OBTAINING AND CHARACTERIZING A POLYMER COMPOUND BASED ON NBR ELASTOMER AND FUNCTIONALIZED POST-CONSUMER RUBBER WASTE

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This work presents the obtaining and characterization of elastomeric compounds based on butadiene-co-acrylonitrile rubber and NBR rubber waste (from the footwear industry) that replaces the active silicon dioxide filler. The rubber waste was cryogenically ground to micrometric dimensions and functionalized with monoethylene glycol (MEG). After grinding, it is functionalized with monoethylene glycol (MEG) in a proportion of 20% at a temperature of 60°C. By recycling and reusing vulcanized rubber waste (NBR), as well as by means of advanced technologies, it is possible to contribute to the improvement of product quality, the protection of the environment through waste recycling, and most importantly the protection of human health through the elimination of noxious substances during their burning and, of course, increasing the turnover of economic agents. The polymer compounds obtained after conditioning at ambient temperatures were characterized according to the standards in force for the footwear industry, in terms of physical-mechanical normal state and accelerated aging at 70°C for 168 h and FT-IR spectroscopy. The polymer composites based on NBR rubber and functionalized rubber waste present optimal values according to the standards and are used in the processing of general-purpose footwear.

Keywords: NBR elastomer, rubber waste, FT-IR spectra, polymer compound, waste recycling

INTRODUCTION

At the global level recently, the industry of processing vulcanized materials aims to recycle them (United Nations Environment Programme, 2015), and the diversification of the chemical compositions and structures of vulcanized rubber is the main reason because it is not biodegradable. The increase in the number of finished products made of vulcanized rubber (tyres, car parts and shoe soles), represents a threat to the environment, as well as to human health (Formela, 2021). By recycling and reusing vulcanized rubber waste (nitrile rubber), as well as advanced technologies, it is possible to contribute to the improvement of product quality, to environmental protection through waste recycling, and most importantly to the protection of human health through the elimination of noxious substances during their burning and, of course, increasing the turnover of economic agents (United Nations Environment Programme, 2015; Chittella *et al*., 2021). The progress made in recent years in the management of elastomer waste has made rubber products, especially used ones, to be perceived as a potential source of valuable raw materials (Sienkiewicz *et al*., 2017). Thus, a series of decisions and regulations appeared in the regulation of waste recycling and reuse. The Romanian government has issued a series of decisions for waste management. One of these decisions is Governmental Decision no. 85/2002 – "Introduction of the waste management record and the European waste catalog". The cryogenically ground rubber (elastomer) waste used in powder form, in elastomeric compounds, has particles with regular shape, a smooth surface and shows a low level of oxidation (Nituica *et al*., 2022). Butadiene-co-acrylonitrile (NBR) rubber mixtures generally contain fillers, plasticizers, antioxidants, vulcanizing agents to improve tensile and tear strength,

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workability, etc. (Alexandrescu *et al*., 2014). Thus, active fillers such as silicon dioxide can be successfully replaced by ground (powder) and functionalized elastomeric waste (Stelescu *et al*., 2020; Nituica *et al*., 2021). The compounds based on NBR rubber and elastomeric waste (from the footwear industry) processed through the mixing technique, in the presence of vulcanization systems, leads to the obtaining of technical products with characteristics necessary for use in the footwear industry (Nituica *et al*., 2022). The vulcanization of the compounds has a major impact on the final properties of the products, representing an important property, and the use of vulcanized rubber waste as filler is important in obtaining elastomeric compounds (Roucoules *et al*., 2007; Alexandrescu *et al*., 2019).

EXPERIMENTAL PROCEDURE

Materials

The materials used were: 1) NBR - butadiene-co-acrylonitrile rubber: acrylonitrile content – 34%, Mooney viscosity (100%) – 32±3, density – 0.98 g/cm^3; 2) ST – stearin: white flakes, molecular weight 284.48 g/mol, dynamic viscosity 9,87 mPa.s at 70°C, volumetric weight approx. 400-500 kg/m^3, moisture – 0.5% max, ash – 0.025% max; 3) ZnO – zinc oxide microparticles (white powder): precipitate 93-95%, density – 5.5 g/cm, specific surface – 45-55 m^2/g; 4) SiO_2 – silicon dioxide: density 1.9-4.29 g/cm^3, molar mass – 60.1 g/mol; 5) $CaCO_3$ – chalk: white powder, molecular weight 100.09; 6) rubber waste – ground rubber from the footwear industry; 7) functionalized rubber waste – ground rubber from the footwear industry functionalized with MEG (monoethylene glycol); 8) mineral oil; 9) IPPD 4010 – N-isopropyl-N'-phenyl-p-phenylenediamine: density – 1.1 g/cm^3, solidification point of over 76.5°C, flat granules brown to dark violet in color; 10) S – Sulphur: vulcanization agent, fine yellow powder, insoluble in water, melting point: 115°C, faint odor; 11) Th – tetramethylthiuram disulfide: curing agent, density – 1.40g/cm^3, melting point <146°C, ultrafast curing accelerator.

Methods

Preparation of Polymer Compound Based on NBR Rubber and Non-Functionalized/ Functionalized Rubber Waste

The polymer compounds obtained are based on butadiene-co-acrylonitrile rubber (NBR) and non-functionalized/functionalized butadiene-co-acrylonitrile rubber waste with monoethylene glycol (MEG), Table 1. Phases of the laboratory-scale technological process for making polymer compounds based on NBR elastomer and non-functionalized/functionalized NBR rubber waste with MEG (monoethylene glycol) are the following: analysis and reception of raw materials; dosing of raw materials; mixing the polymer compound in Brabender mixer; rheological characterization on a Monsanto Rheometer for establishing the optimal vulcanization parameters in the electric press; making the samples (with dimensions according to the elastomer processing standards) in the electric press for quality control of the mixture; quality control of samples made of elastomeric compound based on NBR rubber and non-functionalized/functionalized waste.

The polymer compounds were processed by mixing technology on the Brabender Plasti-Corder (capacity 350 cm^3) with the possibility of adjusting the working parameters (temperature and mixing speed) according to Table 2, with strict observance of the order of introduction of the ingredients.

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Table 1. Formulation of compounds based on NBR rubber and non-functionalized/functionalized rubber waste

Symbol	MU	B0	$B0_2$	BCP_1	BCP_2	BCP_3	BCP_4
Mixing in the Brabender Plasti-Corder							
Butadiene-co-acrylonitrile (NBR)	g	150	150	150	190	190	190
Stearin	g	1.8	1.8	1.8	2.85	2.85	2.85
ZnO (active powder)	g	7.5	7.5	7.5	9.5	9.5	9.5
SiO_2	g	45	-	30	19	0	0
$CaCO_3$ (kaolin)	g	37.5	37.5	37.5	37.5	37.5	37.5
Non-functionalized rubber waste (50%)	g	-	75	-	-	-	-
Functionalized rubber waste (NBR)	g	-	-	15	30	45	75
Mineral oil	g	15	15	15	15	15	15
IPPD 4010 antioxidant		4.5	4.5	4.5	4.5	4.5	4.5
S (Sulfur)	g	2.25	2.25	2.25	2.25	2.25	2.25
Th (tetramethylthiuram disulfide)	g	0.9	1.5	0.9	0.9	0.9	0.9

B0 – composite without rubber waste; $B0_2$ – composite with 50% non-functionalized rubber waste (butadiene-co-acrylonitrile rubber waste)

Butadiene-co-acrylonitrile rubber waste (NBR rubber waste from consumer goods and the footwear industry) was used in elastomeric mixtures in powder form. The waste was ground with a cryogenic mill, in three cycles, at a speed of 12,000-14,000 rpm to a final size of 0.35 mm. After grinding, it was functionalized with monoethylene glycol (MEG) in a proportion of 20% at a temperature of 60°C.

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

The order of introduction of the ingredients	Mixing time (min.)	Mixing speed	Temperature, °C
NBR rubber (plasticization)	1' 30"	40 rpm	40°C
Ingredients (without vulcanizing agents)	3'	35 rpm	40°C
Vulcanizing agents (S and Th)	1'30"	40 rpm	40°C
Homogenization time	4'	100 rpm	80 °C
TOTAL	10'	35-100 rpm	40°C-80°C

After the mixing process, the elastomeric polymer compounds based on NBR rubber and rubber waste are tested from a rheological point of view on a Monsanto Rheometer, at 165°C, for 24', to establish the optimal vulcanization times for pressing in the electric press, in standard molds. After pressing, 150x150x2 mm samples are obtained by pressing in elastomer-specific molds, by compression between its plates. The optimal parameters for obtaining the samples are: working temperature 165°C; pressing time – 5 minutes; cooling time (water cooling) – 10 minutes; pressure – 300 kN. The samples are subjected to characterizations according to the standards in force.

Characterization of Elastomeric Compounds

The elastomeric compounds based on NBR rubber and rubber waste were tested in terms of rheological, physical-mechanical and structural properties (Infrared Spectroscopy) using appropriate techniques.

The elastomeric compounds based on NBR rubber were tested in compliance with the physical-mechanical standards in effect, under normal condition and accelerated ageing: hardness, °ShA – ISO 48-4:2018; elasticity, %, ISO 4662:2017; tensile strength, N/mm^2 – SR ISO 37-2020; tear strength, ISO 34-1:2015 – N/mm; elongation at break, N/mm^2 – SR ISO 37-2020; abrasion, mm^3, SR ISO 4649/2011. Accelerated ageing was carried out

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according to SR ISO 188/2011, using the hot air circulation oven method at 70 ± 1°C and 168h. After performing the aging process, the samples are subjected to conditioning for 16 hours up to 7 days, then they are subjected to physical-mechanical determinations, and the results obtained are compared with those obtained under normal conditions.

Fourier Transform Infrared Spectroscopy (FT-IR Spectroscopy) were performed with a double beam IR molecular absorption spectrometer, in the range 4000-400 cm^{-1}, using the FT-IR Thermo Nicolet iS 50 equipped with ATR with diamond crystal.

RESULTS AND DISCUSSION

Physical-Mechanical Characterization of Polymeric Compounds

The physical-mechanical characterization of samples under normal and accelerated aging conditions was carried out on elastomer-specific equipment.

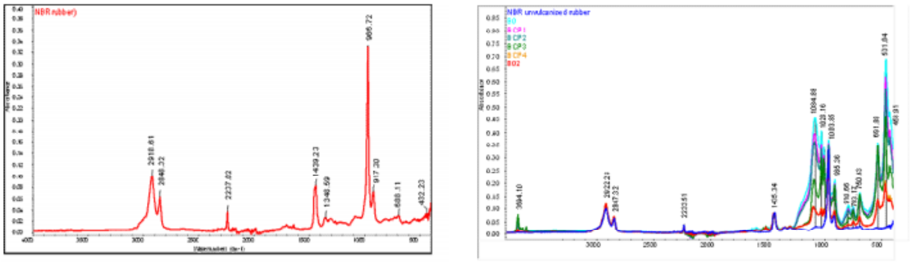
Table 3. Physical-mechanical characterisation of compounds based on NBR rubber and non-functionalized/functionalized rubber waste

Symbol	B0 (control)	$B0_2$	BCP_1	BCP_2	BCP_3	BCP_4
Normal condition						
Hardness, °Sh A	60	55	57	54	47	46
Elasticity, %	20	19	16	19	17	18
Tensile strength, N/mm^2	11.3	8.82	8.68	7.29	4.87	3.06
Elongation at break, %	180	940	740	700	540	380
Abrasion resistance, mm^3	218.39	157.03	223.02	250.63	165.13	66.67
Accelerated aging at 70°C and 168 h						
Hardness, °Sh A	66	61	61	60	53	50
Elasticity, %	24	20	20	18	18	18
Tensile strength, N/mm^2	14.47	8.0	8.0	5.76	3.73	2.8
Elongation at break, %	980	600	600	560	420	360

From the recorded physical-mechanical characteristics, Table 3, it appears that: hardness decreases significantly especially for samples BCP_3 and BCP_4, samples containing 30% and 50% functionalized elastomer waste, respectively, which indicates a stiffness of the characterized samples; elasticity and tensile strength decrease compared to the control sample – B0 by replacing the active charge (SiO_2) with functionalized rubber waste (in different proportions – 10-50%); elongation at break shows a maximum value especially for sample BCP_1 (10% functionalized rubber waste), then decreases with the increase in the amount of elastomeric waste, and the lowest value of elongation at break is for sample BCP_4 – 380%; the abrasion resistance increases with the increase in the amount of rubber waste, by approximately 14% compared to the control sample, having a maximum value for the BCP_2 sample (20% functionalized rubber waste and 20% active filler), followed by a decrease of 69 % for the BCP_4 sample (the active filler being replaced with 50% functionalized rubber waste). Changes in the physical-mechanical characteristics are significant. After the accelerated aging process at 70°C, for 168 h, small variations in hardness of ±1°ShA are observed for the samples with 10-20% functionalized waste and 20% active filler, and for the samples BCP_3 and BCP_4, where the active filler is replaced with functionalized rubber waste, it decreases by ±10°ShA, while variations of elasticity from 17% to 25%, tensile strength from 41% to 80% and elongation at break from 38% to 80% are noticed as well. The changes in the physical-mechanical characteristics are significant for the samples where the active filler was totally replaced with the rubber waste functionalized with MEG.

FT-IR Spectrometric Analysis

The FT-IR spectra recorded for the polymer compounds based on NBR elastomer are shown in Figure 1 (a, b, c). The stretching vibration bands are based on those obtained in the reference spectrum of butadiene-co-acrylonitrile rubber (NBR elastomer).



a) FT-IR spectrum from NBR rubber

b) FTIR spectrum of composites based on NBR rubber and NBR waste functionalized with MEG/non-functionalized

Figure 1. FT-IR spectra of compounds based on NBR rubber with non-functionalized/functionalized rubber waste (B0, $B0_2$, BCP_1, BCP_2, BCP_3, BCP_4)

In the FT-IR spectrum recorded for NBR rubber, the band at 2237.02 cm^{-1} confirms the presence of stretching groups of -CN bonds from nitrile as well as the stretching vibration of double bonds from butadiene =C-H at 966.72 cm^{-1} (Alhareb *et al.*, 2015). In the FTIR spectrum of functionalized and non-functionalized NBR waste, the bands originating from NBR rubber (2917.74, 2848.41, 1454.95, 966.76 cm^{-1}), the presence of silicon dioxide/kaolin (1081.4, 794.28 and 457.01 cm^{-1}) can be visualized (Khalil, 2007). As it can be seen in the case of sample B0 (compound based on NBR rubber without NBR waste), a very high intensity of the bands at 1084.88 and 458.91 cm^{-1} can be observed, compound bands originating from silicon dioxide and kaolin. The high intensity proves that the highest amount of SiO_2 is used in this sample. Moreover, the intensity of these bands decreases as the amount of SiO_2 decreases (samples BCP_1 and BCP_2). Instead, in the case of samples BCP_3 and BCP_4, silicon dioxide is replaced with NBR waste. However, in this region (1084.88 cm^{-1}) characteristic bands can be identified, but these come from kaolin. The presence of monoethylene glycol could not be detected for the samples containing functionalized NBR waste (10, 20, 30 and 50% functionalized NBR waste), because it is either covered with a layer of NBR rubber or is used in low quantities. The presence of compound bands comes from SiO_2 and kaolin, the intensity of these varying depending on the amount added to the mixture.

CONCLUSIONS

The elastomeric compounds were tested by appropriate techniques. In the FT-IR spectra recorded for samples based on NBR rubber and rubber waste in a proportion of 10, 20, 30 and 50%, functionalized with MEG, the bands originating from NBR rubber, from kaolin and silicon dioxide can be visualized. The presence of monoethylene glycol could not be observed for samples containing functionalized NBR waste because it is either covered with a layer of NBR rubber or is used in low quantities. The presence of compound bands originating from SiO_2 and kaolin could be highlighted at 1084.88 and 458.91cm^{-1}, their intensity varying depending on the amount used. From the comparison of the samples that do not contain silicon dioxide, BCP_3 and BCP_4, it is observed that by replacing SiO_2, with rubber waste, there is a decrease in hardness, elasticity and tensile strength, while abrasion resistance increases. The changes in the physical-mechanical characteristics are significant for the samples where the active filler was totally replaced with the rubber waste functionalized with MEG. The polymer composites based on NBR rubber and functionalized rubber waste show optimal values according to the standards and are used in the processing of general-purpose footwear.

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