BEHAVIOUR OF NITRILE RUBBER-BASED MIXTURES TO COMPOSTING TESTS

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

The National Research & Development Institute for Textiles and Leather - Leather and Footwear Research Institute Division, 93 Ion Minulescu Street, 031215 Bucharest, Romania; dmstelescu@yahoo.com

The paper presents the behavior of some samples based on nitrile rubber reinforced with inorganic and organic type of filler, respectively, to composting. The organic filler used was obtained as waste in the leather and footwear industry. Before use, the waste was ground and then functionalized with potassium oleate in order to improve compatibility with the polymer matrix. The samples of rubber mixtures were obtained on a Brabender mixer, the vulcanization agents were added on a laboratory roller, and the vulcanization of the samples was performed in a hydraulic laboratory press, at 165°C, with a pressing force of 300 kN. The aerobic composting test was performed at laboratory scale, using solid, standardized and homogeneous synthetic waste. After a thermophilic incubation period of 42 days (at 58°C), followed by a period of mesophilic incubation (at the room temperature) of 42 of days, a decrease of some physico-mechanical properties was noticed (hardness, 100% modulus, tensile strength), of the gel fraction, and of the crosslinking densities, the largest decrease of these characteristics being observed in the sample with the highest content of organic filler. The results obtained may indicate that the biodegradation of the rubber samples is favored by the organic fillers.

Keywords: NBR, leather waste, composting test, gel fraction, crosslinking density

INTRODUCTION

Acrylonitrile butadiene copolymers (nitrile rubbers) are used to obtain rubber products (technical articles) with high resistance to oils and petroleum products, with a low gas permeability, a very good abrasion resistance, and with a resistance to aging, heat and ozone superior to natural rubber (Degrange *et al.*, 2005; Shen *et al.*, 2016). Nitrile rubber mixtures (NBR) generally contain fillers (to improve the tensile and tear strength), plasticizers to improve processability, vulcanizing agents, antioxidants, etc.

Vulcanized rubber materials are not biodegradable and for these reasons, after use, they represent a problem for the environment. Due to the current concerns regarding environmental protection, in recent years there have been several studies regarding the replacement of inorganic fillers in rubber mixtures with organic, biodegradable ones (Przepiorkowska *et al.*, 2007; Prochoń and Przepiórkowska, 2013; Mendez-Hernandez *et al.*, 2018). However, there are not many studies on the evaluation of the biodegradation properties of these types of rubber mixtures (Prochoń *et al.*, 2012).

This paper aims to analyze the behavior of samples based on reinforced nitrile rubber both with inorganic and organic fillers to biodegradation and disintegration by composting. Thus, a part of the inorganic filler was replaced with cryogenically ground leather waste or with ground waste based on leather and vulcanized butadiene-styrene rubber (SBR). The testing of the samples regarding the aerobic composting behavior was performed in laboratory conditions, during an incubation period of 84 days, of which 42 days at 58°C (thermophilic incubation), followed by 42 days at the ambient temperature (mesophilic incubation). The modification of the physico-mechanical characteristics, the gel fraction, and the crosslinking densities of the samples were determined.

https://doi.org/10.24264/icams-2022.IV.14

EXPERIMENTAL

Materials

In the obtaining of the samples based on nitrile rubber (NBR) subjected to disintegration into compost, both inorganic and organic fillers were used. The organic fillers were functionalized with potassium oleate in order to improve their compatibility with the nitrile rubber. Table 1 shows the composition of the analyzed samples, in parts per 100 parts of rubber (by weight). The main characteristics of the materials used were presented in a previous paper (Nițuică *et al.*, 2021).

Table 1. The composition of the samples

Ingredients	Symbol samples		
	B0 (control)	BCB_4	$BCPP_4$
Polymer matrix: NBR rubber	100	100	100
Plasticizer: mineral oil	10	10	10
Stearin	1.2	1.2	1.2
Inorganic filler:			
- Silicon dioxide (SiO_2)	30	-	-
- Kaolin	25	5	5
Organic filler:			
- Functionalized leather waste with potassium oleate	-	-	50
- Leather and SBR rubber mixed waste functionalized with potassium oleate	-	50	-
Antioxidant: IPPD 4010	3	3	3
Vulcanizing agent:			
- Sulphur (S)	1.5	1.5	1.5
- Zinc oxide (ZnO)	5	5	5
- Tetramethylthiuram disulfide (Th)	0.6	0.6	0.6

Preparation of Samples

The rubber mixtures were obtained on an internal Brabender PlastiCorder mixer. The addition of the sulfur and vulcanization accelerators was carried out on a laboratory roller, and the vulcanization process took place in a hydraulic laboratory press at 165°C, a pressing force of 300 kN, and vulcanization time 5 minutes. The method of obtaining the samples was presented in detail in the paper by Nițuică *et al.*, 2021. The paper also presents the procedure of waste functionalization (leather, and a mix of leather and butadiene-styrene-SBR rubber waste, respectively), characteristics presented in Brabender processing diagrams, as well as rheological characteristics of mixtures.

Measurements

Composting tests of NBR rubber samples was performed using solid, standardized and homogeneous synthetic waste, in accordance with ISO 20200. The aim was to determine the degree of disintegration of the test materials at the laboratory scale, in conditions that simulate an intensive process of aerobic composting. For the test, a transparent plastic box with a lid was used, provided with a hole on both sides of the box (reactor). From the vulcanized rubber sheets, dumbbell-type specimens (with a thickness of 2 mm and a length of 115 mm) were punched, then they were weighed and placed in the plastic box. From each sample, min. 6 test pieces were analyzed. For the composting

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test, synthetic solid waste (inoculated with matured compost) was used as a solid matrix, in the amount of 1100 g, whose composition is specified in Table 2. Over the synthetic solid waste, 1345 g of distilled water were added, representing 55% of the total mass quantity. These were mixed, and then together with the samples (test pieces) were placed in the box (reactor). The reactor with the samples were inserted into the oven at 58°C, it was weighed daily and the evaporated water was replaced with distilled water, evenly distributed. After 42 days, the first series of samples was removed from the box, washed and wiped, dried for 24 hours in the oven at 58°C and then 1 hour at 100°C. After conditioning at room temperature, the samples were reweighed and then tested. After the thermophilic incubation period (at high temperature), the second series of samples, which remained in the box, was maintained for another 42 days at a mesophilic incubation (at ambient temperature). During this period, the reactor was weighed twice a week and distilled water was added to return the mass to 70% of the mass measured at the beginning of the test. The second series of test pieces was removed on the 84th day, and the same procedure of washing, wiping, drying and conditioning was applied.

Accelerated ageing evaluation was carried out according to ISO 188 using the hot air oven method. Test duration was of 168 h and temperature of 70±1°C.

For the samples: (a) in normal state, (b) after accelerated aging, (c) after the thermophilic incubation period (after 42 days) and (d) after the thermophilic incubation period and the mesophilic incubation period (in total 82 days), the physico-mechanical characteristics were determined, namely: tensile strength (using dumb-bell shaped specimens according to ISO 37), hardness in Shore A degrees (according to ISO 48-4) and elasticity (according to ISO 4662).

Table 2. Composition of synthetic solid waste

Material	Mass	Characteristics	Company
Sawdust	400 g	Sawdust of natural wood, sieved with dimensions of max 3 mm	P.W. “Hobby”, P. Matuszewski, Poland
Food for rabbits	300 g	Protein 15.6%, fat 2.8%, fiber 18.5%	Cunipic Animals De Companyia, Spain
Matured compost	200 g	Compost Garden	Agro C.S., Prirodni product, Czech Republic
Corn starch	100 g	Starch soluble from potatoes, P.A. $(C_6H_{10}O_5)_n$	Lachner, Czech Republic
Sucrose	50 g	Saccharosa P.A., D(+)szacharoz G.R.($C_{12}H_{22}O_{11}$, M=342.30 g/mol)	Lachner, Czech Republic
Corn oil	40 g	Unrefined corn oil, polyunsaturated fat 54%	S.C. Man Ro S.R.L, Romania
Urea	10 g	P.A. purity 99.5%	Chimreactiv S.R.L., Romania

In order to be able to evaluate the degree of biodegradation of the samples after the thermophilic and mesophilic incubation period, respectively, the gel fraction and the crosslink density were determined using the Flory–Rehner equation for tetrafunctional networks. For this, the samples were immersed for 168 hours in toluene at room temperature. The procedure and the calculation formulas are presented in several previous papers, with the specification that: the molar volume of toluene is 106.5 cm^3/mol and the Flory-Higgins polymer (NBR) – solvent (toluene) interaction parameter (χ_{12}) is 0.3795 (Stelescu *et al*., 2022; Basu *et al*., 2021).

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RESULTS AND DISCUSSIONS

Analysis of the Samples after the Composting Test of the Samples

During the composting process, the sequence of specific odors mentioned in the ISO 20200 standard was detected, as well as the change in the appearance of composting and the color shifting from slightly yellowish due to the high concentration in sawdust, to dark brown. Figure 1 shows the images of the samples: the initial stage, at 42 days, and at 84 days, after washing, wiping and drying. As shown in Figure 1, after the composting test period, the samples have not disintegrated because, according to the literature (Prochoń *et al.*, 2012), the samples of cross-linked rubber have a high resistance to biodegradation. According to the results obtained during weighing, the samples showed mass variations both negative and positive, of a maximum of ±10%. These variations in mass may be due to the biodegradation reactions that occurred at the interface between the samples, the solid synthetic waste in the wet state (with the composition specified in Table 2) and the microorganisms developed during the thermophilic and mesophilic incubation period, respectively. These changes could be observed with the naked eye immediately after washing and wiping the samples (see Figure 2), but after drying them, the samples darkened (see Figure 1).

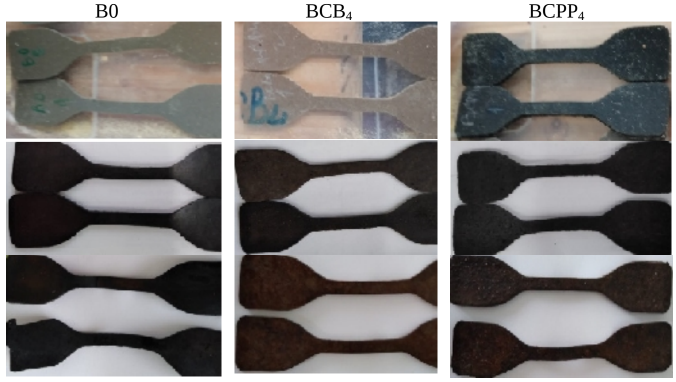

Figure 1. The images of the samples in the initial state, after the thermophilic and mesophilic incubation period respectively (the samples are washed, wiped and dried)

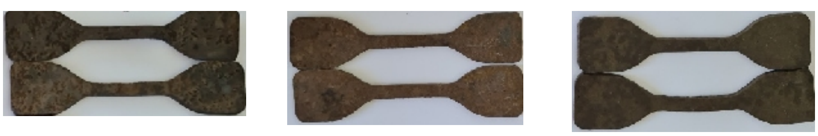

Figure 2. Images of the samples washed and wiped, after the thermophilic incubation period

Physico-Mechanical Characteristics

The physico-mechanical characteristics of the samples in the normal state, after accelerated aging, after the thermophilic and mesophilic incubation period are shown in Figure 3. From analyzing the obtained characteristics the following can be observed: (a) the characteristics are influenced by the type of filler introduced into the mixture

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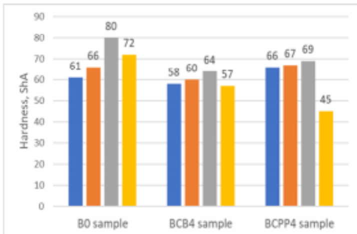
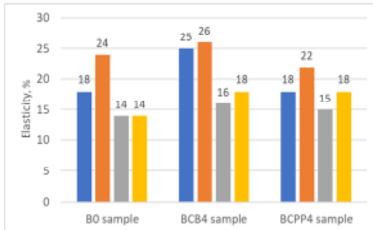
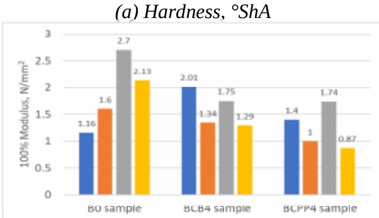
(inorganic or organic); (b) the values of the characteristics obtained after accelerated aging or after the thermophilic incubation period may indicate an increase in the degree of crosslinking due to maintaining the samples at a high temperature (Liu *et al*., 2016; Jiang *et al*., 2019); (c) for samples tested after thermophilic and mesophilic incubation periods (84 days) a decrease in characteristics is observed that may indicate a partial biodegradation of samples, and this is more significant in the sample with a higher content of organic waste ($BCPP_4$).



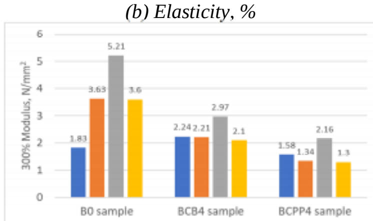
(a) Hardness, °ShA



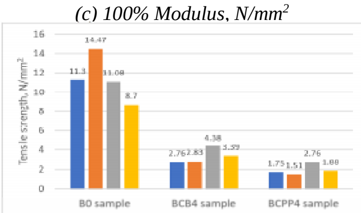
(b) Elasticity, %



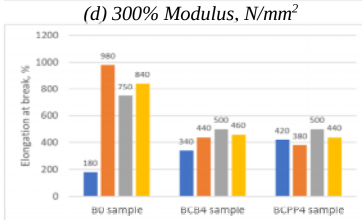
(c) 100% Modulus, N/mm^2



(d) 300% Modulus, N/mm^2



(e) Tensile strength, N/mm^2



(f) Elongation at break, %

Figure 3. Physico-mechanical characteristics of the samples for: normal state (blue), after accelerated aging 168hx170°C (orange), after the thermophilic incubation period of 42 days (gray), and after the thermophilic and mesophilic incubation period 84 days (yellow)

Gel Fraction

The gel fraction and the crosslink density of the samples is shown in Figure 4. A tendency to increase the gel fraction and the crosslink density of the samples after the thermophilic incubation period can be observed, due to the crosslinking reactions that may occur during the maintenance of the samples for a period of 42 days at 58°C (Liu *et al*., 2016; Jiang *et al*., 2019). The values of the gel fraction and the crosslink density decrease significantly after maintaining the samples at a thermophilic and mesophilic incubation period (84 days), the largest decrease being observed in the sample with a high content of organic filler ($BCPP_4$ sample).

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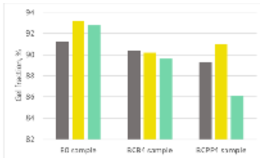
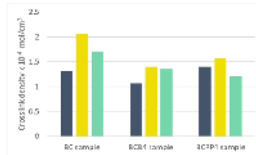


(1) Gel fraction, %



(2) Crosslink density x $^{10\text{-}4}$, mol/cm^3

Figure 4. Gel fraction and crosslink density of samples for: normal state (dark gray), after the thermophilic incubation period of 42 days (yellow), and after the thermophilic and mesophilic incubation period 84 days (green)

CONCLUSIONS

After analyzing the biodegradation behavior by composting of samples based on NBR rubber reinforced with inorganic and organic filler type, respectively, it was observed that after a period of 42 days of thermophilic incubation, followed by a period of 42 days of mesophilic incubation, there is a decrease in: hardness, 100% modulus, 300% modulus, tensile strength, gel fraction and crosslinking density, and these decreases are more pronounced in the sample with a higher content of organic waste.

Acknowledgements

This research was financed by ANCSI through PN 19 17 01 03/2019 project.

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https://doi.org/10.24264/icams-2022.IV.14