Recycling of waste from the rice chain: incorporation of rice husk and rice husk ash in polymeric composites

Reciclagem de resíduos da cadeia do arroz: incorporação de casca de arroz e cinza de casca de arroz em compósitos poliméricos

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ABSTRACT

The high need for polymeric materials and the availability of agro-industrial wastes, such as the rice production chain, demand the development of technologies to obtain polymeric composites based on these waste materials. Therefore, this work aims to develop materials using low density polyethylene (LDPE) as a polymer matrix and rice husk or rice husk ash, prepared by micronization in a whirlwind mill, as reinforcing fillers. The processing was carried out by injection molding, with formulations containing 20%, 30% and 40% of the filler. Tensile strength, hardness and water absorption properties were evaluated. The tensile strength of composites containing rice husk ash was higher than the same parameter for composites containing rice husk as filler. The highest tensile strength of 9.26 N/mm² was found for the material containing 20% of rice husk ash. The shore D hardness of materials containing rice husk ash was slightly higher. Regarding water absorption, the composites containing rice husk ash were those with lower absorption and all developed materials presented water absorption below 1.1%. Based on the results, we concluded that the composites have potential properties for the manufacture of polymeric consumer goods.

Keywords: Rice husk; Rice husk ash; Polymeric composites

RESUMO

A alta necessidade por materiais poliméricos e a disponibilidade de resíduos agroindustriais, como os da cadeia de produção do arroz, demandam o desenvolvimento de tecnologias para a obtenção de compósitos poliméricos a partir destes materiais resíduais. Neste sentido, este trabalho tem como objetivo o desenvolvimento de materiais, utilizando o polietileno de baixa densidade (PEBD) como matriz polimérica e cascas de arroz ou cinzas da casca de arroz, preparadas pela micronização em um moinho turbilhão, como cargas de reforço. Os processamentos foram realizados pela moldagem por injeção, com formulações contendo 20%, 30% e 40% de carga. As propriedades de resistência a tração, dureza e absorção de água foram avaliadas. A resistência à tração dos compósitos contendo as cinzas da casca
de arroz foram superiores aos compósitos contendo a casca de arroz como carga. A maior resistência à tração, de 9,26 N/mm², foi encontrada para o material contendo 20% de cinzas de casca de arroz. A dureza shore D dos materiais contendo as cinzas foi ligeiramente superior. Com relação a absorção de água, os compósitos contendo as cinzas de casca de arroz foram aqueles com menor absorção, sendo que, todos os materiais desenvolvidos apresentaram absorção de água inferior a 1,1%. Com base nos resultados, conclui-se que os compósitos produzidos possuem propriedades potenciais para a fabricação de bens de consumo poliméricos.

**Palavras-chave:** Casca de arroz; Cinza da casca de arroz; Compósitos poliméricos

### 1 INTRODUCTION

The search for sustainable management, the efficient use of natural resources and the need to develop new materials and technologies are relevant topics nowadays (ONU, 2021). Due to the high consumption of contemporary society, natural resources are used excessively, causing negative impacts on the environment and requiring sustainable practices to solve existing environmental problems. In this context, lignocellulosic waste may be an alternative for the production of greener consumer products. Indeed, these wastes are inevitably generated and, when not handled correctly, are eliminated by burning or burying, generating significant pollution (GRYCZAK; BERNADIN, 2021; GUNA et al., 2020).

One of the most abundant agro-industrial waste is rice husk, which can be considered a biodegradable filler, due to its large percentage of cellulose. However, the application of this waste is hampered by characteristics such as its abrasive and irregular surface and, mainly, by the amount of silica in its composition. Therefore, the natural degradation in the soil is limited, which causes environmental problems when large amounts are disposed on the soil. Its use as animal feed is also not recommended, as rice husk has low nutritional values. Thus, the use in the agricultural sector is precarious and alternatives to mitigate environmental impacts are required (VARALA et al., 2019; THOMAS, 2018; HUNER, 2017).

In Brazil, the crop of raw rice recorded in the 2020/2021 harvest was 11.8 million tons. The south and central-west regions are the main producers (CONAB,
From the grain processing, approximately 20% of the amount becomes rice husk, generated during the grain husking process to obtain the husked rice (GRYCZAK; BERNADIN, 2021; MOURA et al., 2018).

As a way to solve the management of this material, the combustion for energy generation is very common, which results in rice husk ash. The burning of this new waste, when performed inappropriately, triggers many environmental impacts, such as air pollution and water and soil contamination (BASTA, 2019). Given this, composite technology is an excellent approach for using agricultural by-products (YUSUF et al., 2017).

The rice husk waste has properties such as biodegradability, low cost, low density, high modulus and proficient mechanical properties. In addition, it is biologically efficient, which enhances its application as a filler in polymer composites. Furthermore, the reliability in the homogeneity of rice husk properties as a filler, regardless of the production region, generates robust and reliable manufacturing processes regarding the characteristics of the composites obtained (MOHAMED et al., 2020; KUMAR et al., 2019; HUNER, 2017).

The properties of this waste, added to the environmental advantages, demonstrate that the application of rice husk as a filler in polymer composites is very promising for obtaining new, weightless and low-cost sustainable materials (SUN et al., 2019). Consequently, the use of rice husk as a filler in polymer composites has gradually increased, as the recycling of this agricultural waste has benefits, in addition to reintegrating it into value chains (ARIDI et al., 2016).

The rice husk ash waste, on its turn, is obtained from rice husk combustion processes that generate energy and heat. The technology used on a larger scale is direct combustion, due to the fact that it presents low investments and low complexity. Nevertheless, due to the high silica content of rice husk, this is not a complete solution, as it generates a great amount of ash (LAWAL et al., 2019; QUISPE et al., 2017). The most studied alternative for the application of these rice husk ash is its incorporation in mortar. However, as combustion is carried out for
the purpose of energy generation and not due to the ash properties, its characteristics such as reactivity and pozzolanic properties are not interesting for application in mortar (SONAT et al., 2019; MARTIRENA; MONZÓ, 2018).

To obtain high quality rice husk ash suitable for application in mortars, the combustion has to be strictly controlled and the ash must be pre-treated. These demands reduce the potential of this solution. Conventional burning technologies for power generation produce ash with little amorphous silica and sometimes even unburnt ash particles, which also hinders the application in scale as a component of mortars (OLUTOGE; ADESINA, 2019; MUTHUIKRISHNAN et al., 2019; MARTIRENA; MONZÓ, 2018). Therefore, the application of rice husk ash as filler in polymer composites is an alternative that should be studied.

There is a growing demand for advanced materials with better properties to meet new requirements or to replace existing materials. The modification of polymers by adding different fillers is an effective method to generate an infinite number of new materials with customized properties (AGRAWAL; SATAPATHY, 2015). Furthermore, the incorporation of these waste as a filler reduces the demand for polymers of non-renewable origin, which are mostly obtained from petroleum, reducing the pressure on this resource. Finally, agro-industrial wastes that are highly available generate value, reducing the loss of these materials, with an adequate management of these lignocellulosic wastes (VERCHER et al., 2020; HUI et al., 2020).

Due to the demand for solutions for these agro-industrial wastes, the objective of this work was to develop polymeric composites through injection molding technology. Low density polyethylene (LDPE) was used as the polymer matrix and rice husk or rice husk ash as reinforcement fillers. The materials were then submitted to physical and mechanical tests, to evaluate the properties of the obtained composites.
2 MATERIALS AND METHODOLOGY

The rice husk (RH) and rice husk ash (RHA) wastes used in the study were tapped from the rice chain agro-industry in the state of Rio Grande do Sul, Brazil. These materials were prepared by micronization in a whirlwind mill, Schilling, model MC 250. Figure 1 depicts the materials before and after the micronization processes. The analysis of the particle size distribution of the wastes before and after micronization was obtained with a Bertel electromagnetic sieve stirrer, with 32, 48, 80, 170, 250 and 500 mesh sieves.

Figure 1 – Rice Husk and Rice Husk Ash - Before and After Micronizations

Low Density Polyethylene (LDPE) BC818, manufactured by Braskem, was selected as the polymer matrix material to obtain the composites. The inputs were oven-dried at 90ºC to remove moisture. Then, the samples were weighed, according to the formulations described in the Table. After weighing, the materials were manually mixed, followed by the processing of the composites in a Bonmaq
injection molding machine, model APTA 80. Injection molding was performed at 180°C, 190°C and 190°C in the three heating zones of the equipment and at 200°C at the injection nozzle.

Table 1 – Formulation of Composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rice Husk (%)</th>
<th>Rice Husk Ash (%)</th>
<th>LDPE BC818 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH20</td>
<td>20</td>
<td>_</td>
<td>80</td>
</tr>
<tr>
<td>RH30</td>
<td>30</td>
<td>_</td>
<td>70</td>
</tr>
<tr>
<td>RH40</td>
<td>40</td>
<td>_</td>
<td>60</td>
</tr>
<tr>
<td>RHA20</td>
<td>_</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>RHA30</td>
<td>_</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>RHA40</td>
<td>_</td>
<td>40</td>
<td>60</td>
</tr>
</tbody>
</table>

Source: Authors, 2021

Figure 2 shows the shape of the injected specimens from one of the RH20 and RHA20 samples. An injection mold was used in the injection molding machine with the cavities in a suitable format to obtain specimens according to the respective characterization tests.

Figure 2 – Injected specimens in the shape of a tie and strap.

Source: Authors, 2021

The tensile tests were carried out in accordance with the ASTM D 638-14 standard, with type IV specimens. For each sample, 3 tie-shaped specimens were
used, as per Figure 2. The preparation for the tests was carried out, keeping them at 23°C for 24 hours, then submitting to tests in a Maqtest universal testing machine. A speed of 50 mm/min was used in the test, obtaining the result of the Tensile Strength in N/mm², by the average of the results of the 3 specimens of each sample.

The shore D hardness of the composites was obtained according to ASTM D 2240-15 standard. For each sample, 3 specimens were used in strip format, as shown in Figure 2. The preparation for the tests was carried out, keeping the samples at 23°C for 24 hours, submitting each strip to 3 measurement processes, using a Pantec Shore D durometer. The final result was obtained by averaging 9 hardness measurements of each sample.

Determination of water absorption was performed according to ASTM D570-98. To carry out this test, the samples were dried in an oven at 50°C for a period of 24 hours. Subsequently, the samples were weighed on a semi-analytical balance with a precision of 0.001 and then immersed in a beaker of ultrapure water, remaining in immersion for 24 hours at 23°C. After 24 hours of immersion, the samples were removed from the water, lightly dried to remove surface water and weighed again. The result was obtained by the average of the 4 samples of each composite.

3 RESULTS AND DISCUSSION

Table 2 shows the results of the tensile strength, hardness and water absorption tests of the composites obtained in the study.

In Table 3, the data from the analysis of particle size distribution of rice husk and rice husk ash is presented. The average particle size of the natural rice husk is larger than the average particle size of the rice husk ash in the natural format. Consequently, when submitting the two wastes to the same micronization process, the average particle size of the micronized ash is smaller. It is important to note
that up to the 250 mesh sieve, only 21.56% of the micronized rice husk ash particles were retained, while for the rice husk they were 87.83%. This difference in particle size of micronized materials can generate different properties in composites when they are applied as fillers (ERDOGAN; HUNER, 2018; SHIRP; BARRIO, 2018).

**Table 2 – Results of Physical and Mechanical Tests**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength (N/mm²)</th>
<th>Shore D hardness</th>
<th>Water Absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHA20</td>
<td>9.26</td>
<td>47.22</td>
<td>0.07</td>
</tr>
<tr>
<td>RHA30</td>
<td>9.20</td>
<td>49.11</td>
<td>0.11</td>
</tr>
<tr>
<td>RHA40</td>
<td>8.79</td>
<td>51.33</td>
<td>0.15</td>
</tr>
<tr>
<td>RH20</td>
<td>8.03</td>
<td>45.78</td>
<td>0.25</td>
</tr>
<tr>
<td>RH30</td>
<td>7.39</td>
<td>47.11</td>
<td>0.49</td>
</tr>
<tr>
<td>RH40</td>
<td>6.42</td>
<td>49.33</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Source: Authors, 2021

**Table 3 – Particle size distribution per material**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage amount of material retained on each sieve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>32 mesh</td>
</tr>
<tr>
<td>Natural Husk</td>
<td>98.78 %</td>
</tr>
<tr>
<td>Micronized Husk</td>
<td>2.83 %</td>
</tr>
<tr>
<td>Natural Ash</td>
<td>79.28 %</td>
</tr>
<tr>
<td>Micronized Ash</td>
<td>0.12 %</td>
</tr>
</tbody>
</table>

Source: Authors, 2021

Graph 1 contains the tensile strength data obtained in the study. An increase in the percentage of the composites containing rice husk reduces the tensile strength. This behavior is related to the compatibility of the hydrophilic rice husk with the hydrophobic thermoplastic polymer, resulting in an inadequate adhesion of the rice husk with the LDPE (HIDALGO-SALAZAR; SALINAS, 2019; ROYAN et al., 2018; ERDOGAN; HUNER, 2018).
The decrease in tensile strength with the increase in the percentage of rice husk in the composite is also justified by the reduction in material flow and lower compaction during mechanical processing. The greater amount of husk in the composites can even generate agglomerations of particles in certain regions of the material. This effect can negatively affect the mechanical properties, as the proper encapsulation of the charge by the polymer matrix is impaired (BHARATHIRAJA et al., 2016; YEH et al., 2015).

The reduction in tensile strength, related to the increase in the percentage of composite rice husk filler, was also observed in the studies of Awang et al. (2019). These researchers used micronized rice husk in blends with polypropylene (PP), processed by an injection molding technology. The authors pointed out that the reduction in tensile strength, due to the increase in the amount of rice husk, was caused not only by the incompatibility of the materials, but also by the incompatible deformation of the husk and the thermoplastic polymer.

Graph 1 shows that in the composites developed with rice husk ash, tensile strength reduces with the increase in the percentage of this filler. Therefore, in the study of Nam et al. (2019), composites containing rice husk waste and also composites containing rice husk ash were evaluated. The authors found from the
results that, as in the present study, there is a reduction in the tensile strength property with the incorporation of these fillers. The loss of this mechanical property is attributed to the incompatibility between the fillers and the polymer matrix. Data from composites containing rice husk and husk ash evidence that the incorporation of ash as filler generates materials with greater tensile strength properties. It is important to note that the polymer matrix is hydrophobic, as it is the silica present in the fillers (FERNANDES et al., 2018). Therefore, as silica is in a higher percentage amount in rice husk ash, it is more compatible with LDPE than rice husk, which has less silica and more hydrophilic components such as cellulose and lignin in its composition.

The transfer of tensions between the polymer matrix and the filler when under mechanical stress is another characteristic that negatively contributes to the tensile strength. Accordingly, a greater amount of filler generates a reduction in this property of the composites. Thus, the incorporation of fillers with different stiffness from the polymer matrix reduces the efficiency of stress transfer. This, added to the reduction of the chemical interactions of the elements of the composites, generates the reduction of the mechanical property verified in the results (BATTEGAZZORE E FRACHE, 2019; PONDONG et al., 2018).

In this study, the processing methodology used to obtain the composites was the injection molding, as well as in the study of Battegazzore e Frache (2019), who also observed a reduction in tensile strength in polyamide and rice husk ash composites. The characteristic of reduced tensile strength by the addition of rice husk ash is also observed with the use of other processing methodologies, such as hot pressing and with the use of different polymeric matrix materials such as biodegradable polymers, rubbers and epoxy resins (Wu et al. 2018; FERNANDES et al. 2018; DISHOVSKY et al. 2017).

The reduction in tensile strength does not preclude the application of rice husk and rice husk ash as fillers in polymer composites. It is, though, a characteristic that impacts the material properties and needs to be observed when
developing new materials. Another property that is impacted by the incorporation of rice waste fillers is the hardness of the materials.

In Graph 2 presents the results of the shore D hardness tests. For rice husk, it is verified that the increase in the concentration of this filler in the composites generates an increase in hardness. Rice husk has greater rigidity than the polymeric matrix of LDPE. In addition, it decreases the mobility of the polymeric matrix chains, due to the incorporation of the rice husk filler. For these reasons, a higher percentage of rice husk generates greater hardness (SADIK et al., 2021; SAJITH et al. 2017).

Graph 2 – Shore D Hardness Test Results

![Graph showing Shore D Hardness Test Results](source)

Source: Authors, 2021

The impact of the percentage increase of rice husk on the hardness of polymeric composites is observed in other studies, such as in Sabbatini et al. (2017), by adding micronized shells to polymethylmethacrylate (PMMA), promoting greater hardness of the composite. Kumar et al. (2019) applied rice husk to obtain panels, with the use of an epoxy binder, also increasing the hardness of the materials. Similarly, Singh et al. (2019) used corn starch as a binder to obtain panels and reported an increase in the hardness properties of the composites by increasing the husk content.
For the hardness property of composites, in addition to the amount of lignocellulosic filler and matrix polymer hardness, the type, structure and particle size of the filler also influence this property, as it reflects the resistance to penetration of the material by other objects (VERCHER et al., 2020).

In the results of the shore D hardness tests of the composites obtained by using rice husk ash, the increase in the filler content also promoted greater hardness of the materials. Compared with rice husk composites, the hardness is higher, and the particles of rice husk ash have a smaller size, as shown in Table 3. It should be noted that the minimization of voids and adequate dispersion of the filler in the polymer matrix increases the hardness of the materials and affects the mobility of the molecular chains of the polymer matrix (BISHT; GOPE, 2018; PONDONG et al. 2015). Therefore, the smaller particle size of the rice husk ash filler promoted a better compaction of the material and a more homogeneous distribution of the particles, resulting in greater hardness.

Regarding studies on composites containing rice husk ash through injection molding processing, Pondong et al. (2018) verified that the incorporation of rice husk ash increases the Young’s modulus of the composites. Consequently, materials with greater rigidity and greater hardness are obtained through the introduction of rice husk ash filler, since this filler is more rigid than the polymer matrix.

In the present study, the water absorption of the composites was also evaluated, as this material property is essential for the definition of suitable practical applications (LAI et al., 2017). Therefore, all materials obtained in the study presented only a minimum of water absorption, with percentages below 1.1%.

In the materials obtained by the incorporation of rice husk, the increase in the percentage of this filler generated a greater water absorption, as shown in Graph 3. This increase in water absorption occurs due to the hydrophilic characteristic of the rice husk (HUNER, 2017; YEH et al., 2015).
These results are in agreement with other studies, in which the absorption of water in composites increases as the percentage of rice husk increases. (ERDOGAN; HUNER, 2018; LAI et al., 2017; LUNA et al., 2015). Depending on the processing methodology, water absorption can be very expressive, reaching up to 45% of water absorption (SOUZA et al. 2017). There are also examples of studies in which rice husk composites present water absorption of less than 0.6%. This occurs due to the adequate compaction of the material and the encapsulation of the filler by the polymeric matrix, resulting in a minimum level of water absorption (SABBATINI et al., 2017).

For composites containing rice husk ash, the data indicate that water absorption is lower than in composites containing rice husk, which is linked to the higher percentage of silica in the ash. As silica is hydrophobic, it does not contribute to water absorption (Fernandes et al., 2018). However, as shown in the results, the composites that contain ash as a filler also absorb a minimum of water. This absorption increases with the increase in the percentage of ash in the samples, which is due to the voids in the microstructure of the composite. Indeed, by increasing the filler amount, the voids where the water will be retained also increase. (BOITT et al., 2014).
4 CONCLUSION

In the present study, polymeric composites were developed from rice husk or rice husk ash, prepared by micronization in a whirlwind mill. Processing was carried out using LDPE as polymer matrix, through an injection molding technology. The percentages of rice husk or rice husk ash as reinforcement fillers were 20%, 30% and 40%. Suitable flow and compaction were observed in all composites during the injection molding processes, thus obtaining suitable samples to carry out the characterization tests. From the characterization results, a reduction in the tensile strength of composites was verified by increasing the percentage of fillers. This reduction was around 5% between the composites CCA40 and CCA20. On the other hand, between the composites CA40 and CA20, the reduction in tensile strength was 20%, due to the increase in the filler. The highest tensile strength, of 9.26 N/mm², was obtained by the material containing 20% of rice husk ash, while the material containing 20% of rice husk presented a tensile strength of 8.03 N/mm². Regarding the shore D hardness of the materials, the percentage increase in fillers resulted in an increase the hardness. In this test, the composites containing the rice husk had hardness values ranging from 45.78 to 49.33 Shore D, while the materials containing a rice husk ash ranged from 47.22 to 51.33 Shore D. In the water absorption test, an increase in absorption was observed in relation to the percentage increase in fillers. The lowest water absorption was found for the composite CCA20, containing rice husk ash, and was 0.07%, as well as for CCA40, which presented 0.15% of water absorption. For the composites containing rice husk, the lowest water absorption was from the CA20 material, with 0.25% of absorption, while the highest water absorption was obtained by the CA40 composite, which was 1.03%. All composites presented water absorption lower than 1.1%, that is, the materials obtained have very low hygroscopicity. Overall, the composites containing rice husk ash showed better results in the tests due to the smaller particle size of the ash and the higher percentage amount of silica. These
samples obtained better compaction, reduced voids and better encapsulation of particles by the polymer matrix. However, all composites showed adequate flow for processing by injection molding technology, showing promising characteristics in terms of tensile strength, shore D hardness and water absorption. The results lead us to conclude that composites containing rice husk or rice husk ash have potential properties for the manufacture of polymeric consumer goods.

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