DESIGNING AND OBTAINING WOOD WASTE AND CHLOROPRENE RUBBER-BASED COMPOSITES

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The aim of this paper is to obtain and study the properties of wood waste reinforced elastomer composites with various fibre contents (10-50 wt%). The composite is based on chloroprene rubber, and added post-consumer recycled wood particles, with dimensions of 500 nm eco-reinforcing material, and active fillers, 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. Wood waste acts as a filling material which leads to the biodegradability of the composite and the decrease in density. Tensile, tear strength, elasticity, hardness, abrasion resistance, melt flow index and morphological study (FT-IR) of those composites were examined in order to determine the viability in various applications domains.

Keywords: composite, wood waste, eco material.

INTRODUCTION

The waste management concept of integrating various materials into a composite, along with various recycling methods, offer new possibilities of reducing the footprint and amounts of wastes. Using those wastes in polymeric materials biodegradable composites can be obtained. Recycling and the use of renewable natural resources offer a new dimension in the discovery of new materials. Nowadays, special attention has been paid to the development of composites with polymer matrix reinforced with natural fibers.

The problem of waste has been addressed over time by several methods: depollution, consumption reduction, waste recovery, recycling, reusing.

The use of natural fibers as a reinforcing agent in the composites (Chaudemanche *et al.*, 2018; Brostow *et al.*, 2016) is gaining new momentum.

Types of natural fibers are:

- wood fibers (wood waste);
- leather fibers (leather waste);
- textile fibers (textile wastes, cloth scraps).

Wood waste is a set of products and materials whose origin comes from all stages of the wood industry, from logging to the manufacture of finished products. Also, the scrap wood (boxes, crates, pallets) represents a significant quantity (Turku *et al.*, 2018; Najafi, 2013; Piao *et al.*, 2014).

The main sources of wood waste are: logging: bark, sawdust, thin wood (small); wood processing industry (cutting, carpentry, furniture factories, parquet): chips, sawdust, scrap; scrap: construction wood, railway crosses, pallets, formwork wood, etc.

Polymer composites are materials that consist of two or more components that are connected, or chemically bind, and offer better properties due to their synergies. Thus, at least two different materials, which are completely immiscible, are mixed to form a composite. Additives such as compatibilizers, plasticizers, pigments, UV radiation stabilizers, nanoparticles are also frequently added in order to improve certain properties. The type and geometry of the discontinuous phase give the composite optimized properties, such as high specific strength, rigidity and hardness, low specific weight, etc. (Navarro *et al.*, 2004).

In this research the composite is based on chloroprene rubber, and added post-consumer recycled wood particles, with dimensions of 500 nm eco-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. Wood waste acting as a filling material which leads to the biodegradability of the composite and the decrease in density.

MATERIALS AND METHODS

Materials

Materials used to obtain the composites were: *chloroprene 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; *chlorinated paraffin* – solid state, powder; *N-Isopropyl-N'-phenyl-1,4-phenylenediamine*, brown flat granules, molar mass: 226,317 g/mol, density: 1.04 g/cm³; *sulfur*, vulcanization agent (fine yellow powder, melting point: 115°C); *tetramethylthiuram disulfide* – vulcanization agent (density 1.40 g/cm³), melting point <146°C, an ultrafast curing accelerator); all ingredients are from Bayer company.

Wood waste was collected from the manufacture of wooden furniture, cryogenically ground at 12.000 rpm for 15s and screened through a 500 nm mesh screen.

Method

Functionalization

The functionalization of wood waste with potassium oleate was achieved by mixing with a mechanical stirrer with 80 rotations/min with heat, at a temperature of 80°C for 8 hours. The ratio between wood 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 PLE-360. The other ingredients like fillers, plasticizers and wood waste are slowly added, in 4 min 30s, twin screw speed set to 20rpm and temperature rise to 90°C. Compound homogenization for another 2 minutes, speed 60 rpm and temperature reach over 100°C. The total processing times was 8 minutes. Table 1 shows tested formulations. The mixture is extracted from the mixer chamber and finished on the electric roller, by adding the antioxidant and vulcanizing agents. The processing parameters are as following: temperature 23-30°C, friction of the rollers 1:2, and 50 rotations/min, for 5 min and homogenization for another 2 min.

Figure 1. Processing stages

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 recipe was adapted to have a higher ecological component, by adding functionalized waste in different amounts, respectively 10, 20, 30, 50% waste compared to the amount of elastomer. The waste used is wood (CL1-CL4).

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

Ingredients / Symbol	M.U.	CO	CL1	CL2	CL3	CL4
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 Wood 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 2, 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 2. Brabender mixing diagram for composites C0-CL4

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

IR spectrum represents the radiant energy absorption curve in the IR domain by the sample molecule, depending on the wave length or radiation frequency. The infrared domain of the electromagnetic radiation is between 0.8 and 200 μm . IR domain for usual organic chemistry is between 2.5 and 25 μm . 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 3. FTIR spectra of composites based on chloroprene rubber/wood waste treated with potassium oleate

In the case of chloroprene rubber/wood waste treated with potassium oleate composite, in addition to the band's characteristic of the treated waste (especially at ~ 1596 , 1515 cm^{-1}) the characteristic band of silica (1090 - 1100 cm^{-1} , $\sim 800 \text{ cm}^{-1}$, 460 - 470 cm^{-1}), calcium carbonate (~ 874 , 712 cm^{-1}) and rubber, can also be observed. Moreover, the presence of wood waste can be proved in CL4 by the fact that the area 1000 - 1100 cm^{-1} contains several overlapping strips including the C-O band from approximately 1027 cm^{-1} of the untreated wood waste. In CL2 due to the presence of SiO_2

there is a merging of the bands, one characteristic of silica between 1000-1100 cm^{-1} and the C-OH strips from the wood waste, which leads to an asymmetry of the peak.

The physical-mechanical characteristics of the composites - CL series (based on chloroprene rubber and wood waste) are shown in table 3.

Table 3. Physical mechanical-characteristics

Physical mechanical-characteristics	Symbol			
	CL1	CL2	CL3	CL4
Hardness, °Sh A	60	57	62	72
Elasticity, %	16	18	18	26
Tensile strength, N/mm^2	12.6	7.83	6.43	5.87
Elongation at break, %	640	600	560	580
Remanent elongation, %	28	28	36	34
Tear strength, N/mm	49.5	45.5	37.5	30
Specific weight, g/cm^3	1.4	1.39	1.36	1.29
Abrasion resistance, mm^3	187.28	189.86	185.41	219.46

Hardness of the control sample is 60°Sh A, when adding the functionalized wood waste increases proportionally with the amount of waste used in the mixture, up to 72°Sh A. This is demonstrated by the fact that the hardness increases with the amount of fillers in the mixture.

The **tensile strength** decreases compared to the control sample, 12.6 N/mm^2 , and proportionally to the amount of wood waste introduced into the composite, reaching 5.87 N/mm^2 for the composite with 50% functionalized wood waste.

Elasticity does vary compared with control sample.

Elongation at break, similar to tensile strength, decreases, from 640% of the control sample, proportional to the amount of wood waste, down to 580% for the composite with 50% wood waste in the composition. Similar values are obtained for **remanent elongation and tear strength**.

Specific weight decreases proportional to the amount of wood waste, from 1.4 g/cm^3 control sample to 1.29 in the CL4 sample with 50% wood waste.

The abrasion increases exponentially with the proportion of wood waste added; thus, the control sample has a value of 187.28 mm^3 , the CL1 sample with 10% wood waste has the value of 189.86 mm^3 , and the CL4 sample with 50% wood waste reaches 219.46 mm^3 . It was observed that composites with 10-20% wood waste have values that fall within the standardized requirements for abrasion, namely 200 mm^3 .

CONCLUSIONS

- Composites based on Chloroprene rubber and semi-active fillers compounded with functionalized post-consumption wood waste were obtained.
- Hardness increase up to 72 °ShA and the elasticity has variable values and are uneven.
- The values of the tensile and the tearing strength decrease as the silicone dioxide is replaced with the wood waste.
- Elongation at break has good values, over 550%.
- Abrasion resistance increases in samples with wood wastes.
- The density of the mixtures decreases as the amount of wood waste increases and replace other components with heavier density.
- Properties like hardness, and increased, indicating that the composite is becoming more rigid and due to the replacement of other components by wood waste, it became lighter.

Thus, the use of post-consumption wood waste in elastomeric composites could contribute to sustainable development in a near future.

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