LOW CARBON FOOTPRINT COMPOSITE BASED ON CHLOROPRENE RUBBER AND ELASTOMER WASTE

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The aim of the paper consists in the treatment of post-consumer and technological waste of elastomers and plastomers, according to the 4R principle (reduction, reuse, recycling and recovery) by transforming them into raw materials with added value and integrating them into different industries. This will lead to the developing of new processing concepts regarding obtaining new biodegradable composite materials, with various waste contents (10-50 wt%). The composite is based on chloroprene rubber, and added post-consumer recycled rubber particles, with size of 45 mesh, eco-reinforcing material, and active fillers, plasticizers, vulcanizing agents, antioxidants. In order to enhance the compatibility and their level of interaction, the elastomer waste was finely ground (cryogenic mill) and functionalized with potassium oleate. Rubber waste acts as a filling material which leads to lower carbon footprint of the composite and lower mass. Tensile, tear strength, elasticity, hardness, abrasion resistance, melt flow index and morphological study (FT-IR) of those composites were examined in order to determine their viability in various application areas. The transformation of waste (cryogenically ground, and functionalized) into new products with added value will lead to remarkable improvements in the life cycle of raw materials and the sustainable use of this waste, contributing to increasing sustainability, improving eco-efficiency and economic efficiency and reducing the carbon footprint on the environment.

Keywords: composite, rubber waste, eco material, carbon footprint

INTRODUCTION

Chloroprene rubber, also known as neoprene, has excellent physical properties, and is characterized by good resistance to elements, flame, ozone and oils. Due to the presence of halogen in the rubber molecule, chloroprene resists burning better than any other hydrocarbon rubbers (Maya *et al*., 2018). Rubbers represent a class of materials that have become an environmental and economic issue, so the evaluation of the end-of-life management of these materials is of primary relevance. The emerging challenges of depletion of raw materials and an increase in rubber demand can be met through circular economy by slowing, closing, and narrowing resource loops. In recent years increasing recycling rates or increasing the product lifetime has become the primary goal for sustainable development. Besides tires, 50% of the world's rubber production is used for the consumption of general rubber goods (GRG). The processed waste can be transformed into cheaper and more sustainable material to feed their production. This cycle of producing tires and GRG from their used, worn-out materials increases sustainability. The use of worn-out tires and scrap GRG granulates in new products can significantly reduce the carbon footprint up to one-third compared to the products produced without recycled material (European Tyre and Rubber Manufacturers' Association, Circular Economy, https://www.etrma.org/key-topics/circular-economy/).

Nowadays, thanks to the development of new processes, there are several different options that can be identified for the end-of-life management of these materials. One of the most common solutions is to use the rubbers as fuel to burn this waste with associated energy recovery (Isayev, 2013; Ramarad *et al*., 2015). Another solution is to recycle this

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material through a mechanical process, by grinding the waste to convert it into powder or granulates, that can be used for different applications: bituminous mixtures, concrete, reinforcing fillers in polymers, rubber pads (Farina *et al*., 2017; Isayev, 2013; Li *et al.*, 2010; Si *et al.*, 2018; Sienkiewicz *et al*., 2017; Zanetti *et al.*, 2015). If rubber materials, in the last part of their life cycle, are not directed towards a recycling process, the remaining destination is landfill disposal, with the consequent possible development of diseases and ecological contaminations (Molino *et al.*, 2018). However, to fulfil the objectives defined by a circular economic model and therefore try to keep the quality of materials unchanged for as long as possible, it is necessary to rely on other processes, which allow a recovery of the material while preserving its physico-mechanical properties.

In this research the composite is based on chloroprene rubber, and added post-consumer recycled rubber particles, having the size of 0.5 µm, ground reinforcing material, and active fillers, such as plasticizers, vulcanizing agents, antioxidants. In order to enhance the compatibility and their level of interaction, the wood waste was finely ground (cryogenic mill) and functionalized with potassium oleate. Using rubber waste as a filling material leads to the lower carbon footprint composite and the decrease in mass.

EXPERIMENTAL

Materials

Materials used to obtain the composites were: c*hloroprene rubber*, from SAFIC ALCAN; *stearin* – powder, white colour, molecular weight 284,48 g/mol; *zinc oxide*, microparticles, white powder, precipitate 93-95%; *magnesium oxide*, microparticles, fine powder, precipitate 93-95%, *silicon dioxide*, molecular mass 60,08 g/mol, white colour, particle size < 0,5 mm; c*hlorinated paraffin* – solid state, powder; *N-Isopropyl-N'-phenyl-1,4-phenylenediamine*, brown flat granules, molar mass: 226,317 g/mol, density: 1.04 g/cm^3; *sulfur*, vulcanization agent (fine yellow powder, melting point: 115°C); *tetramethylthiuram disulfide* – vulcanization agent (density 1.40 g/cm^3), melting point <146°C, an ultrafast curing accelerator); all ingredients are from Bayer company.

Rubber waste was collected from the soles and footwear manufacturers, cryogenically ground at 8.000-10.000 rpm for 20s and screened through a 45-mesh screen (down to 0.5µm).

Methods

Functionalization

The functionalization of rubber waste with potassium oleate was achieved by mixing in a heated mechanical stirrer with 80 rotations/min, at a temperature of 80°C for 8 hours. The ratio between elastomer waste and potassium oleate – 50%.

Composites Processing

The rubber is plasticized for 90s, speed 40 rpm and 45°C, mechanically mixed in a Brabender Plasti-Corder. The other ingredients like fillers, plasticizers and elastomeric waste are slowly added, in 4 min 30s, twin screw speed set to 20rpm and temperature rises to 90°C. Compound homogenization for another 2 minutes, speed 60 rpm and temperature reaches over 100°C. The total processing times was 8 minutes. Table 1 shows

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tested formulations. The mixture is removed from the mixer chamber and finished on the electric roller, by adding the antioxidant and vulcanizing agents. The processing parameters are as follows: temperature 23-30°C, friction of the rollers 1:2, and 50 rotations/min, for 5 min and homogenization for another 2 min.

Table 1 shows the formulations of compound based on chloroprene rubber, with semi-active – MgO and ZnO white mineral fillers, and flame-retardant materials such as chlorinated paraffin, stearin.

This formulation has been altered to have a reduced carbon footprint, by adding functionalized waste in various amounts, 10, 20, 30, 50% waste respectively, compared to the amount of chloroprene rubber. The waste used was rubber (CC1-CC4).

Table 1. Polymer composites based on polychloroprene rubber compounded with rubber waste

Ingredients / Symbol	M.U.	CO	CC1	CC2	CC3	CC4
Processing on Brabender						
Chloroprene Rubber	g	190	190	190	190	190
Stearin	g	2.28	2.28	2.28	2.28	2.28
Zinc oxide	g	9.5	9.5	9.5	9.5	9.5
Magnesium oxide	g	7.6	7.6	7.6	7.6	7.6
Silicon dioxide	g	57	38	19	0	0
Chlorinated paraffin	g	57	57	57	57	19
functionalized rubber waste	g	0	19	38	57	95
Antioxidant IPPD	g	5.7	5.7	5.7	5.7	5.7
Processing on Roller						
Sulfur	g	2.85	2.85	2.85	2.85	2.85
Accelerator	g	2.28	2.28	2.28	2.28	2.28

RESULTS AND DISCUSSIONS

It can be seen in Figure 1 that the torque in the first part which lasts 90 secs at 40 rpm, the elastomer is added into the mixer and therefore the torque increases initially.

The first loading peak corresponds to the introduction of elastomers. As the torque increases, so does the temperature due to friction.

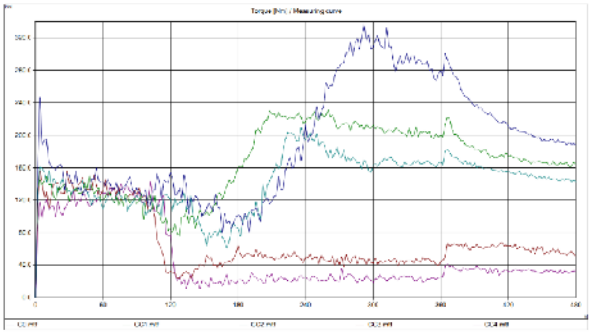

Figure 1. The variation of torque vs time recorded by the Brabender Plasti-Corder during the processing of rubber mixtures (C0-CC4)

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After the loading peak is reached, the torque begins to decrease, mainly due to the homogenization and plasticization of the elastomer, as well as due to the increase in temperature due to shear.

Then the other ingredients are added and the speed is reduced to 20 rpm for 4':30".

After 90 Sec first part, the torque begins to increase due to the incorporation of the ingredients, but also as a result of elastomer reinforcement and energy transfer.

After incorporating the fillers and other ingredients, the second loading peak is observed when a maximum torque is achieved.

The torque starts to decrease, indicating the homogenization of the mixture.

Then the homogenization of the compounds takes place for 120 sec at 60 rpm.

As a result, a maximum value of torque 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 of the mixture temperature due to the friction at a higher rotation speed (60 rpm).

FTIR Spectroscopy

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 pure elastomer spectrum. After the tests were carried out, the following were found:

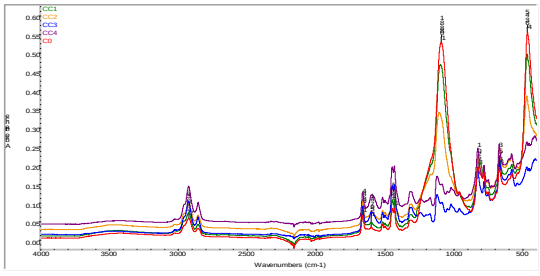

Figure 2. FTIR spectra of composites based on chloroprene rubber / rubber waste modified with potassium oleate

In the case of composites based on chloroprene rubber (control sample CO) and mixtures containing rubber waste modified with oleate CC1-CC4), both bands originating from rubber and the presence of additional bands due to the specific ingredients used in processing (silicon dioxide at 1088.81 cm^{-1}, 463 cm^{-1} as well as the presence of the potassium oleate surface modified rubber waste at 1597 cm^{-1}) can be identified.

The physical-mechanical characteristics of the composites – CC series (based on chloroprene rubber and elastomeric waste) are shown in Table 3.

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Table 3. Physical-mechanical characteristics

Physical-mechanical characteristics	Symbol			
	CC1	CC2	CC3	CC4
Hardness, °Sh A	55	49	49	47
Elasticity, %	18	16	16	20
Tensile strength, N/mm^2	11.86	12.22	13.87	14.18
Elongation at break, %	660	780	670	620
Remanent elongation, %	24	28	24	28
Tear strength, N/mm	46.5	47.9	49.2	50.2
Specific weight, g/cm^3	1.41	1.37	1.33	1.28
Abrasion resistance, mm^3	224.91	395.76	183.94	163.39

The ***hardness*** decreases by a maximum of 8°ShA in the samples that contain less silicon dioxide and more rubber waste.

Elasticity varies unevenly across the samples.

The ***tensile*** and ***tear strength*** gradually increase as the silicon dioxide active filler is replaced by the elastomeric waste, and show good values, of 14.18 N/mm^2 and 50.2 N/mm respectively for sample CC4.

Elongation at break shows good behaviour, and values over 620%.

Specific weight of the mixtures decreases as the amount of the powder increases, indicating, along with the other properties, a good compatibility between the chloroprene polar rubber and the rubber powder.

The abrasion increases with the increase in the amount of powder, shows a maximum value for the CC2 mixture (20 phr silicon dioxide and 20 phr rubber powder), followed by a decrease (an improvement) in the values for the CC4 sample.

Obtaining chloroprene rubber sheets (simple diagram – Figure 3). First part unvulcanized rubber sheet then processed and vulcanized on roller mix.

Figure 3. Obtaining and vulcanisation of rubber sheets

The Life Cycle Assessment methodology was used to carry out the analysis and the main environmental impact categories evaluated were: Climate change, Ozone depletion, Photochemical ozone formation, Acidification, Eutrophication, Ecotoxicity, Resource use. The first step, the analysis focused on the identification and quantification of main environmental hotspots. The results of the hotspots analysis reveal that the main contribution to the environmental impacts of the composite is the material consumption and type and the energy used. In this regard the material has an impact of up to 60% of total. The comparison underlines how the using of recycled of rubber waste allows to reduce the carbon footprint with 20%. Using the rubber waste lower the GWS from 3.02 kg eqCO_2 in processing phase to 2.4 kg eqCO_2.

CONCLUSIONS

- Composites based on Chloroprene rubber and semi-active fillers compounded with functionalized post-consumption rubber waste were obtained.

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- The values of the tensile and the tearing strength increase as the silicon dioxide active filler is replaced by the elastomeric waste, showing good compatibility with the matrix.
- Elongation at break has good values, over 620%.
- Abrasion resistance increases in samples with rubber wastes, property important for soles.
- The density of the mixtures decreases as the amount of rubber waste increases and replace other components with heavier density.

The use of recycled of rubber waste allows to reduce the carbon footprint with 20%, while maintaining good physico-mechanical properties.

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