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PRELIMINARY INVESTIGATIONS OF rPP REINFORCED WITH *EUCALYPTUS* FIBERS AND GRANITE POWDER

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Abstract. *The development of new polymer composites from recycled plastic materials with waste from the wood and ornamental stone industry enables the volume of these surplus quantities to be reduced, minimizing impacts on public and environmental health, such as soil, air and water contamination. These wastes are little valued, thus reducing the economy of the productive chain. The use of these by-products as raw material and transformation into new marketable and / or economically feasible products presents itself as a sustainable technological alternative to companies and public sectors. In this work were prepared composite materials with different mass fractions, from the mixture of untreated eucalyptus fibers and granite powder as recycled polypropylene (rPP) reinforcements, pigmented with carbon black, without the use of compatibilizers. The physical and chemical characterization of eucalyptus fibers and granite powder derived from residual abrasive sludge from granite processing was performed. The composites were made in a single screw extruder and characterized by the melt flow index (MFI). Preliminary results show that the fillers have reinforcement potential in the manufacture of composites, due to their composition and geometry. The MFI of the composites is influenced by the type of filler and impurities present in the rPP, consequence of the recycling process.*

Keywords: *Composite materials, Solid wastes, Thermoplastics, Wood, Ornamental stones*

1. INTRODUCTION

The Brazilian forest-based industry is globally recognized for its high wood volume productivity and the slowest rotation in the world. However, in spite of global hegemony, in recent years, wood production has become more expensive in Brazil. Sector costs have been increasing more than national inflation, making wood production more expensive (IBÁ, 2017).

Wood products are easily recycled and contribute less greenhouse gas emissions than non-renewable materials. Due to the worldwide shortage of trees in many areas and environmental awareness, research on the development of composites prepared using various wastes and recycled materials is actively being sought (HAQ; SRIVASTAVA, 2017). The accumulation of solid waste in the timber industry is an ongoing process, requiring large storage spaces with fire hazards. Part of this volume corresponds to *eucalyptus* wood (IBÁ, 2017). Another environmental problem is related to the residues of the industry of extraction and processing of ornamental rocks in Brazil, they are disposed in the environment without previous treatment, being able to contaminate soils and groundwater. It should be noted that the abrasive sludge from the processing of granite when it dries constitutes fine powder that causes impacts on public health. An alternative to minimize some of these problems is the use of these materials in mixtures with polymer matrices for improvements in the physical, chemical, mechanical and thermal properties of composites. This new concept in the design of products from waste from renewable sources promotes the incorporation of sustainability in different industrial segments.

Nowadays, one of the biggest concerns of society is the use and management of waste. Environmental pollution is alarming, especially in relation to waste produced by large industries. The increase in waste generation presents a serious environmental problem and costly disposal. In this scenario, plastic materials are considered the main polluters of the environment, since the demand for polymeric artifacts has been growing considerably since the last decades to the present. Polypropylene is one of the commodity plastics most used as a raw material in many industrial fields today. This can be attributed to the low cost, the excellent versatility of applications and the performance of this resin. However, because polymeric materials take a long time for spontaneous degradation (on average more than 200 years) and, when burned, can produce different degrees of toxicity, the deposition of this waste is a serious environmental problem. In this regard, researchers point to recycling as the best way to reduce this accumulation, considering factors such as virgin raw material preservation, quality of products formed, low production costs and the possible generation of employment and income (CATTO et al., 2014; FARIA; WISBECK; DIAS, 2015; ABIPLAST, 2017; LAZIM; SAMAT, 2017; RODRIGUES et al., 2017). In this context, no studies were found in the literature using *eucalyptus* fibers and granite powder as reinforcing agents in the same recycled polymer matrix. In view of the above, the use of *eucalyptus* fibers and granite powder becomes an interesting alternative in the preparation of new materials due to the high volume and characteristics of the waste.

Thus, the main objective of the research was to investigate preliminarily recycled polypropylene (pigmented industrially with carbon black) composites reinforced with *eucalyptus* fibers and granite powder, regarding the preparation and characterization.

2. MATERIALS AND METHODS

2.1 Materials

The matrix used was recycled polypropylene (rPP) in the form of pellets of approximately 5 mm, pigmented with carbon black, supplied by Tergo Plásticos Industriais Ltda (Brazil). As dispersed phases, *eucalyptus* (*Eucalyptus* spp.) fibers (EF) were used, without superficial modification, with and without mixtures of granite powder (GP) from the abrasive slab from the cutting and polishing of granitic rocks, provided by SerraMatti Madeireira Ltda (Brazil) and SM Granitos Ltda (Brazil), respectively.

2.2 Filler-matrix characterization

The ash content in the rPP was obtained according to ASTM D5630-13 (Procedure B), and the melt flow index (MFI) of the matrix was determined by the method ASTM D1238-13, measured under conditions 230 ºC/2.16 kg using a JINHAIHU plastometer, model XNR-400B. The *eucalyptus* fibers were dried (natural drying and later in an oven at 105 ± 2 ºC for 48 hours) and stored in sealed plastic containers. Fibers were characterized by granulometry (ASTM D1921-18), bulk density (SCAN-CM 46-92, ABNT NBR 14984-03), moisture content (ABNT NBR 14929-03) and chemical constituents (ABNT NBR 13999-17, ABNT NBR 14853-10, ABNT NBR 7989-10). In order to observe the morphological characteristics of the *eucalyptus* fibers, the image analysis was performed using a scanning electron microscope (ZEISS®), model EVO MA10.

Leaching tests (ABNT NBR 10005-04) and solubilization (ABNT NBR 10006-04) of the residual sludge from the granite processing were performed. The abrasive slurry was dried (natural drying and then oven-dried at 100 ± 2 ºC for 24 hours), then deagglomerated, obtaining a powder. Granulometry of the granite powder was obtained by an test analogous to that used to determine the fineness of the cement (ABNT NBR 11579-12).

2.3 Composite manufacturing process

Figure 1 summarizes, schematically, the steps of the production process to obtain rPP composite materials reinforced with untreated *eucalyptus* fibers and granite powder.

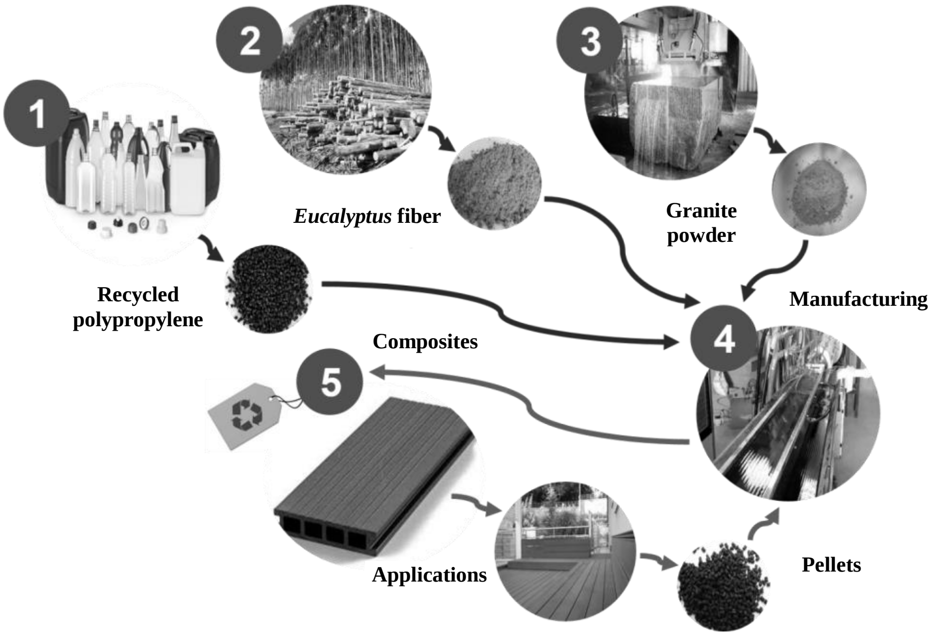

Figure 1 – Simplified illustrative scheme for the production of composites, applications and recycling.

The matrix and fillers were mixed manually for 10 minutes and then placed in the feeder of the extruder, where the feedstock rate of the raw materials was varied to keep untreated *eucalyptus* fibers and the granite powder in the different fractions of 5, 10, 15 and 20% by mass in the matrix, respectively. The materials were homogenized by direct extrusion in a single screw extruder, brand SEIBT, model ES35, with thread diameter of 35 mm, thread and cannon nitrided, ratio L/D of 30, without devolatilization system. Thus, the processing was carried out at temperatures ≤ 200 ºC, taking into account the residence time of the material in the extruder. This is necessary to minimize the process of thermal degradation of cellulose, which occurs at temperatures ≥ 200 ºC. In Table 1 and Figure 2 the processing and configuration parameters of the extrusion profile, respectively, are presented in the five heating zones of the extruder. The MFI of the rPP and formulated composites of Table 2 was determined by the method ASTM D 1238-13 (230 ºC/2.16 kg).

Table 1 – Conditions of preparation of the composites in single screw extruder.

Parameters	Value	Unity
Feeding temperature to matrix	190 - 200 - 200 - 200 - 200	ºC
Thread rotation	90	rpm
Feed rate	2	kg h^{-1}
Mixing time in camera	3	min

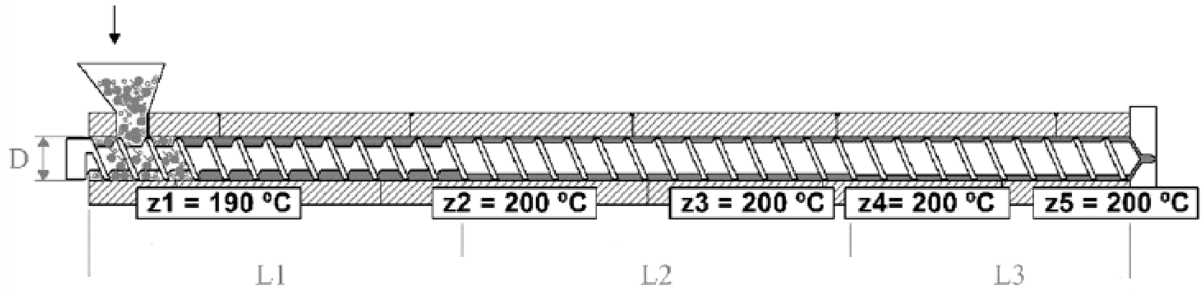

Figure 2 – Configuration and schematic profile of the cannon and thread.

Table 2 – Formulations and abbreviations of the samples.

N.	Samples	Code	Recycled polypropylene	*Eucalyptus* fibers	Granite powder

			rPP (% m/m)	EF (% m/m)	GP (% m/m)
1	A	rPP100	100	0	0
2	B	rPP95EF5	95	5	0
3	C	rPP90EF10	90	10	0
4	D	rPP85EF15	85	15	0
5	E	rPP80EF20	80	20	0
6	F	rPP95GP5	95	0	5
7	G	rPP90GP10	90	0	10
8	H	rPP85GP15	85	0	15
9	I	rPP80GP20	80	0	20
10	J	rPP90EF5GP5	90	5	5
11	K	rPP80EF10GP10	80	10	10
12	L	rPP70EF15GP15	70	15	15
13	M	rPP60EF20GP20	60	20	20

3. RESULS AND DISCUSSION

3.1 Characterization of *eucalyptus* fibers

The retained mass frequencies showed that 78.4% of the fibers are between 0.149 and 0.075 mm. The distribution of fiber size is an important factor in the preparation of composites, since it increases the homogenization and dispersion of the short fibers in the polymer matrix. Figure 3 shows the geometric characteristics of *eucalyptus* fibers.

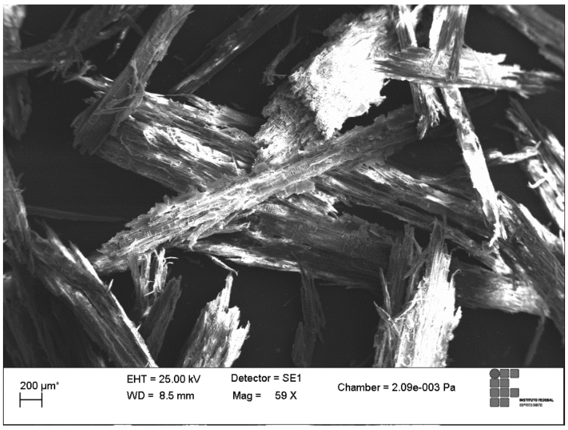

Figure 3 – Micrograph of *eucalyptus* fiber

The micrograph of the fibers shows the predominance of rough surface with uneven texture, being interesting in the filler/matrix interfacial adhesion. However, lignocellulosic components are observed on the surface of the fibers, which may compromise the wettability of the resin in the substrate. The density of the EF was 0.12 ± 0.01 g cm^{-3}. This result represents an advantage in obtaining low-density composites compared to other mineral fillers with a density of 2.7 g cm^{-3} (CARASCHI, LEÃO, 2002). The moisture content of the EF for processing was 3.0 ± 0.1%. According to Rodolfo Júnior and John (2006), the moisture must be less than 8.0% for processing, because the higher the moisture, the greater the volume of gases generated inside the extruder, surface staining and difficult filler/matrix adhesion.

The properties of tensile strength, flexural strength and modulus of elasticity in composites can reach higher values with the correct selection of the type of vegetal filler (GRISON et al., 2015). Considering the fact that there are variations in the different regions of the tree, in the wood and by environmental conditions, the determination of the constituents of the wood is important, because they characterize the mechanical and thermal properties of the materials (KLYOSOV, 2007). The values of the constituents of each residue are in agreement with the results obtained by Klock et al. (2005).

The mass values of the chemical constituents of the EF are shown in Figure 4.

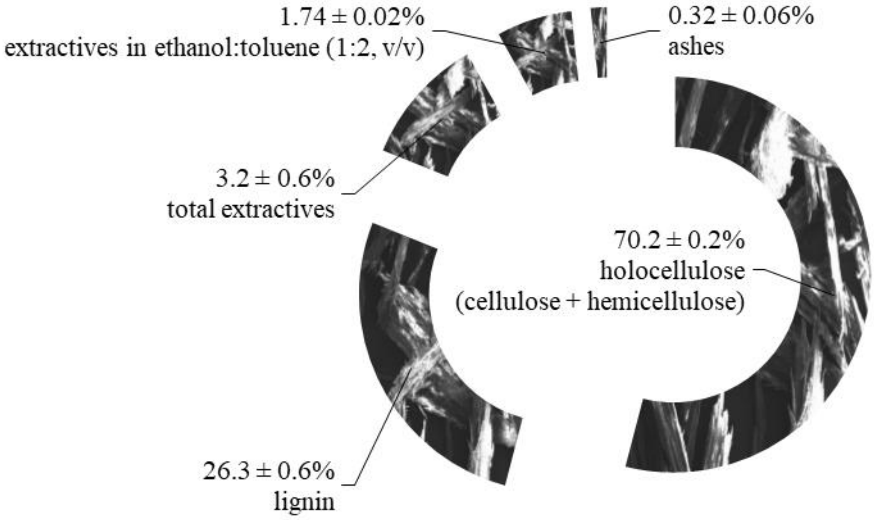

Figure 4 – Chemical composition of *eucalyptus* fibers, dry mass fraction (% b.s.)

3.2 Characterization of residual abrasive sludge - granite powder

The result of the fineness of the granite powder was 31.95%. Thus, approximately 70% of the residue used in the preparation of the composites has a particle size of less than 0.075 mm. The results of the abrasive sludge leaching and solubilization test are presented in Table 3.

Table 3 – Leaching and solubilization of abrasive sludge.

Parameters	Leached (pH 4 ± 1)		Solubilized (pH 9 ± 1)	
	Value ($mg\ L^{-1}$)	Maximum limit	Value ($mg\ L^{-1}$)	Maximum limit
Al	4.92 ± 0.14	-	1.85 ± 0.13	0.2
Ba	0.22 ± 0.011	70	< 0.005	0.7
Cd	< 0.13	0.5	< 0.0002	0.005
Pb	< 0.12	1	< 0.002	0.01
Cl	12 ± 0.089	-	10 ± 0.03	250
Cu	0.05 ± 0.04	-	< 0.5	2
Cr	0.015 ± 0.008	5	< 0.0011	0.05
Sn	< 0.005	-	< 0.005	-
Fe	30.9 ± 0.60	-	0.09 ± 0.002	0.3
F	0.2 ± 0.0023	150	0.1 ± 0.002	1.5
Mn	1.42 ± 0.11	-	< 0.088	0.1
Ni	0.08 ± 0.0069	-	< 0.005	-
Ag	< 0.11	5	< 0.001	0.05
Si	6.84 ± 0.063	-	0.48 ± 0.0083	-
V	< 0.011		< 0.011	
Zn	0.11 ± 0.0084	-	< 0.021	5

The granite sludge was classified as Class II A (non inert) waste, according to the ABNT NBR 10004-04, because it presented aluminium (Al) above the maximum limit allowed for the solubilized extract. Similarly, Bertossi et al. (2012) verified the non-inerticity of a sludge sample from granite processing due to the copper (Cu), iron (Fe), manganese (Mn) and sodium (Na) concentrations that exceeded the maximum limit. Gonçalves, Moura and Dal Molin (2002) analyzed residual granite sludge from a granite processing industry, which was also classified as Class II A waste, because the concentration of chemical element fluorine (F) exceeded the maximum solubilization limit. The difference of parameters from one industry to another corresponds to the different blocks of processed granites, each granite rock has unique elements and characteristics. In this way, the residual sludge may also have different characteristics within the same industry, according to the quantity and diversity of the sawn stones. The moisture content of the solubilized extract was 13 ± 0.066%.

3.3 Determination of ash content and melt flow index

The ash content in the rPP was 2.48 ± 0.36%. From the experiment it is shown that the MFI of sample A is higher than the other samples. This means that rPP is less viscous compared to formulated composites because the melt flow rate is an indirect measure of molecular weight with high melt flow rate corresponding to low molecular weight (HAQ; SRIVASTAVA, 2017). It is observed for the same class of dispersed phase incorporated in the matrix, that losses occur in the fluidity. Granite powder reduces the flowability of rPP more than *eucalyptus* fibers, due to the higher density of the mineral filler. As well, mixtures of fibers (20% m/m) and fine powder (20% m/m) further hinder the flowability of rPP compared to other formulations. Another factor that restricts melt flowability is the impurities present in the rPP in the recycling process and pigmentation with carbon black in the segregation unit.

Table 4 shows the melt flow index with a 30 second cut-off time of the samples according to the formulations.

Table 4 – Sample flow index.

Samples	**A**	**B**	**C**	**D**	**E**	**F**	**G**
MFI (g/10min, 230 ºC/2.16 kg)	0.438 (0.107)	0.246 (0.051)	0.227 (0.018)	0.199 (0.015)	0.186 (0.012)	0.216 (0.014)	0.206 (0.011)
		H	**I**	**J**	**K**	**L**	**M**
		0.192 (0.037)	0.166 (0.014)	0.214 (0.013)	0.201 (0.019)	0.174 (0.011)	0.133 (0.012)

Value in parentheses is the standard deviation

4. CONCLUSION

The characteristics of *eucalyptus* fibers and fine granite powder are interesting for potential reinforcement use in composite fabrication. It has been found from the melt flow index that the formulated composites have lower flowability capacities compared to rPP, and that this decrease is accentuated in the formulations with the blended fillers.

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