BIODEGRADABLE POLYMER COMPOSITE BASED ON NBR RUBBER AND PROTEIN WASTE

MIHAELA NIȚUICĂ (VÎLSAN)*, MARIA SÖNMEZ, MIHAI GEORGESCU, MARIA DANIELA STELESCU, LAURENȚIA ALEXANDRESCU, DANA GURĂU

INCDTP - Division Leather and Footwear Research Institute, 93 Ion Minulescu St., sector 3, Bucharest,

mihaela.nituica@icpi.ro, mihaelavilsan@yahoo.com

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ABSTRACT. The aim of this work is to characterize a biodegradable polymer composite based on butadiene-co-acrylonitrile rubber (NBR) and protein waste (ground leather). The biodegradable polymer composite was obtained by the mixing technique on a Brabender Plasti-Corder mixer and then on an electric roller (without heating), between its rollers, with sulfur vulcanization activators and Th accelerator, relative to 100 parts plasticized elastomer, obtaining 3-4 mm thick sheets, with strict observance of the technological recipe, but also of the established mode of operation. The obtained mixtures are then subjected to rheological characterization to determine the vulcanization time using the Monsanto rheometer (to determine the optimum temperature and vulcanization times in the laboratory electric press in specific molds for obtaining specimens to be subjected to subsequent characterization). Biodegradable polymeric composites based on butadiene-co-acrylonitrile rubber (NBR) and protein waste (leather waste from the footwear and leather goods industry) were made at optimal working parameters, and the characterization was performed on equipment specific to elastomers and according to standards in force for the footwear and consumer goods industry such as: plates for general purpose footwear soles as well as for water and mud environments, but also for the food industry, car mats, gaskets and components used under normal working conditions, technical plates, insoles, etc.

KEY WORDS: NBR rubber, protein waste, biodegradable, vulcanized, composite

COMPOZIT POIMERIC BIODEGRADABIL PE BAZĂ DE CAUCIUC NBR ȘI DEȘEU PROTEIC

REZUMAT. Scopul acestei lucrări este de a caracteriza un compozit polimer biodegradabil pe bază de cauciuc butadien-co-acrilonitril (NBR) și deșeuri proteice (piele măcinată). Compozitul polimeric biodegradabil a fost obținut prin tehnica amestecării pe un amestecător Brabender Plasti-Corder și apoi s-a completat pe un valț electric (fără încălzire), între rolele acestuia, cu activatori de vulcanizare sulf și accelerator Th, raportate la 100 părți elastomer plastifiat, obținându-se recepturi sub formă de foi de 3-4 mm grosime, cu respectarea strictă a rețetei tehnologice, dar și a modului de operare stabilit. Apoi amestecurile obținute sunt supuse caracterizării reologice pentru determinarea timpului de vulcanizare cu ajutorul reometrului Monsanto (pentru stabilirea temperaturii și timpilor de vulcanizare optimi în presa electrică de laborator în matrițe specifice pentru obținerea de epruvete ce vor fi supuse caracterizării ulterioare). Compozitele polimerice biodegradabile pe bază de cauciuc butadien-co-acrilonitric (NBR) si deșeu proteic (deșeu de piele provenit din industria de încălțăminte și marochinărie) au fost efectuate la parametrii de lucru optimi, iar caracterizarea s-a efectuat pe aparatura specifică elastomerilor și conform standardelor în vigoare pentru industria de încălțăminte și a bunurilor de larg consum precum: plăci pentru tălpi pentru uz general, apă și noroi, dar și pentru cele utilizate în industria alimentară, covoare auto, garnituri și repere utilizate în condiții normale de lucru, plăci tehnice, branțuri, etc.

CUVINTE CHEIE: cauciuc NBR, deșeuri proteice, biodegradabil, vulcanizat, compozit

COMPOSITE POLYMÈRE BIODÉGRADABLE À BASE DE CAOUTCHOUC NBR ET DE DÉCHETS PROTÉIQUES

RÉSUMÉ. Le but de ce travail est de caractériser un composite polymère biodégradable à base de caoutchouc butadiène-co-acrylonitrile (NBR) et de déchets protéiques (cuir broyé). Le composite polymère biodégradable a été obtenu par la technique de mélange sur un mélangeur Brabender Plasti-Corder puis sur un rouleau électrique (sans chauffage), entre ses rouleaux, avec des activateurs de vulcanisation au soufre et un accélérateur Th, pour 100 parties d'élastomère plastifié, obtenant de feuilles de 3 à 4 mm d'épaisseur, dans le strict respect de la recette technologique, mais aussi du mode de fonctionnement établi. Les mélanges obtenus sont ensuite soumis à une caractérisation rhéologique pour déterminer le temps de vulcanisation à l'aide du rhéomètre Monsanto (pour déterminer la température optimale et les temps de vulcanisation dans la presse électrique de laboratoire dans des moules spécifiques pour l'obtention d'échantillons à soumettre à une caractérisation ultérieure). Des composites polymères biodégradables à base de caoutchouc butadiène-co-acrylonitrile (NBR) et de déchets protéiques (déchets de cuir issus de l'industrie de la chaussure et de la maroquinerie) ont été réalisés à des paramètres de travail optimaux, et la caractérisation a été réalisée sur des équipements spécifiques aux élastomères et selon les normes en force pour l'industrie de la chaussure et des biens de consommation tels que : semelles à usage général, eau et boue, mais aussi pour celles utilisées dans l'industrie alimentaire, tapis de voiture, joints et pièces utilisés dans des conditions normales de travail, plaques techniques, semelles, etc.

MOTS CLÉS : caoutchouc NBR, déchets protéiques, biodégradable, vulcanisé, composite

INTRODUCTION

Waste designates a material emerging as a result of a biological or technological process that can no longer be used as such. The Romanian government has issued a series of government decisions regarding waste management, but the most important is G.D. no. 856/2002, which refers to "Introduction of waste management records and the European Waste Catalog". The European Commission adopted in December 2015 a package of measures on the circular economy to help European businesses and consumers make the transition to an economy

* Correspondence to: Mihaela NIȚUICĂ, INCDTP - Division Leather and Footwear Research Institute, 93 Ion Minulescu St., sector 3, Bucharest, mihaela.nituica@icpi.ro, mihaelavilsan@yahoo.com

in which resources are used sustainably [1, 2]. By using new and advanced technologies, but also by reusing and recycling waste, we can contribute to both environmental protection, protection of human health by eliminating toxins released during their incineration and increasing the turnover of economic agents globally [3, 4].

Recently, in the competition of polymer composites, new improvements appear in the synthesis of elastomers, in their processing in the presence of new materials, which when used can restore predetermined properties [5, 6]. Polymer composites based on elastomers have been intensively studied lately, especially in fields such as the automotive, electrical, household, gardening and plastic packaging of any type or shape. The structure of composite materials includes: elastomers, activators, anti-degradants, etc. [7-9]. After the vulcanization process elastomers keep their solid shape, but vulcanization influences the physical-mechanical characteristics such as elasticity, elongation at break, abrasion resistance, etc. [10, 11]. Thus, butadiene-co-acrylonitrile rubber (NBR)-based vulcanized elastomers have very good resistance to mineral oils, petroleum products, aging resistance, abrasion resistance and low gas permeability. The addition of vulcanization accelerators (Vulcacite Th - tetramethylthiuram disulfide) improves the physical-mechanical properties, and the antioxidants (IPPD - N-isopropyl-N'-phenyl-p-phenylenediamine) are introduced into the rubber mixture in order to prevent or reduce effects of time degradation of vulcanized elastomers (aging) under the action of various factors such as: oxygen, ozone, copper, manganese, iron, light, high temperature, repeated mechanical stress [12].

Biodegradable polymeric composites based on butadiene-co-acrylonitrile rubber (NBR) and protein waste (leather waste from the footwear and leather goods industry) were processed by mixing technique in a Brabender mixer, then on an electric roller provided with water cooling, then rheologically tested to determine the optimal vulcanization times for pressing in the electric press (in molds specific to elastomeric polymer composites) at controlled times, temperatures and pressures, to obtain products with characteristics necessary for use in the footwear and consumer goods industry such as: plates for general purpose footwear soles as well as for water and mud environments, but also for the food industry, car mats, gaskets and components used under normal working conditions, technical plates, insoles, etc. [13-15].

EXPERIMENTAL

Materials

Materials used to obtain the biodegradable composite based on butadiene-co-acrylonitrile and protein waste 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) protein waste - ground leather from the footwear and leather goods 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-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 Biodegradable Composite based on NBR Rubber and Protein Waste

Biodegradable polymer composites are made by blending on a Brabender mixer. After dosing each component according to the recipe, Table 1, by the mixing technique on a Brabender Plasti-Corder mixer with a capacity of 350 cm^3, establishing the initial working temperature of 36°C, the butadiene-co-acrylonitrile (NBR) rubber is introduced for plasticization for 1'30'', at 40 rpm, then the rest of the ingredients (without vulcanizing agents) are added: stearin plasticizer, active filler - ZnO microparticle, kaolin (mineral filler), ground waste, in proportion of 10, 20, 30 and 50% and functionalized with potassium oleate, mineral oil, IPPD antioxidant, strictly observing the order of introduction of ingredients, for 4’, at 20 rpm, continuing to mix until it is homogenized for 2’, at temperatures between 60-100°C, 80-100 rpm.

Before being added to the formulation, the leather waste was ground to a size of 0.35 mm using a cryogenic mill at a speed of 12000-14000 rpm and functionalized with a proportion of 20% potassium oleate at the temperature of 60°C. Then between the rollers of an electric roller without heating, the mixture is completed with sulfur vulcanization activators and Th accelerator, relative to 100 parts of plasticized elastomer, obtaining 3-4 mm thick sheets. Afterwards, the biodegradable polymeric composites are rheologically tested on a Monsanto Rheometer at 165°C for 24’ to determine the optimal vulcanization times by pressing in the electric press, from which 150x150x2 mm specimens will be obtained by pressing in molds specific to elastomeric polymer composites, by the method of compression between its plates, for the physical-mechanical, chemical and morpho-structural tests. The optimal parameters for obtaining test specimens by pressing in the electric press are: pressing temperature - 165°C; pressing time - 5 minutes; cooling time - 10 minutes (water cooling); pressure - 300 kN. The test pieces obtained are left for 24 hours at ambient temperature, then subjected to the corresponding characterizations according to the standards in force: normal state and accelerated aging at 70°C and 168 hours.

Table 1: Formulation of biodegradable polymer composite based on butadiene-co-acrylonitrile rubber (NBR) compounded with protein waste (ground leather)

Symbol	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
Functionalized leather waste 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	1.5	0.9	0.9

RESULTS AND DISCUSSIONS

Characterization of Brabender Processing Diagrams

According to the registered Brabender diagrams, Figure 1, it can be observed that for the mixtures obtained by the mixing technique on the Brabender Plasti-Corder, the working method presented above is observed (when preparing the polymer composites). Thus, in the first portion (A-B) which lasts 1’30” at 40 rpm, the elastomer, butadiene-co-acrylonitrile rubber is introduced into the mixer and therefore the torque increases. The first loading peak, A, corresponds to adding the rubber. As the torque increases, so does the temperature due to the friction of the mixer screws. The torque begins to decrease near A to B, mainly due to the homogenization and plasticization of the butadiene-co-acrylonitrile rubber, as well as due to the increase in temperature from shearing. Then the other ingredients are introduced and the rotation speed is reduced to 20 rpm for 4’, keeping the mixer open (until all the ingredients are incorporated according to the recipe). Between point B and point X, the torque begins to increase due to the incorporation of the ingredients, but also as a result of the compaction and reinforcement of the elastomer. After incorporating the fillers and other ingredients, the second loading peak, X, is observed when a maximum torque point appears. The torque begins to decrease, indicating the homogenization of the mixture. Afterwards, the compound is homogenized for 2’ at 80 rpm, during which time the mixer is kept closed, obtaining a maximum value of the torque 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 with the mixer closed, Table 2.

Table 2: Characteristics presented in Brabender processing diagrams for butadiene-co-acrylonitrile rubber (NBR) compounded with protein waste

Characteristics	BO (control)	$BCPP_0$	$BCPP_1$	$BCPP_2$	$BCPP_3$	$BCPP_4$
Temperature at peak load, °C	70	86	63	73	95	59
Inflection point temperature, °C	94	118	92	97	118	84
Maximum temperature, °C	106	118	109	109	120	90
Energy at peak load, kNm	138.8	104.0	15.9	138.7	69.7	12.6
Maximum energy, kNm	138.7	139.1	133.7	122.3	154.9	242.2
Gelling zone energy, kNm	30.2	4.0	48.7	40.3	0.4	3.3
Specific energy, kNm/g	1.3	0.9	1.3	1.2	0.8	1.0
Gelling rate, Nm/min	-28.0	-3.6	240.5	47.6	114.0	-516.3

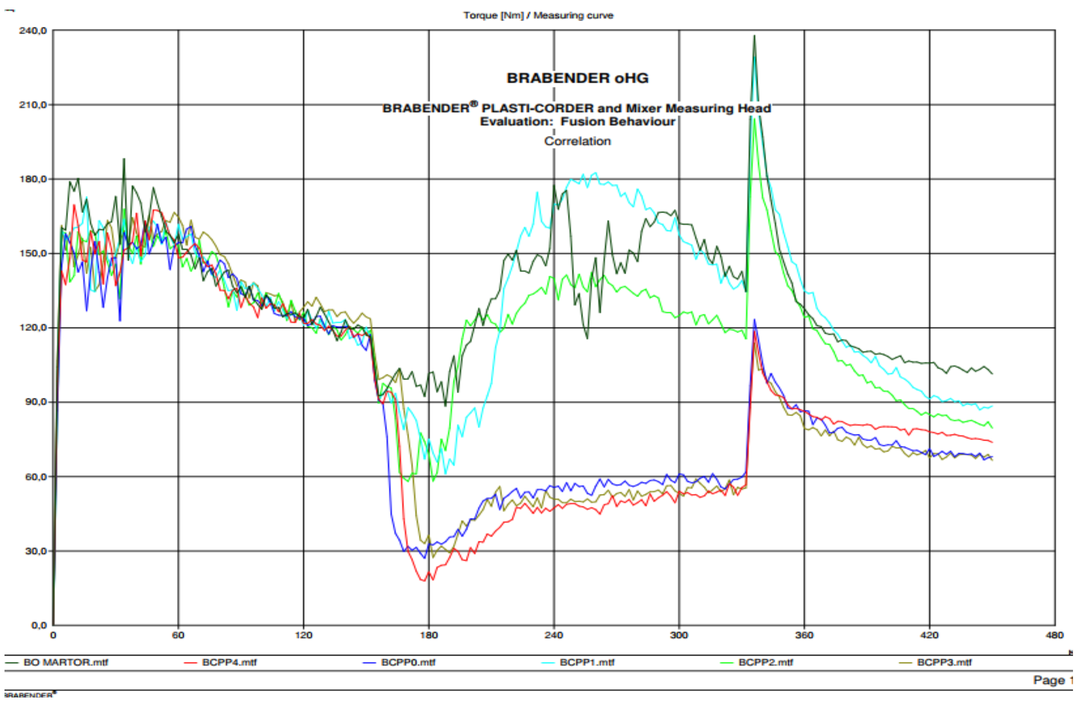


Figure 1. Variation of the torque with time recorded on the Brabender Plasti-Corder when obtaining polymeric composites based on NBR rubber compounded with leather waste functionalized with potassium oleate

Rheological Characterization of Biodegradable Polymer Composites

Biodegradable polymeric composites are rheologically tested on a Monsanto Rheometer at 165°C for 24’. Following the rheological test, the optimal vulcanization times in the press are established in order to obtain the specimens that will be subjected to the physical-mechanical test.

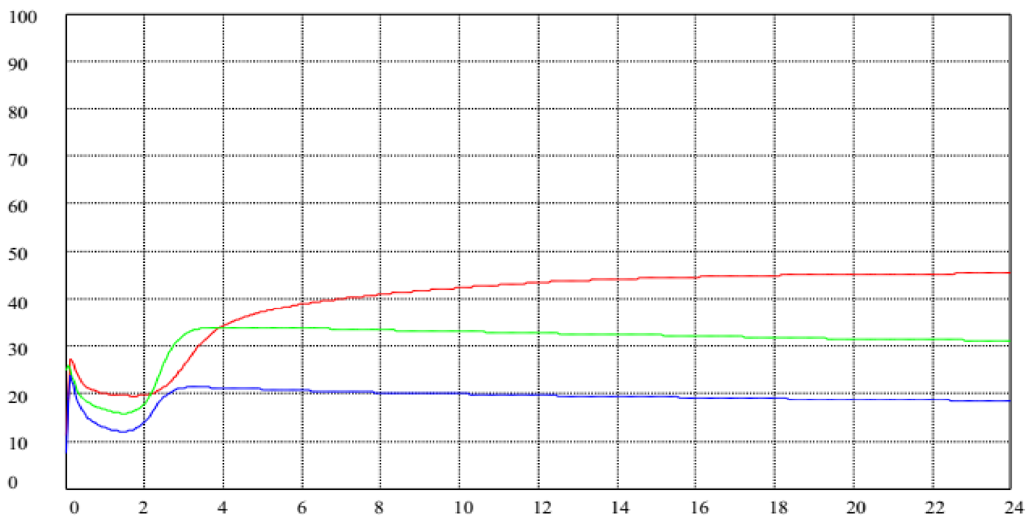
Rheological characteristics of mixtures based on NBR rubber compounded with leather waste (non-functionalized and functionalized with potassium oleate) are shown in Table 3.

Table 3: Rheological characteristics of mixtures based on NBR rubber compounded with leather waste

Rheological characteristics at 165°C	BO (control)	$BCPP_0$	$BCPP_1$	$BCPP_2$	$BCPP_3$	$BCPP_4$
ML (dNm)	17.3	12.8	19.5	18.4	15.7	11.9
MH (dNm)	46.9	29.3	45.3	43.1	33.8	21.4
ΔM = MH-ML (dNm)	29.6	16.5	25.8	24.7	18.1	9.5
t_{s2} (min)	2.91	2.3	2.48	2.67	1.95	1.98
t_{50} (min)	6.38	2.72	3.66	3.58	2.38	2.22
t_{90} (min)	18.61	3.47	10.79	5.18	2.88	2.64

From the rheological analysis made by comparing the samples, Figure 2, it is observed that by replacing the amount of silicon dioxide active filler with functionalized/non-functionalized leather waste powder, the rheological characteristics of the mixtures are modified as follows:

- the minimum torque (ML) as well as the maximum torque (MH) decrease as the amount of leather waste powder functionalized with potassium oleate increases;
- the variation of the torque (ΔM = MH-ML) decreases as the amount of leather waste powder functionalized with potassium oleate increases, to the detriment of the amount of silicon dioxide; this indicates a stiffness of the mixtures in the unvulcanized state which may be due to the agglomeration of the leather waste powder or its larger size compared to the size of the silicon dioxide particles;
- for all the samples the reversal phenomenon is observed, which is specific to the vulcanized mixtures with sulfur and vulcanization accelerators (Figure 1), indicating a degradation of the mixtures at high temperatures by loosening some crosslinking bonds;
- the scorching time (t_{s2}) has very good values, over 1.9’, and the optimal vulcanization time (t_{90}) decreases with the replacement of the active filler of silicon dioxide with the filler of functionalized / non-functionalized leather waste powder.



Physical-Mechanical Characterization of Biodegradable Polymeric Composites

Physical-mechanical characterization of normal state and 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 4 shows the values of the physical-mechanical characteristics obtained.

Table 4: Physical-mechanical characterization of biodegradable polymer composites based on NBR rubber compounded with leather waste non-functionalized/functionalized with potassium oleate

Sample	BO (control)	$BCPP_0$	$BCPP_1$	$BCPP_2$	$BCPP_3$	$BCPP_4$
Physical-mechanical characteristics: 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
Physical-mechanical characterization: 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

From the physical-mechanical analysis performed, Table 4, the following can be seen:

- The hardness of biodegradable polymer based on NBR rubber compounded with leather waste non-functionalized/functionalized with potassium oleate increases with the amount of leather waste added in the mixture with maximum 12°Sh A;
- Elasticity decreases in proportion to the percentage of leather waste functionalized with potassium oleate introduced into the mixture;
- The values of tensile strength decrease as the active filler of silicon dioxide is replaced by the leather waste, and has values between 1.7-9.4 N/mm^2;
- After accelerated aging for 168 h at 70°C there are increases in hardness and elasticity for all samples, while tensile strength decreases significantly, due to the replacement of the active filler with leather waste functionalized with potassium oleate.

CONCLUSIONS

The paper presents the rheological, physical-mechanical Brabender Plasti-Corder mixer diagrams characterization of biodegradable polymeric composites based on elastomer, butadiene-co-acrylonitrile rubber, compounded with leather waste (from the footwear and leather goods industry, ground using a cryogenic mill at a speed of 12000-14000 rpm, in the form of leather powder at a size of 0.35 mm) non-functionalized/functionalized with potassium oleate in a proportion of 20% at 60°C, vulcanization activator - sulfur, Th accelerator and elastomer-specific ingredients. The characterization was performed using the equipment specific to elastomers and according to the standards in force.

Following the characterization performed, it can be seen that the mixtures were made according to the working recipes at the optimum parameters and working times, and from the physical-mechanical characterization performed, the polymer composites based on butadiene-co-acrylonitrile elastomer and leather waste (non-functionalized/functionalized with potassium oleate) it results that they have optimal values that meet the standards and have potential applications for general purpose footwear and in the industry of elastomeric components without special characteristics.

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