POLYMER COMPOSITE BASED ON NBR RUBBER COMPOUNDED WITH RUBBER WASTE FUNCTIONALIZED WITH POTASSIUM OLEATE

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Received: 21.01.2022 Accepted: 18.03.2022 https://doi.org/10.24264/lfj.22.1.5

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ABSTRACT. Waste is a material that occurs as a result of a biological or technological process that can no longer be used as such. Recycling and reusing waste make it possible to contribute to environmental protection and, of course, to the protection of human health by eliminating toxins during waste incineration. The purpose of this paper is to process and characterize polymer composites based on NBR rubber (butadiene-co-acrylonitrile rubber) and rubber waste functionalized with potassium oleate in terms of rheological characteristics (to determine the optimal vulcanization time), Brabender diagrams and physico-mechanical properties in normal state and after accelerated ageing at 70°C, for 168 h (using elastomer-specific equipment). Functionalized rubber waste (with potassium oleate up to 20% at 60°C) is introduced into the mixture in proportions of 10; 20; 30; 50%. The polymeric composites based on butadiene-co-acrylonitrile elastomer and rubber waste (ground with a cryogenic mill at 10,000 rpm, at the size of 0.35 mm) were compounded on a mixer with a capacity of 350 cm3 according to the working recipes. The mixtures were supplemented with vulcanization activators and accelerators on an electric roller, resulting in formulations in the form of 4 mm thick sheets, which are then subjected to the relevant characterizations according to the standards in force for the footwear industry.

KEY WORDS: NBR rubber, rubber waste, compounding, vulcanization, polymer composite

COMPOZIT POLIMERIC PE BAZĂ DE CAUCIUC NBR COMPOUNDAT CU DEȘEU DE CAUCIUC FUNCȚIONALIZAT CU OLEAT DE POTASIU

REZUMAT. Deșeul este un material ce apare în urma unui proces biologic sau tehnologic ce nu mai poate fi utilizat ca atare. Prin reciclarea și reutilizarea acestora se poate contribui la protecția mediului și, bineînțeles, la protejarea sănătății umane prin eliminarea toxinelor din timpul incinerării acestora. Scopul acestei lucrări este procesarea și caracterizarea din punct de vedere reologic (pentru determinarea timpului de vulcanizare optim), al diagramelor Brabender și fizico-mecanic în stare normală și la îmbătrânire accelerată la 70°C, timp de 168 h (pe aparatură specifică elastomerilor), a compozitelor polimerice pe bază de cauciuc NBR (cauciuc butadien-co-acrilonitril) și deșeu de cauciuc funcționalizat cu oleat de potasiu. Deșeul de cauciuc funcționalizat (cu oleat de potasiu până la 20% la temperatura de 60°C) este introdus în amestec în proporții de 10; 20; 30; 50%. Compoundarea compozitelor polimerice pe bază de elastomer butadien-co-acrilonitril și deșeu de cauciuc (măcinat cu o moară criogenică la 10.000 rot/min, la dimensiunea de 0,35 mm) s-a realizat pe un malaxor de capacitate de 350 cm3 conform rețetelor de lucru. Amestecurile au fost completate cu acceleratori și activatori de vulcanizare pe un valț electric, obținându-se recepturi sub formă de foi de 4 mm grosime. Apoi acestea sunt supuse caracterizărilor aferente conform standardelor în vigoare pentru industria de încălțăminte.

CUVINTE CHEIE: cauciuc NBR, deșeu cauciuc, compoundare, vulcanizat, compozit polimeric

COMPOSITE POLYMÈRE À BASE DE CAOUTCHOUC NBR MÉLANGÉ AVEC DES DÉCHETS DE CAOUTCHOUC FONCTIONNALISÉ AVEC DE L'OLÉATE DE POTASSIUM

RÉSUMÉ. Un déchet est un matériau résultant d'un processus biologique ou technologique qui ne peut plus être utilisé en tant que tel. En le recyclant et en le réutilisant, il est possible de contribuer à la protection de l'environnement et bien sûr à la protection de la santé humaine en éliminant les toxines lors de l'incinération des déchets. Le but de cet article est de traiter et de caractériser un composite polymère à base de caoutchouc NBR (caoutchouc butadiène-co-acrylonitrile) et de déchets de caoutchouc fonctionnalisés avec de l'oléate de potassium en termes de caractéristiques rhéologiques (pour déterminer le temps de vulcanisation optimal), de diagrammes de Brabender et de propriétés physico-mécaniques à l'état normal et après vieillissement accéléré à 70°C, pendant 168 h (sur équipement spécifique pour l'élastomère). Des déchets de caoutchouc fonctionnalisés (avec de l'oléate de potassium jusqu'à 20% à 60°C) sont introduits dans le mélange dans des proportions de 10 ; 20 ; 30 ; 50 %. Le compoundage des composites polymériques à base d'élastomère butadiène-co-acrylonitrile et de déchets de caoutchouc (broyé au broyeur cryogénique à 10 000 rpm, à la taille de 0,35 mm) a été réalisé sur un malaxeur d'une capacité de 350 cm3 selon les recettes de travail. Les mélanges ont été complétés avec les activateurs et accélérateurs de vulcanisation sur rouleau électrique, obtenant des feuilles de 4 mm d'épaisseur, qui sont ensuite soumis aux caractérisations pertinentes selon les normes en vigueur pour l'industrie de la chaussure.

MOTS-CLÉS : caoutchouc NBR, déchets de caoutchouc, compoundage, vulcanisé, composite polymère

INTRODUCTION

In December 2015, the European Commission adopted a "circular economy" package to help businesses and European consumers make the transition to a sustainable resource economy. The Romanian government has also issued a series of government decisions related to waste management. Government Decision no. 856/2002 - "Introduction of waste management records and the European Waste Catalogue" is the most important in this context [1-3]. Recycling and reusing waste make it possible to contribute to the environmental protection and, of course, to the protection of human health by eliminating toxins during waste incineration, and implicitly to a turnover increase for economic agents [4, 5]. Reusing and recycling polymeric waste are real options to reduce the amount of waste and thus their impact on the environment, as required by Directive 2008/98/EC [6]. A possible alternative is the transformation of long-lasting polymer waste into biodegradable polymer composites, thus considerably reducing their life span. The reprocessing of polymer waste involves decontamination, grinding, densification, as well as the storage of flakes, fibers or waste granules and their reuse [7].

The disposal of polymeric waste generates serious economic and environmental concerns, and waste management is becoming an important social issue. Given the environmental awareness in society, the most viable option for the treatment of polymer waste remains recycling [1, 6]. Thermal decomposition of polymer waste in an incinerator causes environmental problems, through the release of carbonic acids, sulfur oxides, carbon oxides, etc.

Recently, polymer composites based on elastomers have been intensively studied especially for the domestic, gardening, automotive and aeronautical fields, but also for the footwear industry [7-9]. In the structure of composite materials there are also elastomers that allow vulcanization to occur. Once the vulcanization process takes place, the elastomers keep their shape, but this process also influences their characteristics. NBR elastomer (butadiene-co-acrylonitrile rubber is an elastic elastomer) is used due to properties such as high abrasion resistance and high temperature stability, from -40 to +108°C (-40 to +226°F), making it an ideal material for aeronautical applications [10-14]. It also has a very good resistance to mineral oils, petroleum products, aging resistance and low gas permeability, being used to produce castings, footwear, adhesives, sponges, expanded foam, etc. and conveyor belts for tires (for trucks and cars) in the automotive industry. By adding other substances such as vulcanization activators and accelerators – sulfur, tetramethyl thiuram, etc. – the physical and mechanical properties of the resulting products are improved [15, 16].

Polymer composites based on NBR elastomer (butadiene-co-acrylonitrile) and rubber waste (ground to a size of 0.35 mm with a cryogenic mill at a speed of 10,000 rpm) were obtained on a Brabender Plasti-Corder mixer with a capacity of 350 cm^3, according to working recipes. The mixtures were completed with the same vulcanizing agents and activators (sulfur and tetramethyl thiuram – Th) on an electric roller at a temperature of 25-30°C, friction of the rollers 1:2, with 50 rpm, obtaining recipes in the form of 4 mm thick sheets. Then the rheological test was performed on a Monsanto Rheometer to determine the optimal vulcanization times for the electric press, in molds specific to elastomeric composites. Plates are obtained from which specimens for physical-mechanical characterization are stamped according to the standards in force. After conditioning for 24 hours at room temperature, the specimens are subjected to physical-mechanical determinations: normal state at room temperature and after accelerated aging at 70°C for 168 hours [17-19].

EXPERIMENTAL

Materials

Materials used were: (1) butadiene-co-acrylonitrile rubber (NBR 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) zinc oxide microparticles (ZnO): white powder, precipitate 93-95%, density – 5.5 g/cm, specific surface – 45-55 m^2/g; (4) silicon dioxide (SiO_2): density – 1.9-4.29 g/cm^3, molar mass – 60.1

g/mol; (5) Kaolin: white powder, molecular weight 100.09; (6) protein waste: ground leather functionalized with potassium oleate; (7) rubber waste - ground rubber from the footwear industry; (8) mineral oil; (9) 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); (10) Sulphur (S): vulcanization agent, fine yellow powder, insoluble in water, melting point: 115°C, faint odor; (11) tetramethylthiuram disulfide (Th): curing agent, density – 1.40g/cm^3, melting point <146°C, an ultrafast curing accelerator.

Methods

Preparation of Polymer Composite Based on NBR Rubber and Functionalized Rubber Waste

Vulcanized polymer composites with functionalized rubber waste were made by compounding technology on a Brabender Plasti-Corder mixer with the possibility of adjusting the temperature and mixing speed, with a capacity of 350 cm^3, in strict compliance with the order of introduction of ingredients, Table 1. The mixtures made in Brabender Plasti-Corder were completed with vulcanizing agents on a laboratory roller. The processed recipes are rheologically tested with the help of a Monsanto 100S Rheometer to determine the optimal vulcanization times in the electric press at controlled pressure and temperature. In the first phase, plates are processed from which specimens for physical-mechanical and physical-chemical characterization are stamped at the optimal technological processing parameters established after the rheological testing. After conditioning for 24 hours at room temperature, the plates are subjected to physical-mechanical determinations in normal state (at room temperature) and after accelerated aging at 70°C for 168 hours.

Table 1: Formulation of polymer composite based on butadiene-co-acrylonitrile rubber (NBR) compounded with butadiene-co-acrylonitrile (NBR) rubber waste functionalized with potassium oleate

Symbol	MU [g]	BO (control)	$B0_1$	BCO_1	BCO_2	BCO_3	BCO_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	37	37	37	37	37
Functionalized rubber waste (NBR) with potassium oleate	g	-	-	15	30	45	75
Non-functionalized rubber waste – NBR, (10%)	g	-	15	-	-	-	-
Mineral oil	g	14.9	14.9	14.9	14.9	14.9	14.9
IPPD 4010	g	4.5	4.5	4.5	4.5	4.5	4.5
	Roller mixing						
Sulfur (S)	g	2.3	2.3	2.3	2.3	2.3	2.3
Tetramethylthiuram disulfide (Th)	g	1	1	1	1	1	1

BO – composite without waste;
$B0_1$ – composite with 10% non-functionalized waste

For the good processing of polymeric composites based on butadiene-co-acrylonitrile rubber and functionalized rubber waste in a proportion of 10, 20, 30, 50%, the initial working temperature was set at 40°C. For each mixture, the variation of torque and temperature over time was recorded, Table 2.

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

Order of introducing ingredients	Time (minutes)	Rate	Temperature, °C
Butadiene-co-acrylonitrile rubber (plasticizing)	1'30"	40 rpm	40°C
Ingredients (without vulcanization agent)	4'30"	20 rpm	40°C
Homogenisation	3'	80-100 rpm	80-100°C

Before being introduced into the polymer mixture the NBR rubber waste was ground to a size of 0.35 mm using a cryogenic mill at a rate of 10,000 rpm. After the grinding process, the resulting waste was functionalized with potassium oleate in a proportion of 20%, at a temperature of 60°C.

After the mixture is processed using the Brabender mixer, it is then processed on an electric roller, adding vulcanizing agents, sulfur and TH, at temperatures of 25-30°C, friction of the rollers 1:2, at 50 rpm. The working method is as follows:

- the raw materials, sulfur (S) and tetramethylthiuram (Th) are dosed;
- the composite is plasticized using the Brabender Plasti-Corder mixer;
- vulcanizing agents (S and Th) are introduced and mixed for 5-7 minutes;
- the mixture is homogenized on a roller for 1-2 minutes and removed in the form of a sheet about 4 mm thick. The mixture is then left at ambient temperature for 24 hours for characterization.

RESULTS AND DISCUSSIONS

Characterization of Brabender Processing Diagrams

According to the recorded Brabender diagrams, Figure 1, it can be observed that the samples obtained by the mixing technique on the Brabender Plasti-Corder were made using the working method presented in Table 2. In the first portion, A-B, which lasts 1’30’’ at 40 rpm, the NBR elastomer (butadiene-co-acrylonitrile rubber) is introduced into the mixer, so that the torque increases. Therefore, the first loading peak, A, corresponds to the introduction of the NBR elastomer. As the torque increases, so does the temperature due to the friction of the screws of the Brabender Plasti-Corder mixer. Due to the homogenization and plasticization of the NBR elastomer, as well as due to the increase in temperature due to shearing, we can see that the torque begins to decrease near A towards B. Then the other ingredients are introduced and the rotation speed is reduced to 20 rpm for 4’30’’. The mixer is kept open until all the ingredients are incorporated according to the recipe, Table 1.

As a result of the incorporation of the ingredients, but also of the compaction and reinforcement of the elastomer, the torque between point B and point X begins to increase. After incorporating the fillers and other ingredients into the mixture, the second loading peak, X, is observed, thus appearing a maximum torque. When the torque begins to decrease, it indicates that homogenization of the compound is taking place for 3’ at 80-100 rpm, during which time the mixer remains closed. As a result, a maximum torque value is obtained due to the compaction and homogenization of the elastomer mixture. Then there is a decrease in torque, which indicates the homogenization of the mixture, as well as an increase in its temperature due to friction at a higher rotational speed, with the Brabender mixer kept closed.

Table 3: Characteristics presented in Brabender processing diagrams for composites based on butadiene-co-acrylonitrile rubber (NBR) compounded with rubber waste

Characteristics	BO (control)	$B0_1$	BCO_1	BCO_2	BCO_3	BCO_4
Temperature at loading peak, °C	70	88	50	68	64	85
Temperature at inflection point, °C	94	95	96	93	86	69
Maximum temperature, °C	106	107	107	104	92	79
Energy at loading peak, kNm	138.8	118.6	159.8	14.04	5.0	130.6
Maximum energy, kNm	138.7	107.2	124.0	119.1	215.6	1.9
Gelation area energy, kNm	30.2	39.2	38.4	31.4	2.7	25.9
Specific energy, kNm/g	1.3	1.0	1.2	1.1	0.9	0.6
Gelation rate, Nm/min	-28.0	-20.5	-18.8	-21.7	-85.4	188.4

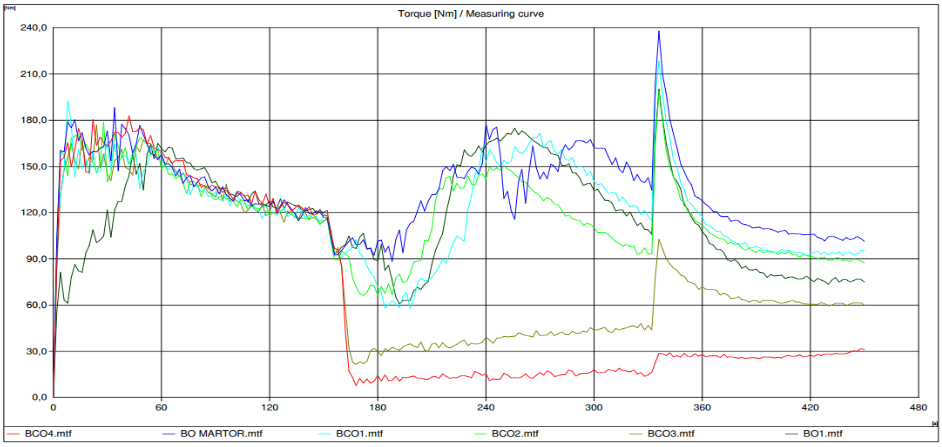

Figure 1. Torque variation over time, recorded with Brabender Plasti-Corder when obtaining polymer composites based on NBR rubber compounded with rubber waste functionalized with potassium oleate

Rheological Characterization of Polymer Composite Based on NBR Rubber

The rheological characteristics of the polymer composites based on NBR rubber compounded with NBR rubber waste functionalized with potassium oleate are obtained using a Monsanto Rheometer, at 165°C, for 24', Table 4, establishing the optimal vulcanization times in the electrical press to obtain specimens that will then be subjected to physical-mechanical, chemical and morpho-structural testing.

The analysis is performed as follows: a sample of maximum 8-10 g is sealed in a cavity of the device, at a controlled and constant temperature, 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 the vulcanization time.

Table 4: Rheological characteristics of polymeric composite based on NBR rubber compounded with rubber waste

Rheological characteristics at 165°C	BO (control)	BO_1	BCO_1	BCO_2	BCO_3	BCO_4
ML (dNm)	1.3	15.7	17.1	17	11.9	12.9
MH (dNm)	46.9	37.4	47.8	44.5	36.1	38.2
ΔM = MH-ML (dNm)	29.6	21.7	30.7	27.5	24.2	25.3
t_{s2} (min)	2.91	2.64	2.78	2.48	2.03	1.68
t_{50} (min)	6.38	3.6	3.87	3.39	2.86	2.51
t_{90} (min)	18.61	8.68	5.45	4.94	8.78	11.21

From the presented data, Figure 2, it is observed that by replacing the quantity of precipitated chalk as inactive filler with elastomeric waste, the rheological characteristics of the mixtures are modified as follows:

- the minimum torque (ML) shows a variation of +5-(-20)%, the maximum torque (MH) shows a decrease of max. 28%, and the variation of the torque (ΔM) decreases by max. 41% as the amount of NBR rubber waste increases, to the detriment of the amount of mineral filler, indicating the decrease of the rigidity of the rubber mixtures in vulcanized state;
- for all samples the reversal phenomenon is observed, which is specific to the mixtures vulcanized with sulfur and vulcanization accelerators, indicating a degradation of the mixtures at high temperatures by breaking some crosslinking bonds;

- the scorching time (t_{s2}) decreases as the amount of rubber waste increases and the amount of mineral filler decreases, and the optimal vulcanization time increases by replacing it with elastomeric waste.

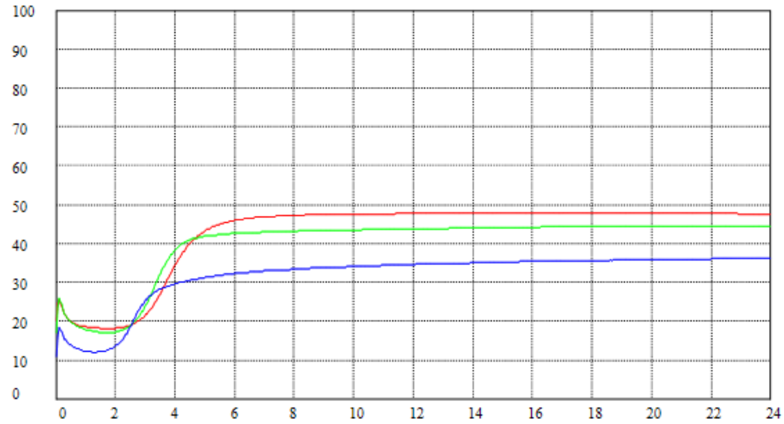

Figure 2. Torque variation expressed in dNm (OY axis) over time expressed in minutes (OX axis) for samples with rubber waste functionalized with potassium oleate: BCO_1 (red) – 10% waste, BCO_2 (green) – 20% waste, BCO_3 (blue) – 30% waste

Physical-Mechanical Characterisation of Polymer Composites Based on NBR Rubber

Physical-mechanical characterization of samples in normal state and after accelerated aging at 70°C and 168 hours was performed according to the standards in force by the following methods: hardness, elasticity, tensile strength. Table 5 shows the values of the physical-mechanical tests performed according to the standards in force.

Table 5: Physical-mechanical characterisation of polymer composites based on NBR rubber compounded with rubber waste

Sample	BO (control)	BO_1	BCO_1	BCO_2	BCO_3	BCO_4
Physical-mechanical characteristics: Normal State						
Hardness, °Sh A	61	47	57	55	50	47
Elasticity, %	18	20	18	18	16	16
Modulus 100%, N/mm^2	1.16	0.82	1.18	1.19	0.96	0.93
Tensile strength, N/mm^2	11.3	3.29	9.15	6.77	3.8	2.6
Elongation at break, %	180	480	760	700	560	380
Residual elongation, %	80	16	28	28	24	20
Tear strength, N/mm	42.9	16.05	33.25	30.6	17.8	14.56
Specific weight, g/cm^3	124	1.08	1.19	1.19	1.15	1.07
Resistance to abrasion, mm^3	218.39	80.62	181.12	138.17	112.08	79.87
Physical-mechanical characterization: Accelerated ageing at 70°C and 168 h						
Hardness, °Sh A	66	51	61	57	54	48
Elasticity, %	24	24	22	22	20	16
Modulus 100, N/mm^2	1.6	0.97	1.44	1.41	1.22	0.92
Tensile strength, N/mm^2	14.47	2.86	10.14	6.86	32	2.02
Elongation at break, %	980	400	740	580	400	320
Residual elongation, %	60	16	32	20	20	12
Tear strength, N/mm	53.7	16.4	44.1	34.950	18.5	1.22

From the presented data it is observed that by replacing the amount of silicon dioxide with NBR rubber waste, the physical-mechanical characteristics of the mixtures are modified as follows:

- hardness decreases by max. 6°ShA in samples containing less silicon dioxide and more rubber powder;
- the elasticity decreases proportionally with the increase of the waste percentage;
- the values of tensile and tear strength gradually decrease as the active filler of silicon dioxide is replaced by elastomeric waste, but has good values, of 3.8 N/mm^2, respectively 17.8 N/mm for sample BCO_3;
- elongation at break has good values, over 700%, in the BCO_3 sample (composite with 30% elastomeric waste);
- the abrasion resistance decreases proportionally with the increase of the waste quantity and presents a value that falls within the standard (minimum 200 mm^3);
- the density of the mixtures decreases as the amount of powder increases, indicating, in conjunction with the other properties, a better compatibility between NBR rubber and the waste of the same type of elastomer;
- after accelerated aging for 168 h at 70°C of the samples, the following are observed: increases in hardness of +2-6°ShA and smaller variations of the tensile and tear strength (of max. 21%, respectively of max. 10%).

CONCLUSION

This paper presents the technology for making polymer composites based on NBR rubber compounded with rubber waste, but also the characterization of Brabender Plasti-Corder mixer diagrams, from a rheological and physical-mechanical point of view according to the standards in force using equipment specific for elastomers. The rubber waste was ground with a cryogenic mill at a size of 0.35 mm at a rate of 10,000 rpm and then functionalized with potassium oleate. Functionalization was performed at temperatures of 60°C.

Following the rheological characterizations of the polymeric composites based on NBR rubber compounded with NBR rubber waste functionalized with potassium oleate, the optimal vulcanization times in the electrical press were established for obtaining specimens. According to the recorded Brabender diagrams, the samples are obtained by the mixing technique, complying with the established working mode. Following the physical-mechanical characterization of samples in normal state and after accelerated aging at 70°C, for 168 h, it is observed that the mixtures were carried out according to the working recipes at the optimal parameters and working times.

Polymer composites based on butadiene-co-acrylonitrile (NBR) elastomer and rubber waste functionalized with potassium oleate have optimal values according to the standards and have potential applications in the domestic field, in consumer goods for general use, but also in automotive and aeronautics.

Acknowledgements

This research was financed by ANCSI through 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)”.

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