in the frame of LIFE GREENSHOES 4 ALL (LIFE17ENV/PT/000337) project and PN 19 17 01 03/2019 project: "Biodegradable composites from technological and post-consumption polymeric wastes by designing and applying 4R eco-innovative technologies (4R-ECO-MAT)".

DISCLAIMER

LIFE GREENSHOES 4 ALL, (LIFE17ENV/PT/000337) project is been co-funded with support from the European Commission under the LIFE- programme. This publication reflects the views only of the author, and the Commission cannot be held responsible for any use which may be made of the information contained therein.

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