

Sustainable composites of eco-friendly polyethylene reinforced with eggshells and bio-calcium carbonate

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Abstract

This work aimed to obtain and analyze composite materials made from green polyethylene and calcium carbonate extracted from chicken eggshells. The shells were collected and prepared for later extraction of calcium carbonate. With the X-ray diffraction analysis it was possible to confirm that both the in natura reinforcement and the calcined one, have the same polymorph mineral (calcite). With regard to thermal behavior, compounds with in natura reinforcement showed greater mass loss due to the moisture contained in them. The results showed a significant increase in Young's moduli of the composites compared to the pure polymer. The scanning electron microscopy showed good dispersion and adhesion between the reinforcement materials and matrix. In view of the results, eggshells have the potential to be used as fillers, where greater rigidity is required. Since these materials come from a waste material, with low cost, their use becomes even more viable.

Keywords: biopolymers, calcium carbonate, composites, eggshells, polyethylene.

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1. Introduction

A Brazilian petrochemical company created the green polyethylene named "*I'm green*" to develop a sustainable product from renewable raw materials. Unlike other polymers extracted from fossil fuel sources, such as oil and natural gas, low density green polyethylene (LDGPE) is obtained from sugarcane-derived ethanol. In this way, this product reduces the emission of greenhouse gases while keeping the same properties and performance as conventional polyethylene^[1].

Brazil has kilometers of land with sugarcane plantations, thus making the use of a product from this renewable source more viable. An interesting fact in contributing to the development of a network with a more sustainable profile, such as green polyethylene, is that in its production chain it contributes to a cleaner atmosphere, since sugarcane plantations carry out photosynthesis, and thus absorb carbon dioxide from the atmosphere.

The absorption of carbon dioxide (CO_2) by green polyethylene occurs in sugarcane plantations that photosynthesize and capture CO_2 from the atmosphere, making green polyethylene a "carbon sequestrant". This process can remove around three tons of CO_2 from the atmosphere for each ton of green polyethylene (PE) produced, for conventional polyethylene the opposite is true, its production process releases two tons of CO_2 into the atmosphere^[2].

From an economic point of view, the cost of production and the value of the green product is higher than conventional polyethylene. This difference can reach 30% for each kilogram of green polyethylene^[3]. Several reasons explain this difference such as the need for a vast land area for planting sugarcane, adequate weather conditions, increased water consumption, equipment, capital, and direct competition with ethanol production based on sugarcane^[2].

According to the Brazilian Association of Animal Protein (ABPA)^[4], Brazil consumes many eggs, consumption of eggs by each Brazilian in 2021 was 257 units, this consumption generates a considerable amount of waste^[4]. Eggshell is a porous ceramic material that, despite being light, has high strength^[5]. Eggshell is rich in mineral salts, and its main constituent is calcium carbonate (CaCO₃), around 94%. The organic part of the egg (6%) includes internal and external membranes composed of collagen types I, V and X and glycosaminoglycans^[6,7].

Due to the fact that eggshells are highly deposited in the environment, there is a need to explore more applications for their use. Therefore, this research encompassed two materials that are not usually combined because the eggshell, when used in composites, acts as a filling filler and not as the main filler of the composite. Thus, one of the differentiating points of this study is the use of eggshells as the main load. Furthermore, another interesting novelty of this study is the comparison between different types of reinforcement material.

Calcium carbonate has been applied as a filler in some noteworthy composites. It can be prepared as nanoparticles, optimizing the homogenization between the matrix and the dispersed phase. Charde et al.^[8] added calcium carbonate (CaCO₃) to a polycarbonate matrix and improved the tribological properties of the composite. Hafez et al.^[7] produced a biofilm combining nanocellulose and calcium carbonate. The CaCO₃ increased the thermal stability and retarded the thermal degradation of the cellulose at high temperatures.

Currently, there are numerous works considering that eggshell reinforces composite matrices. But, regarding its use and comparison to the calcium carbonate, obtained through eggshell there is a lack of research and information on the subject. In this way, this comparative study developed composites reinforces with eggshells and calcium carbonate extracted from them. Thus, it is possible to understand better the influence of organic matter present in the eggshell and to indicate possible fields of application for both composites.

Following the above and to promote sustainable development, this work aimed to obtain, characterize, and analyze composite materials made from green polyethylene reinforced with chicken eggshell particles (*in natura*) and biologically derived calcium carbonate (bio-CaCO₃) extracted from the eggshells. The extraction of calcium carbonate was done by the method of calcination of egg shells. At the end of the experimental development, the reinforcements and composites were characterized for the investigation of their microstructural, elemental, thermal and mechanical properties.

2. Experimental

2.1 Materials

The polymeric matrix used was a low-density green polyethylene (LDGPE) from Braskem (*I'm green*TM),

which is commercially known as SLD4004 resin. The chicken eggshells used as reinforcement material were donated by a bakery of the city of Pelotas-RS (Brazil). Finally, polyethylene grafted with maleic anhydride (PE-g-MA) was provided by Crystal Master and used as compatibilizing agent.

2.2 Preparation of in natura eggshell powder

First, the eggshells were collected, cleaned and washed in running water to remove dirt and dried at 100°C for 24h in a Quimis oven, model Q317M-52. After drying, the peels were ground in a Marconi knife mill, MA model. After that, the peels went through a second milling. For this went through a second milling using a IKA A11 Basic analytical mill. Thus, a fine powder was obtained, which was sieved through a Tyler 200 mesh to obtain a better granulometry.

2.3 Extraction of calcium bio-carbonate

The extraction of bio-CaCO₃ from the egg shells takes place by removing the organic matter from the shell. For this, the powder obtained by grinding the eggshells underwent a calcination heat treatment for 2h at 600°C in a Quimis muffle, model Q-318. This simple and affordable procedure removes organic matter, because with the temperature used in the calcination process, the organic matter in the eggshell is degraded and the moisture present in it evaporates, thus leaving only CaCO₃. Figure 1 shows the powders obtained.

2.4 Production of the composites

A Quimis oven, model Q317M-52 was used to dry the polymer matrix and reinforcement materials (in natura and bio-CaCO3) for 24h at 60°C before being processed. After drying, the pellets and reinforcement materials were manually mixed in a glass container to obtain better mixing homogeneity. Table 1 presents the mixture formulations. Then, a single screw extruder from Eco Soluções with a L/D of 20 was used to process and mix the material in the molten state. The pure polymer (unfilled) was also processed following the same conditions used for the composites. The temperature profile used to process the materials was 140°C/145°C/150°C. The die temperature was set at 90°C and the screw speed at 60 rpm.



Figure 1. (a) ground eggshell; (b) in natura powder; and (c) the bio-CaCO₃,

An amount of 5% by weight of each reinforcing material was incorporated into the LDGPE. Formulations were made with and without the compatibilizing agent for a better analysis of the results. A 3 wt% concentration by weight of PE-g-MA was used for the formulations that considered it. The extruded material was granulated to obtain pellets and stored for subsequent injection molding. Table 1 shows the specific formulations.

A mini bench injector, AX Plastics brand, model AXINJET, performed the injection molding. The specimens followed the dimensions presented in ASTM D638 (Type IV) and ASTM D 256A for tensile and impact tests, respectively. The processing conditions used were an injection temperature of 190°C and a mold temperature of 50°C. Eight specimens of each composition were selected for each mechanical characterization. The specimens were measured with a Starret digital caliper, model EC799. In addition, were weighed on a Shimadzu precision scale, model UX8200S.

2.5 Characterization of in natura eggshell powder and bio-CaCO₃ particles

The powders were characterized by scanning electron microscopy (SEM) using a Tescan VEGA3 to evaluate their morphology. SEM analysis was used to visualize the geometry of the reinforcing particles as well as particle size uniformity.

The powders obtained from eggshells were also characterized by X-ray diffraction (XRD) to determine the crystal structure and the degree of crystallinity. A Bruker D8 ADVANCE diffractometer was used. Analyses were performed at a wavelength (λ) of 1.541 Å, operating at 40 kV and 40 mA, using a scan speed of 1°/min, for 20 between 10° and 90°.

The powders were also characterized by Fourier transform infrared (FTIR) spectroscopy to evaluate their functional groups and bonds. A Shimadzu Prestige-21 was used. The analyses were performed in duplicate in the 400 to 4000 cm⁻¹ wavenumber range. An equipment from the brand Shimadzu, model Prestige-21 performed this analysis.

The analysis of the thermal stability of the powders was performed by thermogravimetry using a TA Instruments TG Q500, with a heating rate of 10°C/min, from room temperature to 800°C, under a nitrogen atmosphere.

2.6 Characterization of the polymer matrix and composites

The morphology of the composites was analyzed using SEM under the same conditions and equipment described above. SEM images were obtained from the fractured surface of the specimens after tensile testing.

TGA was performed to evaluate the thermal stability of the composites using a TA Instruments TG Q500 with a heating rate of 10°C/min, from room temperature to 800°C, under an argon atmosphere.

Differential scanning calorimetry (DSC) characterized the melting temperature (T_m), crystallization temperature (T_c), and the degree of crystallinity of the pure polymer and the composites. The samples were initially heated from room temperature to 190°C at a heating rate of 10°C/min and kept at this temperature for 5 min. Then, the samples were cooled to 30°C at a rate of 10°C/min and heated again to 190°C at a rate of 10°C/min, following the ASTM D3418-15 standard. Crystallization and melting thermograms were recorded from the first cooling and second heating cycles. For this analysis, a TA Instruments Q2000 was used, with nitrogen as the carrier gas, at a constant flow of 50 mL/min. From the DSC analysis, the degree of crystallinity of the matrix and composites follows the Equation 1:

$$Xc(\%) = \frac{\Delta Hf}{\Delta H^* f} \times \frac{1}{W} \times 100\% , \qquad (1)$$

Where Xc is the degree of crystallinity (%), ΔH_r is the enthalpy of crystal fusion (J/g), ΔH^*_r is the enthalpy of fusion of a 100% crystalline sample (the theoretical ΔH^*_r value used for LDGPE was 293 J/g^[9]); and W is the amount of polymer (wt%).

One of the mechanical tests used was an Izod-type impact test. The notched specimens were measured using a Ceast pendulum impact instrument, Impactor model, coupled to a DAS 4000 data acquisition system via software. The injection-molded specimens were notched in a Ceast notching machine, to a depth of 2.54 ± 0.1 mm, with a minimum notching speed. According to ASTM D256A standard, the depth of the notch was checked with an appropriate micrometer when performing the analysis.

A uniaxial tensile test was conducted to investigate the mechanical properties of the composites. The tensile tests were carried out following the ASTM D638 Type IV standard in an Instron testing system, model 5569, at 5 mm/min. A 50 kN load cell was used and the specimens were deformed until rupture. It was not possible to use the strain gauge to measure the elastic strain due to the size of the specimens. Eight samples of each formulation were analyzed for each mechanical test.

3. Results and Discussion

3.1 In natura eggshell powder and bio-CaCO₃ particles

Figure 2 shows the micrographs of the *in natura* and bio-CaCO₃ powders, which are irregularly shaped and have smooth surfaces. However, the uniformity of the particle size was not achieved. Ivanović et al.^[10] obtained eggshell particles with geometry and morphology similar to those presented in this study.

Table 1. Formulations of pellets obtained by the extrusion process.

Formulation of pellets (v	vt%)
Pure LDGPE	100
LDGPE/in natura	95/5
LDGPE/bio-CaCO3	95/5
LDGPE/in natura/PE-g-MA	92/5/3
LDGPE/bio-CaCO3/PE-g-MA	92/5/3

Tm is the crystalline melting temperature measured in the second heating cycle; ΔH_m is the enthalpy of crystal melting measured on the second heating; Tc is the crystallization temperature measured in the cooling cycle; ΔH_c is the enthalpy of crystallization measured in the cooling cycle; and Xc is the degree of crystallinity calculated in the second heating cycle.

As expected, bio-CaCO₃ had smaller particles than the *in natura* powder. This reduction in particle size is a result of the calcination process. A smaller particle size gives bio-CaCO₃ increased surface area compared to the fresh powder. In this case, large surface area values guarantee greater viability for the reinforcement. Large surface area usually has better adhesion to the polymer matrix^[9].

Figure 3 shows the X-ray spectra of the powders. It can be seen that the peaks are well defined, which can be explained by the ordering of the atoms when forming the crystalline structure of the particles, as Callister and Rethwisch^[11] comment. The peak of greatest intensity occurs at approximately 29.5° (2 θ). This aspect indicates that the *in natura* powder and the bio-CaCO₃ contain calcite as the main constituent phase, identified from the rhombohedral structure, corroborating Nawar et al.^[12] and Kareem and Naji^[13].

There is no difference between the diffractograms presented, due to the fact that the two reinforcement materials have the same constituent phase, (calcite), that is, the same crystalline arrangement of the atoms that form the particle.

Figure 4 presents the FTIR spectra of the reinforcement particles produced. In both spectra of Figure 4 it is possible to observe broad band at 1415 cm⁻¹, which is associated with the C-O bond. Other two bands, at 711 and 875 cm⁻¹, also occur due to the C-O bond. The fresh powder and bio-CaCO₃ presented similar bands, except for the very weak band at 2360 cm⁻¹. This weak band happened due to the N-H bond and results from the amines and amides present in the organic part of the eggshell. These results agree with previous studies published by Rezk et al.^[14] and Hossain et al.^[15].



Figure 2. SEM micrographs of in natura and bio-CaCO₃ powders (200×, 500×, and 1000× magnification).

Figure 5 presents the TG/DTG (derivative thermogravimetry) curves of the thermal decomposition analysis of *in natura* and bio-CaCO₃ powders. In the TG/DTG curves in Figure 5, it is possible to observe three stages of weight loss in the *in natura* powder. The first stage between 0 and 100°C, due to the loss of moisture from the material. A more accentuated second stage that occurred between 200 and 400°C. This stage is a result of the decomposition of organic matter.



Figure 3. X-ray spectra of in natura and bio-CaCO₃ particles.



Figure 4. FTIR spectra of the particles of interest (*in natura* and bio-CaCO₂).

The third stage is at 750°C. This characteristic temperature range of the thermal decomposition of calcium carbonate (CaCO₃), releasing carbon dioxide (CO₂) and transforming into calcium oxide (CaO). The bio-CaCO₃ particles, as do not contain an organic part and water, did not present the same first stages as the *in natura* particles. Bio-CaCO₃ particles showed only one stage of weight loss (750°C). This stage is a consequence of the conversion of CaCO₃ into CaO. Similar behavior have been reported by Nath et al.^[16] and Razali et al.^[17].

3.2 Composite materials

The specimens of LDGPE and composites were subjected to an Izod impact test using an 11J pendulum. None of the specimens broke (Figure 6). Therefore, the impact resistance values were not quantified. Although the composites did not allow the collection of numerical impact strength data, from the analysis of SEM images below, one can observe that the reinforcement and matrix particles had a satisfactory adhesion to each other.

With regard to tensile strength, there is little variation in behavior when comparing the matrix to the composites produced. Behera et al.^[18] introduced eggshell particles into epoxy resin and, likewise, did not obtain a differential in tensile strength properties. However, the flexural strength properties showed improvement.

The composites should have considerable impact resistance since good adhesion between matrix and reinforcement favors its improvement. The use of eggshells and calcium carbonate as reinforcement might have the same effect, as reported by Oladele et al.^[19] where the mechanical properties were improved for the two types of reinforcement used in an epoxy matrix. Through the SEM analysis, the calcined particulate had a smaller particle size when compared to the *in natura* particulate.

The particle size of the reinforcement materials is another factor that can influence the impact strength of composites. Sosiati et al.^[20] have reported that composites reinforced with smaller particles have better impact resistance since this materials have a high surface area., This surface area allows a better adhesion between the matrix and the reinforcement.



Figure 5. (a) TG; and (b) DTG curves of in natura and bio-CaCO₃ powders.

Table 2 shows the results obtained by the uniaxial tensile test. Among the properties analyzed, Young's modulus presented a significative difference when one compares the composite with the pure polymer. The best properties were observed in LDGPE/*in natura* composite (an increase of approximately 124%). This increase can be explained by the reinforcement particles being well incorporated into the matrix, which is somehow linked to the geometry and size of the particles, facilitating the interaction with the matrix and not forming agglomerates.

Similar results have been reported by Gbadeyan et al.^[21], which improved the Young's modulus with the addition of eggshells at 5 and 10 wt% in an epoxy matrix. Mustapha et al.^[22] used eggshells and calcium carbonate extracted from them as reinforcement materials in a polypropylene matrix. As in the study mentioned above, the Young's modulus of the composite increased by incorporating the reinforcement material.

The elongation at break decreased by incorporating the reinforcing materials into the polymer matrix, as reported by Williams et al.^[23]. This indicates that the composites are less ductile than the pure polymer. Composites do not suffer great deformation until reach rupture. Thus, break more easily.

In composites with the compatibilizing agent, there was no significant improvement in the mechanical results compared to composites without it. This might have happened because a small amount of compatibilizing agent was used. Perhaps, there were insufficient functional groups to improve the mechanical properties.

In the study presented by Brząkalski et al.^[24], the results of the mechanical properties of LDPE obtained from extrusion were 19 MPa for tensile strength and 213 MPa for Young's modulus. In their research, Liew et al.^[25] found the value of 15 MPa for the tensile strength of LDPE. The mentioned values are in agreement with the results of mechanical properties found for LDGPE in this study.

Figure 7 shows the SEM micrographs of the composite materials. The images were obtained from the ruptured area of the specimens. From the images, one can visualize that the reinforcement materials presented a well-dispersed distribution in the matrix. Besides, the presence of large agglomerates was not observed. Despite the voids at the interface, polymer–particle interactions are strong, resulting in good adhesion between the phases of the composite material. The composites do not suffer great deformation until they reach to rupture, breaking more easily.

Particle size can influence the adhesion between the matrix and the reinforcing phase. Based on the micrographs of the composites, the smaller particles presented better incorporation into the matrix. Thus, controlling the particle size can be used to improve adhesion. With the use of the compatibilizing agent, one can observe an improvement in the covering of the reinforcement particles by the matrix.

In other words, the agent partially improved the adhesion between the matrix and the reinforcement particles. Wu et al.^[26] obtained particles of uniform size which resulted in achieving good dispersion of the reinforcement in the matrix of the films. The analysis of the properties showed that Young's modulus and tensile strength increased as the eggshell content increased. Sosiati et al.^[20] reports that composites reinforced with smaller particles have better adhesion with the composite matrix. According to the author, this is due to the fact that the size of the particles, as are smaller, have a greater surface area, enabling good adhesion.

Figure 8 shows the TG/DTG curves of the polymeric matrix and the composites. These thermograms have only one stage of weight loss. Thus, the thermal degradation process of LDGPE occurs in a single step. The only stage of weight loss was at approximately 475°C for all samples, in agreement with Hajinezhad et al.[27], Duque et al.[28] and Saber et al.[29] in similar studies using LDPE. However, each formulation had a different amount of weight loss. Pure LDGPE lost around 78% of its mass, as did the composite LDGPE/bio-CaCO₂/PE-g-MA. The composites reinforced with in natura particles had very similar weight losses (88-90%). These formulations showed the largest decreases in mass, probably due to organic matter present in them. For this reason, the in natura particles are not very stable at high temperatures. The composite that showed the lowest weight loss (~70 wt%) was LDGPE/bio-CaCO,. This can be explained by the reinforcement particles calcined at high temperatures, which provided greater thermal stability to the composite.



Figure 6. Specimens after impact test (*no break*) in (a) pure LDGPE; (b) LDGPE/*in natura*; (c) LDGPE/*in natura*/PE-g-MA; (d) LDGPE/bio-CaCO₃; (e) LDGPE/bio-CaCO₃/PE-g-MA.

Table 2. Mechanical properties of pure LDGPE and composites.

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	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Pure LDGPE	242.4 ± 132.1	19.7 ± 1.2	33.7 ± 3.5
LDGPE/in natura	544.8 ± 150.3	20.1 ± 0.9	22.7 ± 2.9
LDGPE/ in natura/PE-g-MA	494.3 ± 66.6	19.5 ± 1.2	23.7 ± 1.4
LDGPE/bio-CaCO ₃	463.4 ± 24.4	19.1 ± 1.1	25.3 ± 2.2
LDGPE/bio-CaCO ₃ /PE-g-MA	458.8 ± 23.6	18.6 ± 0.6	24.1 ± 1.8



Figure 7. SEM micrographs of the composites at 200×, 500×, 1050×, and 2250× magnification.



Figure 8. (a) TG; and (b) DTG curves of the composites.



Figure 9. DSC curves obtained for the composites produced in (a) cooling; and (b) second heating.

Table 3. Thermal parameters obtained from the DSC anal	ysis
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	Pure LDGPE	LDGPE/in natura	LDGPE/in natura/PE-g-MA	LDGPE/bio-CaCO ₃	LDGPE/bio-CaCO ₃ /PE-g-MA
Tm (°C)	104	104	104	107	104
$\Delta H_{m}(J/g)$	114	104	93	8	100
Tc (°C)	97	98	97	97	97
$\Delta H_{c}(J/g)$	74	74	57	55	69
Xc (%)	39	37	39	39	39

Figure 9 shows the DSC curves of the pure LDGPE and polymer composites samples during cooling and second heating. The endothermic melting peak of LDGPE and the composites appears at approximately 112°C (Figure 9B). This aspect is a characteristic value expected for this polymer. All samples showed similar peak shapes, but with some variation in width and intensity. Similar behavior has been reported by Santos et al.^[30].

Table 3 shows the thermal parameters obtained from the DSC analysis for the matrix and the composites. The obtained values show no significant variation in the Tg, Tm, and Tc parameters. However, there was a reduction in the enthalpy variation values due to the reinforcement particles that do not melt during the heating step.

Li et al.^[31] and Saikrishnan et al.^[32] have reported values of crystallinity for LDGPE and LDPE between 30 and 50%. In this study, the pure LDGPE had 39% crystallinity. The presence of main-chain branches explains this low value. These short "branches" did not fit into the crystal lattice, leading to a large disorder. The same happened in the study by Alkaron et al.^[33], where he comments that with the addition of calcium carbonate there was a slight influence on the crystallinity of his composites, however with the reinforcement of eggshells the crystallinity suffered a decrease. The composites containing the compatibilizing agent had a slight increase in crystallinity, but the value did not outweigh pure LDGPE.

Brząkalski et al.^[24] processed the LDPE through a flat die extruder. The DSC results showed that its melting

temperature peak (Tc) at 98°C. Zhan et al.^[34] indicated that Tm can vary from 105-116°C for the LDPE. These values are similar to the ones found for LDGPE, which were 112°C for the endothermic melting peak, 104°C for Tm, and 97°C for Tc, as shown in Figure 9B and Table 3. The crystallinity value found for LDGPE also

temperature peak (Tm) was around 112°C and crystallization

corroborates studies in the literature that investigate the crystallinity of conventional LDPE, such as Yu et al.^[35] and Li et al.^[31] found around 36% and 38% for the crystallinity of conventional LDPE.

In general, both *in natura* and bio-CaCO₃ reinforcement particles did not strongly influence the thermal properties of the polymer. This can be explained by the low amount of reinforcement incorporated into the matrix.

4. Conclusion

The thermal treatment by calcination proved to be a simple method to obtain calcium carbonate from eggshells (bio-CaCO₃), as confirmed by XRD and FTIR analyses. There was no significant difference when the reinforcement materials (*in natura* and bio-CaCO₃) were compared. The organic matter and water present in the *in natura* particles did not decrease the properties of the composite. The fresh *in natura* powder proved to be as effective as the bio-CaCO₃ powder. The low-density green polyethylene (LDGPE) showed properties and characteristics similar to conventional low-density polyethylene.

The Young's modulus and impact strength of the composites were the remarkable properties. The composites, when compared to each other, do not present a significant difference. However, when comparing the pure polymer to them, the Young's modulus was improved with the incorporation of both reinforcements. It is observed that eggshell powders, *in natura* or calcined, act mainly on the stiffness and energy absorption during impact tests.

Some factors can be improved in this study to improve certain properties, such as tensile strength. Having a better control of the particle size, aiming to obtain particles of smaller and uniform size. It would be interesting to use a source of PE-g-AM that contains a higher maleic anhydride content or to use a different compatibilizing agent. Incorporate a greater amount of reinforcing particles into the polymeric matrix, with the aim of better understanding the properties that remained the same when comparing pure polymers and composites.

Given the excellent properties of stiffness and impact resistance, some applications for the materials purchased can be pointed out, such as parts for vehicles (windshield wipers, rear-view mirror box), electrical devices (sockets, switches), street lighting, police shield etc.

5. Author's Contribution

- Conceptualization Kássia Peçanha Vieira; Amanda Dantas de Oliveira.
- Data curation Kássia Peçanha Vieira.
- Formal analysis Kássia Peçanha Vieira.
- Funding acquisition Amanda Dantas de Oliveira.
- Investigation Kássia Peçanha Vieira; Alexandra Augusta Reichert.
- Methodology Kássia Peçanha Vieira; Alexandra Augusta Reichert; Dielen Marin; Gabriel Monteiro Cholant; Cesar Augusto Gonçalves Beatrice; Amanda Dantas de Oliviera.
- **Project administration** Kássia Peçanha Vieira; Amanda Dantas de Oliveira.
- **Resources** Amanda Dantas de Oliveira.
- Software NA.
- Supervision Amanda Dantas de Oliveira.
- Validation Kássia Peçanha Vieira.
- Visualization Kássia Peçanha Vieira.
- Writing original draft Kássia Peçanha Vieira.
- Writing review & editing Kássia Peçanha Vieira.

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