

POLYMER COMPOSITE BASED ON NATURAL RUBBER AND FUNCTIONALIZED RUBBER WASTE

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ABSTRACT. In this work, biodegradable polymer composites were made based on natural rubber and post-consumer vulcanized rubber waste functionalized with potassium oleate, in various proportions (5, 10, 20, 30, 50%), cryogenically ground to dimensions of min. 500 nm and polyethylene grafted with maleic anhydride as compatibilizer between the two phases. This composite will be made into a low-density product, with low cost, and last but not least, biodegradable, with the recovery and reuse of waste, containing post-consumer polymers. 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, is carried out on a roller and the mixtures are 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: biodegradability, polymer composite, post-consumer

COMPOZIT POLIMERIC PE BAZĂ DE CAUCIUC NATURAL ȘI DEȘEU DE CAUCIUC FUNCȚIONALIZAT

REZUMAT. În această lucrare s-au realizat compozite polimerice biodegradabile pe bază de cauciuc natural și deșeurile de cauciuc vulcanizate post-consum funcționalitate cu oleat de potasiu, în proporții variate (5, 10, 20, 30, 50%), măcinat criogenic la dimensiuni de min. 500 nm și compatibilizator între cele două faze, polietilenă grefată cu anhidridă maleică. Acest compozit va fi transformat într-un produs cu densitate scăzută, cu costuri reduse, și nu în ultimul rând, biodegradabil, valorificând și reutilizând deșeurile care conțin polimeri post-consum. 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. Compoundarea, cea mai importantă operațiune, se realizează pe un valț, iar amestecurile sunt 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 deșeurile, contribuind la sustenabilitate, îmbunătățirea eco-eficienței și a eficienței economice, precum și la reducerea „presiunii” deșeurilor asupra mediului.

CUVINTE CHEIE: biodegradabilitate, compozit polimeric, post-consum

COMPOSITE POLYMÈRE À BASE DE CAOUTCHOUC NATUREL ET DE DÉCHETS DE CAOUTCHOUC FONCTIONNALISÉS

RÉSUMÉ. Dans ce travail, des composites polymères biodégradables ont été fabriqués à base de caoutchouc naturel et de déchets de caoutchouc vulcanisé post-consommation fonctionnalisés avec de l'oléate de potassium, dans diverses proportions (5, 10, 20, 30, 50 %), broyés cryogéniquement à des dimensions de min. 500 nm et compatibilisant entre les deux phases, polyéthylène greffé anhydride maléique. Ce composite sera transformé en un produit à faible densité, à faible coût, et, enfin et surtout, biodégradable, en récupérant et en réutilisant des déchets contenant des polymères post-consommation. 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, est réalisé sur rouleau et les mélanges sont 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: biodégradabilité, composite polymère, post-consommation

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INTRODUCTION

The European Commission adopted the new Circular Economy Action Plan to stimulate Europe's transition from a linear towards a circular economy. This ambitious initiative: "Closing the Loop - An EU Action Plan for the Circular Economy" is promoting the transition to a more circular economy, where the value of products, materials and resources is maintained in the economy for as long as possible and the generation of waste is minimized, being an essential contribution to the EU's efforts to develop a sustainable, low carbon, resource efficient and competitive economy. Nowadays, the circular economy is an irreversible, global trend. It was foreseen that the proposed actions would contribute to "closing the loop" of product lifecycles through greater recycling and re-use, and bring benefits for both the environment and the economy [1-5]. The paper presents a recycling route for post consumption rubber wastes in order to obtain biodegradable composites for green products manufacturing. Composites represent a very valuable group of materials, which can solve a series of existing problems in various applications/industries, because they facilitate the introduction of new properties in materials. Recycling and using renewable natural resources offer a new dimension in the discovery of new materials.

The dynamic increase in the production of rubber products, especially those used in the automotive industry, is responsible for obtaining a large amount of vulcanized rubber waste, especially in the form of used tires, of which more than 17 million tons are globally generated every year. China, the European Union (EU), the USA, Japan and India produce the largest amounts of used tire waste – almost 88% of the total number of tires withdrawn worldwide [6, 7]. The diversification of chemical compositions and three-dimensional structures existing in vulcanized rubber from tires is the main reason why they are highly resistant to biodegradation, photochemical decomposition, chemical reagents and high temperatures. The increased number of used tires makes them a serious threat to the natural environment. End-of-life tires and other rubber waste (containing high-quality natural and synthetic rubbers) have become the source of materials for obtaining "environmentally

friendly" composites with utilitarian properties. The advantages of using such materials include the sustainable management of the large quantities of used polymer articles that currently burden the environment and the reduction of costs of composite materials produced from cheap polymer waste [8]. The increasing level of consumption of rubber recycling products shows that rubber waste is used in the rubber industry as a raw material for the production of composites with practical utilitarian properties and in an economical way. For high-quality and high-strength rubber products, the use of rubber waste is limited. Therefore, rubber composites obtained using rubber waste are used in practice for the manufacture of inexpensive items where strength is not a priority, such as: floor materials, windshield wipers, washers, tapes, molds, cable housings and shoe soles [9].

Currently, the amount of used tires recycled by grinding in the EU, USA, Japan and China is estimated at about 3.6 million tons/year. According to the analysis of the tire recycling market, it can be said that rubber powder is no longer considered a cheap filler, but a valuable component of durable rubber composites, used in large-scale applications by manufacturers of molded and extruded products, gaskets, manufacturers of playgrounds, artificial sports surfaces, or in the automotive industry, etc. [6, 7, 9-13]. It is known in the literature that the properties of rubber powder depend on the method of obtaining them (cryogenic grinding or at ambient temperature), the grain size, crosslinking, filler content and the type of natural or synthetic rubber that the initial products had. The mechanical properties and performances of the polymer composites obtained from rubber powder from waste, depend on the type of polymer matrix used and, therefore, on the nature of the interactions between the matrices, the type and size of the rubber granules and their amount in the composites. For example, the studies carried out by Yehia [8] on compounds based on natural rubber with 0-50 phr HAF and 0-50 phr rubber powder with a particle size of 125-500 μm , showed that by oxidizing the surface of the rubber particles from the powder, there is an improvement in traction and accelerated aging properties. The same conclusions were reached by Zhang *et al.* [14], who modified the

surface of the rubber particles from the powder using plasma treatment. They made composites based on acrylonitrile-butadiene rubber (NBR) with 0-20 phr rubber powder with a rubber particle size of 250 μm , and observed that by using the powder modified by plasma treatment there is an improvement of the interfacial adhesion between the components, which leads to an improvement of the mechanical properties compared to the composites in which the unmodified powder was used.

The aim of this paper is to study the properties of natural rubber reinforced composites with differential rubber 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/Waste Rubber 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) rubber waste – ground rubber functionalized with potassium oleate from the footwear industry; (7) mineral oil; (8) N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD 4010): density – 1.1 g/cm^3 , 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/cm^3 , melting point $93\text{-}100^\circ\text{C}$; (11) diphenyl guanidine (D): curing agent, density – 1.34 g/cm^3 ; (12) PEG – Polyethylene glycol: plasticizer, white pellets.

Preparation of Various Types of Biodegradable Polymer Composite

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

Table 1: Polymer composites based on natural rubber compounded with elastomeric waste functionalized with potassium oleate

Material	UM	N0	NC1	NC2	NC3	NC4
Brabender mixer processing						
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
Elastomeric 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
Roller processing						
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, NC1-NC4 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. from the Brabender mixing diagrams, Figure 1.

According to the diagrams (Figures 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 rotational 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 incorporation 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 value of the torque, which indicates both the homogenization of the mixture and the increase in the temperature of the mixture due to friction at a higher rotational speed (60 rpm) with the mixer closed.

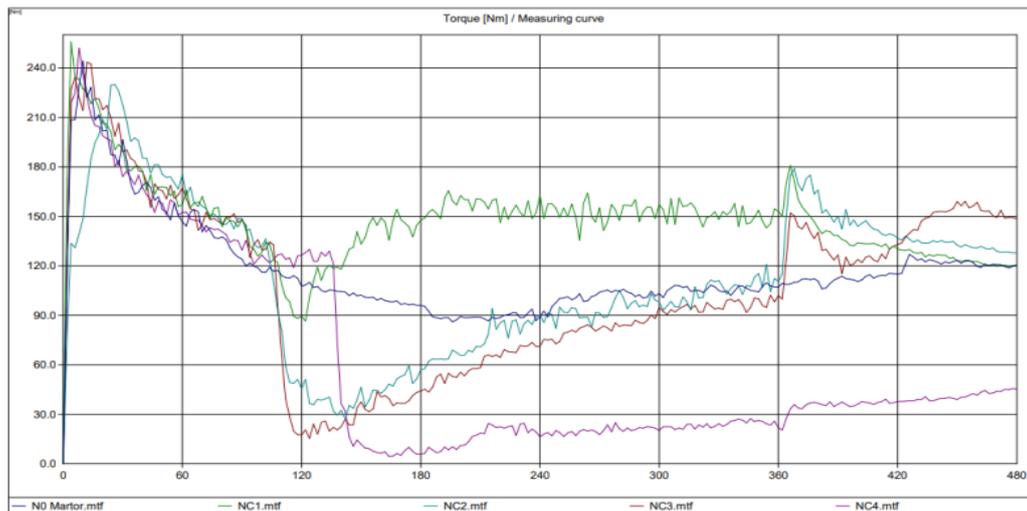


Figure 1. Torque variation with time recorded using the Brabender Plasti-Corder when obtaining NC rubber mixtures

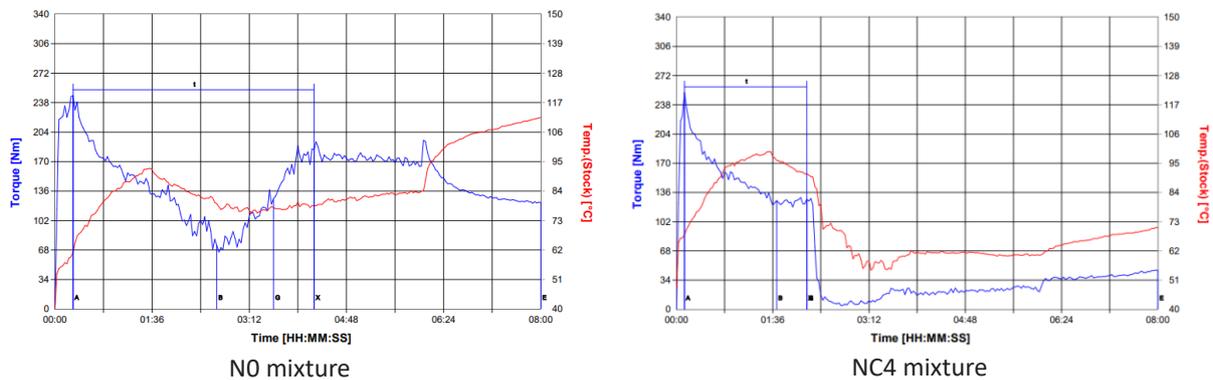


Figure 2. Torque and temperature variation with time recorded using the Brabender Plasti-Corder when obtaining NO and NC4 samples

From the diagrams shown in Figures 1 and 2, it can be seen that the temperature in the mixing chamber increases, depending on the percentage of elastomeric waste introduced into the polymer composite (starting from 78-80°C, it decreases to 69°C – NC3 then increases to 91°C – NC4, the last being the composite with a percentage of 50% elastomeric waste). Also, the mixing forces increase proportionally with the percentage of elastomeric waste in the composite, starting at a temperature of 61°C and reaching a maximum at 30 seconds of mixing of 246 Nm for sample NO and increasing proportionally to 252.1 Nm for sample NC4. The maximum torque

is reached when the natural rubber plasticizes, mixes with the mixing ingredients (plasticizer, filler, antioxidants) and begins to disperse the waste rubber particles. After reaching the maximum torque, it decreases uniformly (171.4-128.2), being constant in the last minute, which indicates the homogenization of the mixture. This decrease is due to the elastic behavior of the rubber waste and its functionalization with potassium oleate, which also acts as a plasticizer. Table 2 shows the processing characteristics presented in the Brabender diagrams, for each processed composite.

Table 2: Characteristics presented in Brabender processing diagrams for NC polymer composites

Characteristics	Sample code				
	NO	NC1	NC2	NC3	NC4
Temperature at peak load, °C	61	64	66	63	68
Temperature at the inflection point, °C	78	80	77	69	91
Maximum temperature, °C	112	109	112	107	91
Energy at the peak load, Nm	246.0	255.9	230.0	243.6	252.1
Maximum energy, Nm	183.5	171.4	169.6	159.1	128.2
Gelation zone energy, kNM	10.3	33.7	33.1	94.7	1.0
Specific energy, kNm/g	0.7	0.8	0.6	0.6	0.3
Gelation rate, Nm/min.	142.5	171.2	22.0	26.3	-52.5

Vulcanizing agents are added to the mixtures made using the Brabender Plastimeter on the roller. The working method on the laboratory electric roller for adding vulcanizing agents to the mixtures is as follows, with the mixture executed on the roller at a temperature of 23-30°C, roller friction 1:2 and 50 rotations/min:

- The composite is plasticized;
- The vulcanization agents are added 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 this case 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 inactive filler (precipitated chalk) with functionalized elastomeric waste, the rheological characteristics of the mixtures are changed as follows:

- the minimum torque (ML) shows a variation of +5 – (-20)%, the maximum torque (MH) shows a decrease of max. 28%, and the torque variation (ΔM) decreases by a maximum of 41% as the amount of waste increases, indicating the decrease in the stiffness of the rubber mixtures in the vulcanized state;

- for all the samples, the reversion phenomenon is observed, indicating a degradation of the mixtures at high temperatures through the breaking of some cross-linking bonds.

- the scorching time (t_{s2}) decreases as the amount of rubber powder increases and the amount of precipitated chalk decreases, and the optimal vulcanization time shows a slight increase by replacing the precipitated chalk with elastomeric waste.

Table 3: Rheological characteristics of NC mixtures

Rheological characteristics at 165°C	Sample codes				
	N0	NC1	NC2	NC3	NC4
ML (dNm)	8	7.6	8.9	10	10.2
MH (dNm)	54.3	54.4	45.2	39	37.4
$\Delta M = MH-ML$ (dNm)	46.3	46.8	36.3	29	27.2
Mf - Reversion (dNm)	47	48.5	43	35	35
t_{s2} (min)	1.2	1.07	1.01	0.99	1.04
t_{50} (min)	1.67	1.74	1.79	1.79	2
t_{90} (min)	2.54	2.75	3.15	3.26	4.06

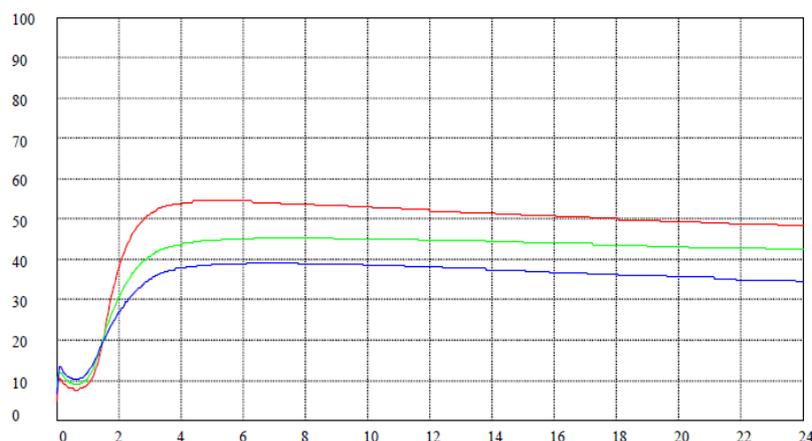


Figure 3. Torque variation expressed in dNm (OY axis) with time expressed in minutes (OX axis) for mixtures based on natural rubber: NC1 (red), NC2 (green) and NC3 (blue)

The vulcanization parameters were established based on the data from the rheograms, presented in Table 4.

Table 4: Vulcanization parameters for making samples in the press for NC mixtures based on natural rubber and elastomeric waste)

Vulcanization parameters	Sample code				
	N0	NC1	NC2	NC3	NC4
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

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.

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 bending 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 done using the FT-IR 4200 JASCO, Herschel series instrument, equipped with ATR having diamond crystal and sapphire head within the spectrometric range $2000\text{--}530\text{ cm}^{-1}$.

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 NC mixtures

Physical-mechanical characteristics	Sample code				
	N0	NC1	NC2	NC3	NC4
Normal state					
Hardness, °Sh A	44	35	32	30	30
Elasticity, %	32	24	22	22	24
100% modulus, N/mm ²	1.0	0.51	0.05	0.046	0.046
300% modulus, N/mm ²	2.0	1.02	0.84	0.77	1.21
500% modulus, N/mm ²	4.52	2.21	1.68	1.97	2.88
Tensile strength, N/mm ²	14.23	10.46	6.2	3.17	5.31
Elongation at break, %	740	800	780	620	660
Residual elongation, %	28	30	26	24	20
Tear strength, N/mm	24.39	19.23	16.9	15	23
Specific weight, g/cm ³	1.2	1.16	1.11	1.08	1.02
Abrasion resistance, mm ³	123.45	320	-	265.36	231.71
Rosflex repeated flexions SR ISO 132/2018	Resist up to 150.000 cycles			90.000 cycles crack appears, resist up to 109.000 cycles	
After accelerated ageing for 168 hours at 70°C					
Hardness, °Sh A	51	41	39	36	35
Elasticity, %	34	38	32	34	24
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	8.3	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 44 °ShA in the control sample to 30 °ShA in the composite based on natural rubber with functionalized rubber 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 inactive filler (precipitated chalk) 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%.

- Abrasion resistance 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 composites NC3 and NC4 with rubber waste content of 30% and 50% respectively, do not fall within this value (crack appears after 90,000 cycles, resist up to 109,000 cycles). The others

have values over 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 on 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 $-\text{CH}_3$ bonds, and the one at 1375.58 cm^{-1} represents the in-plane deformation vibration, namely the shear (δ^{s}) of $-\text{CH}_3$ bonds, the band at 841.97 cm^{-1} represents the out-of-plane deformation vibration (γ) of $-\text{CH}-\text{CH}$ bonds 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 $\text{C}=\text{C}$ bonds [15].

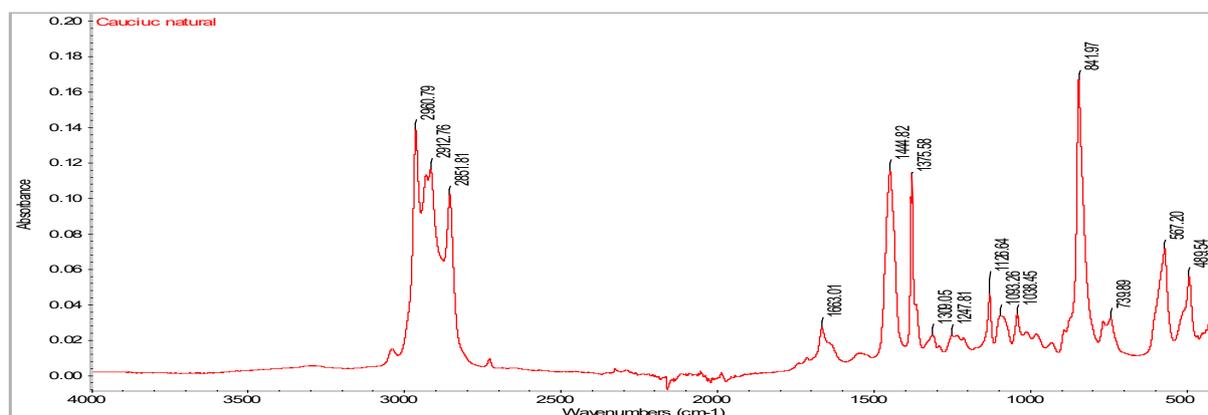


Figure 4. FTIR spectrum of unvulcanized natural rubber

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 on 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 group 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 styrene 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^- bonds. The band at 1463.59 cm^{-1} comes from the CH_2 bond vibration [16]. The band at 719.08 cm^{-1} is due to $-(\text{CH}_2)_n-$ bond deformation [17].

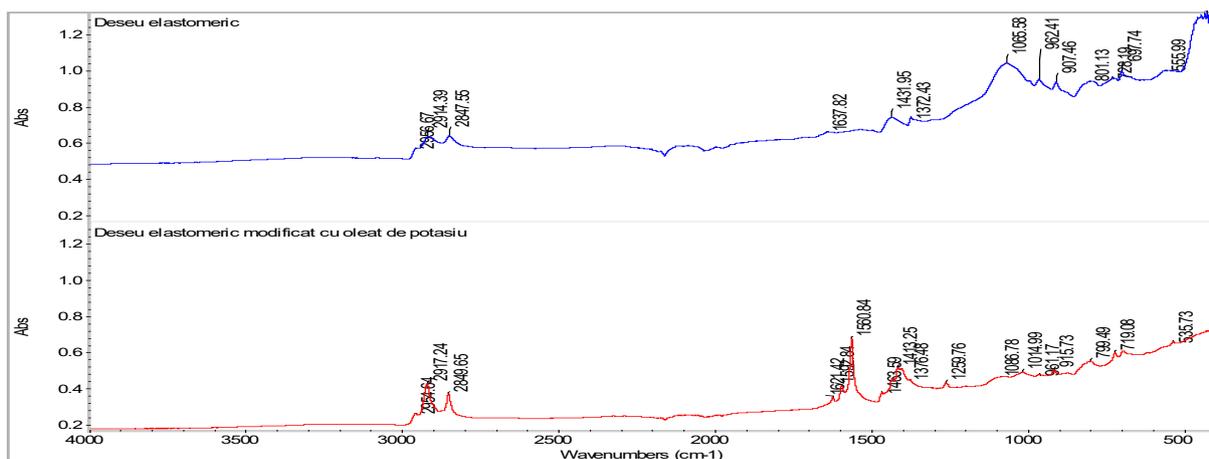


Figure 5. FTIR spectrum of unmodified elastomeric waste and modified with potassium oleate

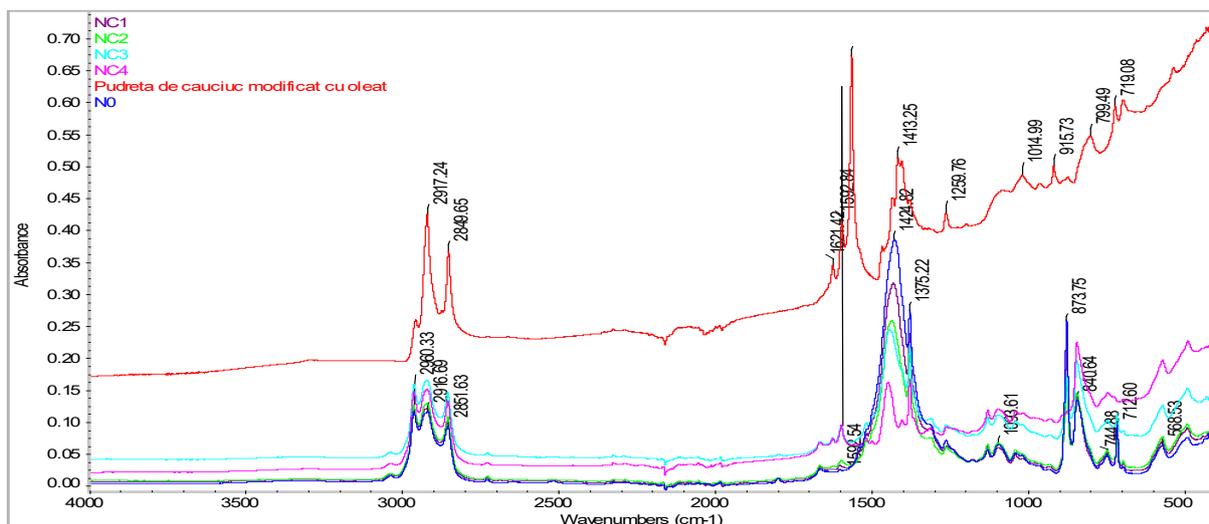


Figure 6. FTIR spectra of mixtures based on natural rubber reinforced with varying percentages of elastomeric waste modified with oleate

In the case of the NO 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 NO contains the highest amount of calcium carbonate, following that in the mixtures NC1-NC3 the amount of carbonate is gradually replaced with the elastomeric waste modified with oleate. Instead, in the case of the NC4 mixture, the calcium carbonate was completely replaced with rubber waste, which led to the disappearance of the bands associated with CaCO_3 . The characteristic bands of the rubber waste modified with oleate, and especially the band at $\sim 1592 \text{ cm}^{-1}$ (due to the vibration of the C=C bonds in the aromatic styrene ring) and 1621 cm^{-1} (the stretching vibration of the C=O bonds in the oleate) can be visualized in all processed mixtures NC1-NC4, their intensity being the greater the greater the amount of rubber waste modified with oleate [18]. 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 bonds (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 antibiotic bottle stoppers for zootechnical use was modified by replacing the inactive filler (precipitated calcium carbonate) with cryogenically ground post-consumer rubber waste with a particle size of 500nm and functionalized with potassium oleate. These polymer composites were processed on a Brabender mixer and laboratory roller using elastomeric waste with different proportions (10, 20, 30 and 50%). The polymer composite samples with percentages of 10 and 20% post-consumer elastomeric waste presented the best physical-mechanical performances 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 – NC0, and the hardness decreased by 9-14 units. The tensile strength of the composition decreased to about half that of NC0. Although the values are lower, the NC1-NC3 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.

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