

Obtaining and characterization of a composite with polymer matrix and corn cob waste filler

Obtenção e caracterização de um compósito com matriz de resina poliéster e carga de resíduos do sabugo de milho

Obtención y caracterización de un compuesto con matriz de resina de poliéster y carga de residuos de sabugo de maíz

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Abstract

It was studied the feasibility of using corn cob to obtain a polymer composite. It was used of the corn cob in Three-grain sizes, and some formulations of the composite of polyester resin and powders were used, and the most appropriate formulation was chosen. For the characterization of the composite thermal and mechanical properties were determined. The main advantage of the composite was the low density, about 1.06 kg/m³ for the thick powder formulation. The composite presented an inferior mechanical behavior concerning the resin for all the studied particle sizes and formulations. The composite presented better mechanicals

results for the bending strength, reaching 25.3 MPa for the thick powder formulation. The composite also proved itself to be viable for thermal applications since it has average thermal conductivity inferior to 0.21 W/m, being classified as thermal insulation and can be used to manufacture structures that do not require significant mechanical strength, such as tables, chairs, benches, panels, works of art, crafts and solar prototypes, such as ovens and stoves.

Keywords: Polymer composites; Agricultural waste; Corn cob; Low density and strength; Thermal insulation.

Resumo

Foi estudada a viabilidade do uso de sabugo de milho para obtenção de um compósito polimérico. Utilizou-se o sabugo de milho em tamanhos de grãos Três, sendo utilizadas algumas formulações do compósito de resina poliéster e pós, sendo escolhida a formulação mais adequada. Para a caracterização do compósito foram determinadas propriedades térmicas e mecânicas. A principal vantagem do compósito era a baixa densidade, cerca de 1,06 kg / m³ para a formulação de pó espesso. O compósito apresentou comportamento mecânico inferior em relação à resina para todos os tamanhos de partículas e formulações estudados. O compósito apresentou melhores resultados mecânicos para a resistência à flexão, chegando a 25,3 MPa para a formulação em pó grosso. O compósito também se mostrou viável para aplicações térmicas por apresentar condutividade térmica média inferior a 0,21 W / m, sendo classificado como isolante térmico e podendo ser utilizado na fabricação de estruturas que não requeiram resistência mecânica significativa, como mesas, cadeiras, bancos, painéis, obras de arte, artesanato e protótipos solares, como fornos e fogões.

Palavras-chave: Compósitos de polímero; Resíduos agrícolas; Espiga de milho; Baixa densidade e resistência; Isolamento térmico.

Resumen

Se estudió la viabilidad de utilizar mazorcas de maíz para obtener un compuesto polimérico. Se utilizó mazorca de maíz en tamaños de Tres granos, y se utilizaron algunas formulaciones del compuesto de resina de poliéster y polvos, y se eligió la formulación más adecuada. Para la caracterización del composite se determinaron las propiedades térmicas y mecánicas. La principal ventaja del material compuesto fue la baja densidad, aproximadamente 1,06 kg / m³ para la formulación de polvo espeso. El composite presentó un comportamiento mecánico inferior a la resina para todos los tamaños de partícula y formulaciones estudiadas. El composite presentó mejores resultados mecánicos para la resistencia a la flexión, alcanzando 25,3 MPa

para la formulación de polvo espeso. El composite también demostró ser viable para aplicaciones térmicas ya que tiene una conductividad térmica media inferior a 0,21 W / m, siendo clasificado como aislante térmico y puede utilizarse para fabricar estructuras que no requieran una resistencia mecánica significativa, como mesas, sillas, bancos, paneles, obras de arte, artesanías y prototipos solares, como hornos y estufas.

Palabras clave: Compuestos poliméricos; Residuos agrícolas; Mazorca de maíz; Baja densidad y resistencia; Aislamiento térmico.

1. Introduction

Sustainability has gained increasing importance in society, and environmental issues have been increasing, the focus of studies worldwide. The literature presents some works on composite materials on the use of particulate composites for the manufacture of industrial panels.(Akinyemi, Afolayan, & Ogunji Oluwatobi, 2016).

Brazil is one of the largest grain producers in the world. Projections of the Ministry of Agriculture indicate that Brazil will have in 2021 a 195 million tones production of grains, in an area more than 50.7 million hectares. (Rossi, 2011).

One of the current problems in agriculture and associated agribusiness is the little concern concerning the generation of wastes and their subsequent destination or treatment. According to the Ministry of Agriculture, Brazil is the third-largest producer of corn, totaling 70.0 million tons in 2015. According to the Brazilian Association of Biomass Industries - ABIB, corn processing residues consist of straw and corncobs, with a residual factor of 58%. (MAPA, 2012).

Biomass resources are plentiful, renewable, and not competitive to human and animal consumption. Making value-added products from agricultural lignocellulosic biomass waste is attractive in terms of cost and pollution management, (Liu, Li, Gai, Yang, & Mao, 2016).

Corn is produced for feeding and is one of the crops generators of waste, and the grains provide a series of industrial products. However, some parts of the plant do not have direct use, and the corncob enters the category of waste from agriculture that has not yet had their potential fully exploited, (Silveira, 2010).

As one of the waste-generating crops, maize is produced for food, and grains provide several industrialized products. Some parts of the plant have no direct use, and corncob falls into the category of agricultural waste that has not yet fully exploited its potential.

The corncob is the central part of the corncob, where the corn kernels are fixed. For

every 100 kg of corn cobs, approximately 18 kg is formed by the cob. With so much waste being discarded comes the concern with the environment and how it would be possible to reuse such waste.

Corn cob can also be used as a thermal insulator in the applications focused on developing biological and sustainable materials. (Pinto et al., 2011)

Facing the environmental problem caused by the accumulation of polymeric materials that take hundreds of years to decompose after their disposal, alternatives that promote the reduction of the use of these materials are needed. (Chen et al., 2012)

These environmental concerns give priority to the development of innovative technologies for new polymeric materials from renewable raw materials, (Zhang, Garrison, Madbouly, & Kessler, 2017).

The composites emerged from the need for the application of materials having specific properties that are not found in metals, polymers, and ceramics. It is desired that the composite materials present the lightness of the polymers, the resistance of the metals, and the thermal capacity of the ceramic materials. Can be said that compound materials have the characteristics of each material component in only one material. (Callister & Rethwisch, 2016)

A corn cob particleboard can be an alternative affordable and sustainable thermal and sound insulation product fit to be applied in the building industry. (Faustino et al., 2012)

Panels made of particulate composite materials may represent an alternative for use as thermal and acoustic insulators, with secure processing, low cost, good aesthetics, and ecologically sustainable characteristics suitable for industrial applications.

The use of corn residues or corn cob byproducts is still incipient in obtaining composite materials. Few articles were found in the polymer composites literature, object of this work, and none of them using a polyester resin matrix. Among the few works found, none had a polyester resin matrix.

Ramos, (2013), in his Master's dissertation obtained and characterized a polypropylene matrix composite and corn cobs from agricultural residues. Cob and polypropylene powders were mixed in an extruder, injection molded and characterized. Mass loads of cob powder of 5, 10, 20 and 30% were used and a low adhesion between the matrix and the load was observed, producing a decrease in the mechanical strength of the composites.

Panthapulakkal and Sain, (2007), studied the feasibility of using agro-residues such as wheat straw and corn cob embedded in a high density polyethylene matrix, producing composites. They proved that it was possible to process these composites for temperatures below 200°C.

Guan and Hanna, (2004), assessed the physical and mechanical properties of composites of starch acetate and cellulose acetate with corn bucket. they assessed the resistance to compression and concluded that it grewed in accordance with the increased content of sabugo.

Obasi, (2012) studied the biodegradability and mechanical behavior of composites with polyethylene mariz and corn cob flour. It demonstrated that corncob flour caused an increase in the young modulus of the composites and that the use of coupling agents caused an improvement in the mechanical performance of the composites.

Faludi, Dora, Renner, Móczó, and Pukánszky, (2013), obtained and studied composites with PLA (lactic polyacid) matrix and corn cob flour. demonstrated the good interaction between natri and load, favoring an increase in mechanical strength.

Yimsamerjit, Surin, and Wong-On, (2007), evaluated the viability of composites with corncob and acetate and amidium. used cob loads of up to 30% to obtain composites by compression molding. They have proven increases in density and tensile strength with increased load.

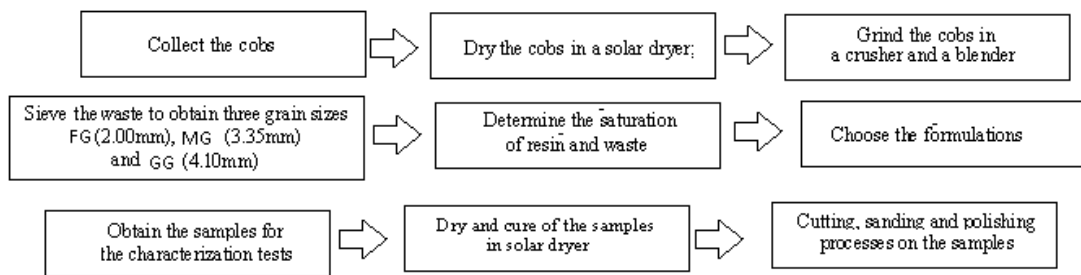
This paper presents a study to obtain and characterize a polymeric matrix composite material using residues generated by corn cobs crushing. It will be demonstrated the viability of using the waste generated for the fabrication of structures with low mechanical load demand and good thermal properties results, which may be a differential of applicability concerning other composite materials that use waste in its composition.

It is considered that the process of obtaining corn cob powders and composites for three different granulometry represents a significant advance towards the use of corn by-products in Brazil, due to their vast corn production, reducing waste, in addition to providing environmentally friendly use.

2. Materials and Methods

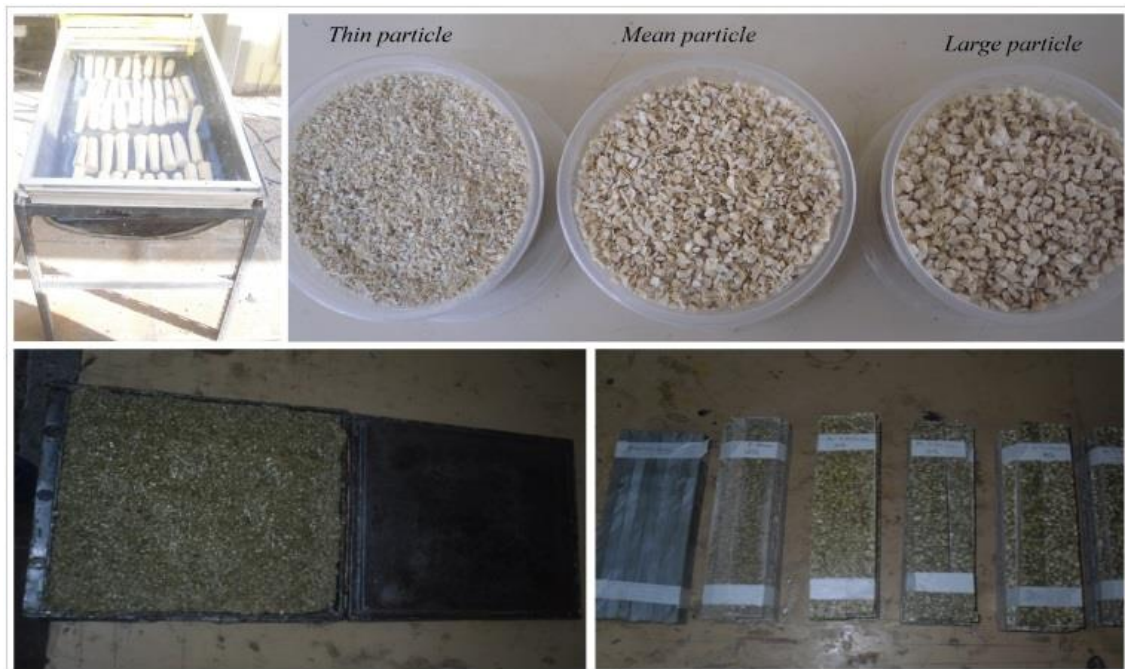
The procedures for obtaining the powders of the corn cob and the composites for three different granulomere are described in the flowchart of Figure 1 and shown in Figure 2.

Figure 1. Procedures for obtaining the powders of the corn cob and the composites.



Source: Authors.

Figure 2. Obtained composites and manufactured plates.



Source: Authors.

The matrix of the composite was terephthalic polyester. The release agent was the carnauba wax to obtain a better surface finish as well as to facilitate the removal of mold plates in the process of obtaining the test sample. The catalyst used was methyl-ethyl-ketone peroxide into phthalate dimethyl provider or curing primer for unsaturated polyester resin and vinyl ester.

The saturation between the matrix and the residue was obtained for 20% by weight for the Thin Particle (TP), 30% to the Mean Particle (MP), and 40% for the Large Particle (LP). This saturation was characterized by the impossibility of manual mixing between the composite elements. For the comparative analysis of the obtained powders, the formulation with 20%

residue corncob was chosen.

All formulations with the composite had a load of corn cob powder corresponding to 20% of the total mass, thus having 80% resin. The formulations used in the study were TP 20% ((Thin Particle 20%) + Resin (80%)); PM 20% (Medium Particle (20%) + Resin (80%)); LP 20% (Large Particle + Resin (80%). To fill the mold, 400 g of resin and 80 grams of residue in its three grain sizes were used.

Tensile and flexural strength, as well as thermal resistance parameters, such as thermal conductivity, thermal capacity, thermal diffusivity, and thermal resistivity, were determined. Density and water absorption percentage were also determined. It was also performed microstructure analysis with SEM image.

Procedures used for the tensile test, including the specimens measurements, were taken from (ASTM-D638, 2014). The three-point bending test was performed according to (ASTM-D 790, 2003). A digital densimeter, DSL 910 with repeatability of $\pm 0.003 \text{ g/cm}^3$ was used to obtain the density of the composite with different granulometry.

The water absorption test was conducted according to (ASTM D570, 2014). To obtain the thermo-physical properties, thermal properties analyzer, Decagon Devices KD2 Pro, was used. The thermal conductivity, specific heat, thermal resistance, and thermal diffusivity of the fiber and the proposed composite were determined.

SEM tests were performed in the fracture surfaces of the composite and mapping of the existing elements, verifying its phases and homogeneity through a Hitachi TM 3000 Scanning Electron Microscope.

3. Results and Discussion

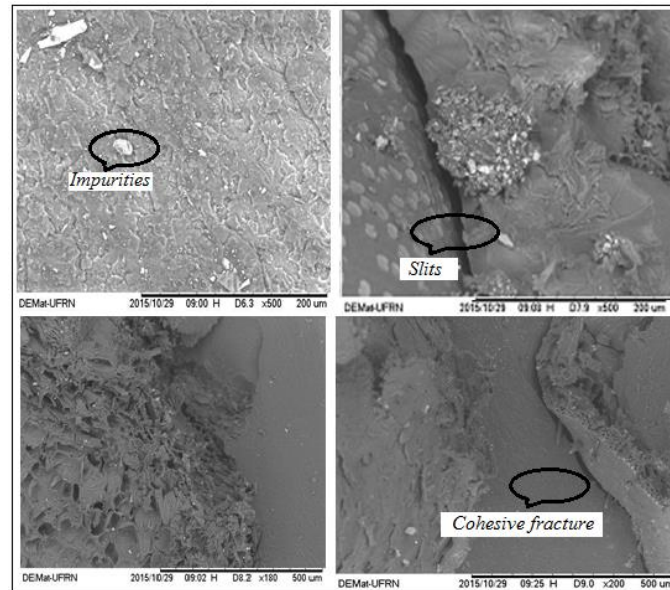
The results of the performed tests for the characterization of the proposed and studied composite are presented for three different granularities.

3.1 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy (SEM) test was used to investigate the adhesion between the particulate and the matrix and to study the fracture mechanisms. The behavior of fracture in composites can be affected by the particulate/matrix interaction, some voids in the analyzed sample, load, and environment in which the sample was submitted. Figure 3 shows the micrographs (500X) for matrix, TP, MP, and LP in the proportion of 20% by mass between

particulate/matrix.

Figure 3. SEM (500X) of the matrix, TP, MP and LP in the proportion 20%.



Source: Authors.

The SEM analysis showed that there was a deficiency of adhesion between matrix and residue, cohesive fracture in the matrix, presence of impurity (which may be substance contained in the particulate), no penetration of resin inside the structure of the particulate and fragile fracture.

3.2 Mechanical Strength

Table 1 presents the results of the parameters measured in mechanical tests for resin and composites formulations.

Table 1. Results of the tensile and flexural strength.

MATRIX/COMPOSITES	Tensile Strength (MPa)	Flexural Strength (MPa)
RESIN	20.4 ±1.25	60.4±3.56
C₁ - TP 20%	3.25 ±0.29	18.70±1.15
C₂ - MP 20%	2.94 ± 0.22	19.30± 1.89
C₃ - LP 20%	2.80 ± 0.21	25.30 ± 2.32

Source: Authors.

The results show that as the granulometry increases, there is a decrease in tensile strength. The same behavior can be observed to strain. These conclusions are associated with a more homogeneous mixture of the composite for the powder of smaller particle size, resulting in better mechanical behavior. The formulation with the best result concerning tensile strength was 20% TP.

The composite in its three granulometry presented a much lower tensile strength than the polyester resin. It indicates a certain composite fragility and that the materials not suitable for use when medium and significant tensile stresses are presented.

About the elongation, it showed a decrease concerning the matrix, but much smaller than the one verified regarding the tensile strength.

The composite and matrix had the same relative behavior. The flexural strength of the composites for the three granulometry was much lower than the matrix, but with values more significant than the tensile strength.

Regarding the deflection, the decrease was lower than the one related to the flexural strength. The composite can be used in its three granulometry, with the same proportion of residue, for applications that do not require great bending efforts. The granulometry that presented better flexural strength was LP 20%.

3.3 Water absorption

The methods adopted for the water absorption test were those established by ASTM D570-9820. The water absorption test was performed with distilled water and seawater. In all, the composites saturated within 50 days of immersion (on average). Table 2 shows the mean

data obtained in the water absorption test by the resin and the studied composite formulations.

Table 2. Water absorption by resin and composites.

MATRIX/COMPOSITES	DISTILLED WATER (%)	SEA WATER (%)
RESIN	0.582	0.561
C₁ - TP 20%	7.264	6.852
C₂ - MP 20%	6.747	7.977
C₃ - LP 20%	12.020	10.805

Source: Authors.

The average water absorption behavior in the two media demonstrated very high resin supremacy over the studied composite formulation in its three granulometry. This higher capacity of water absorption was due to the great hygroscopy of the residue of the corn cob.

The LP, 20% formulation, was the worst result, and the TP 20% had better behavior with this parameter. Although much higher than that of the resin, the water absorption of the composite does not impair its exposure in aqueous media.

The resin presented almost identical water absorption for the two media. The TP had a better result for seawater; MP for distilled water and LP for seawater.

3.4 Thermal analysis

Table 3 presents the results of Volumetric Specific Heat, Thermal Diffusivity, Thermal Conductivity and Thermal Resistivity obtained in the thermal analysis test.

Table 3. Thermal properties of the composite's formulations.

MATRIX/COMPOSITES	Volumetric Specific Heat C (MJ/m³K)	Thermal Diffusivity D (mm²/s)	Thermal Conductivity K (W/mK)	Thermal Resistivity R (°C·m/W)
RESIN	2.586 ± 0.028	0.090 ± 0.002	0.232 ± 0.005	4.438 ± 0.78
C₁ - TP 20%	1.788 ± 0.019	0.091 ± 0.001	0.163 ± 0.004	6.134 ± 0.96
C₂ - MP 20%	1.770 ± 0.015	0.105 ± 0.004	0.186 ± 0.004	5.480 ± 0.84
C₃ - LP 20%	1.820 ± 0.023	0.109 ± 0.004	0.202 ± 0.004	5.025 ± 0.82

Source: Authors.

In addition to the properties of the composite formulations, the properties of corn cob and powders in their three-grain sizes were also measured, which helped to explain the behavior and variation of the thermal properties of the composite produced.

These properties vary for each batch of resin purchased, which makes it indispensable to survey properties each time a new resin is used. It is believed to be associated with additives that are added to the resin.

All composite formulations showed thermal properties characteristic of thermal insulators superior to those of polyester matrix resin.

It was noticed that there was an improvement of the thermal properties, analyzing them as an improvement of the thermal insulation capacity, as the particle size decreased.

The formulation with fine grains presented a lower thermal conductivity, explained by the greater homogeneity between grains and resin. As the grains have lower conductivity than resin, 0.163, 0.186, and 0.202, for fine, medium, and coarse grains, respectively, the composite formulation with fine grain showed a lower thermal conductivity in 19.3% than the presented at the coarse grain formulation.

All formulations tested can be used as thermal insulators as they have thermal conductivity below 0.21W / m.K, which represents good applicability for the composite produced (Souza, 2019).

Concerning other composites already produced and studied, it presented, together with the composite material that used coffee grounds, the best thermal properties as possible thermal insulation (Varela, 2017), (Vieira, 2018).

3.5 Density

Table 4 presents the results of the density test for the matrix and the studied composite in the three formulations.

Table 4. Densities of the resin and composite formulations studied.

MATRIX/COMPOSITES	DENSITY (g/cm³)
RESIN	1.20
C₁ - TP 20%	1.16
C₂ - MP 20%	1.10
C₃ - LP 20%	1.06

Source: Authors.

According to the manufacturer, the terephthalic resin density ranges from 1.10 to 1.15 g/cm³. All the studied composite formulations, for three particle sizes, had densities lower than of the matrix, with a gross particle size of 11.7%. The average density for the studied formulations was 1.106 g/cm³.

This property is the one that provides a higher potential of use for the composite, allied to the thermal behavior. Light and sturdy structures could be fabricated for some applications such as furniture, automotive parts, and crafts with good aesthetics. Some prototypes were built to test the performance of the composite material. A shelf board and bench top are shown in Figure 4.

Figure 4. Practical applications of the composite studied.



Source: Authors.

4. Conclusions and Suggestions

The composite was feasible, in the three studied granulometry, for the fabrication of parts and structures applicable to systems subjected to low mechanical stresses, being able to have massive applicability in the furniture and automobile industries. The residue of corn cob reduces the use of resin, confirming the economic character of the use of the residue as a filler in the composite. The corn cob residue was present in the composite as a filler, since its mechanical strength was inferior to that of the matrix resin. The reduction of the mechanical performance of the composites when compared to the original matrix can be justified by the low adhesion between the interface load and matrix verified by scanning electron microscopy (SEM). The average behavior for water absorption demonstrated resin supremacy over the composite formulations studied. The LP formulation was the one with the worst result and the TP with the best behavior. Due to the great resin impregnation capacity of the residue, its maximum viable addition was 40% by mass, for PG, by manual mixing technique. All formulations of the studied composite, for three particle sizes, had densities lower than that of the matrix, with a maximum reduction of 11.7%. Obtain and study the composite from a corn grain of smaller particle size. Produce a hybrid composite from the polyester resin and the lower granulometry to increase mechanical strength. Study the obtaining of the composite using other polymeric matrices. Test the composite obtained for impact strength. Perform composite aging analysis. Test the absorption of the composite for contact with oils. Study the acoustic behavior of the proposed composite. Manufacture other structures with the obtained composite.

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