

Evaluation of the Mechanical and Morphological Properties of a Rice Husk Mixture with Recovered Polypropylene and High-Density Polyethylene, using Sulfur-Silane as the Coupling Agent

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Agro-industrial and plastic waste constitute a significant percentage of generated solid waste, leading to serious environmental problems and elevated final disposal costs for industries and municipal final disposal systems, due to its large volume and limited amount of available use options. It is for this reason that this research article focuses on using rice husk (RH), an agro-industrial byproduct, mixed with polypropylene (PP) and high-density polyethylene (HDPE) found in household solid waste, using the sulfur-silane coupling agent to aid the interfacial adhesion between the materials. This mixture was created through mechanical recycling techniques, for a subsequent evaluation of its mechanical properties, specifically tension, flexural and impact tests, in addition to examining its morphological characteristics via a scanning electron microscope (SEM).

1. Introduction

Agro-industrial and plastic waste represent a significant percentage of solid waste generated (Solano et al., 2019), leading to serious environmental problems and elevated final disposal costs for industries and municipal final disposal systems, due to its large volume and limited amount of available use options. As such, several research studies have been carried out to incorporate this type of waste into the production cycle.

Using mixed plastic waste as an alternative has been the subject of several studies, which have yielded positive results in obtaining mixtures and identifying their physical and mechanical properties, as is the case of the polypropylene and expanded polystyrene mixture, in which the latter has limited use options in the recycling chain (Solano et al., 2017). Another type of widely developed mixtures are those that combine polymers from municipal solid waste (MSW) with agro-industrial waste, such as rice husks, which is the primary focus of this study.

These types of mixtures between municipal solid waste and agro-industrial waste, not only uses these raw materials, but also inputs such as compatibility and coupling agents. The former promote interfacial adhesion between the polymers used and the latter promote interfacial adhesion between the polymer matrix or polymer and rice husk particles. The agents' use is not necessary, but when used, there is evidence of certain properties improving. However, when they exceed a specific percentage content, they cause certain mixture properties to decrease. The most commonly used coupling agents are maleated polypropylene (MAPP), maleated polyethylene (MAPE) (Chen et al., 2016), Struktol (Aridi et al., 2016), and aminopropyltrimethoxysilane (APS) (Santiago et al., 2011).

2. Materials and Methods

The mixing percentages used (Table 1), along with a description of the materials, variables and methods adopted for this research project are presented below (Figure 1).

Table 1. Experimental Design

Mixture	Polymer (%)	Husk (%)	Coupling agent * (%)
75% HDPE - 25% PP	100	-	-
80% HDPE/PP - 20% RH	80	20	5
60% HDPE/PP - 40% RH	60	40	5
40% HDPE/PP - 60% RH	40	60	5
20% HDPE/PP - 80% RH	20	80	5

Uncertainty (± 0.001)

* The amount of coupling agent used is equal to 5% of the quantity of husk used in each mixture.

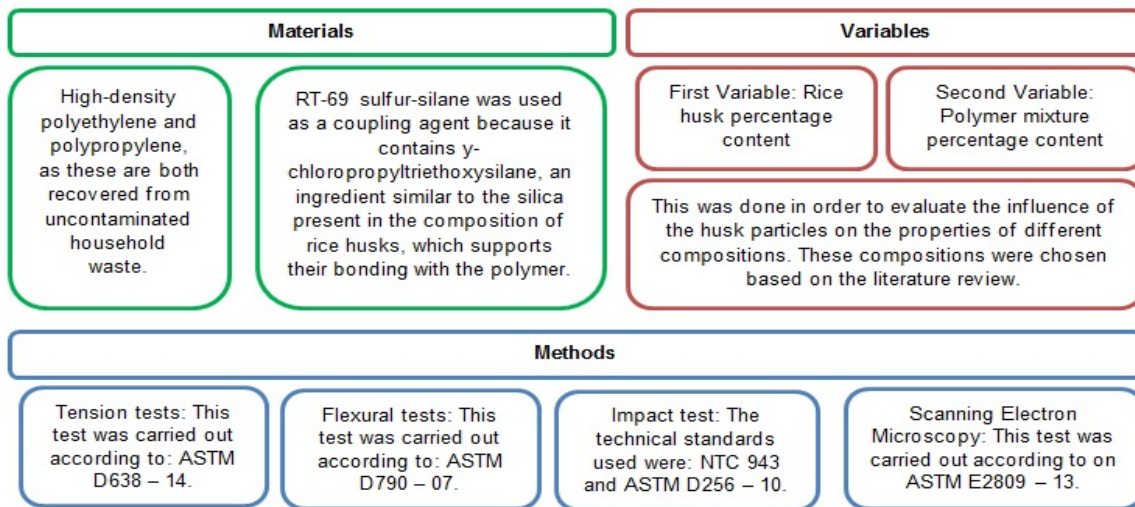


Figure 1. Materials and Methods

3. Results and Discussion

3.1 Mechanical characterization

Tension tests: This type of test is performed in order to analyze the deformation, elongation or breakage that occurs in a material when it is subjected to a specific force at a constant speed along the major axis of a specimen of the material being studied (Fombuena et al., 2016). Table 2 shows the experimental values obtained in the tension test.

Table 2. Tension Test Results

Sample	Tensile Strength at Break (Mpa)	Tensile modulus (Mpa)	Elongation at break (%)
75% HDPE/ 25% PP	4.76 \pm 1.16	1146.04 \pm 0.613	100.1 \pm 61.51
80% HDPE/PP - 20% RH	14.77 \pm 0.739	2701.693 \pm 276.048	1.058 \pm 0.112
60% HDPE/PP - 40% RH	13.334 \pm 1.065	2093.026 \pm 157.357	2.151 \pm 0.671
40% HDPE/PP - 60% RH	14.957 \pm 0.613	1483.418 \pm 277,614	7.614 \pm 2.278
20% HDPE/PP - 80% RH	6.216 \pm 2.152	2774.841 \pm 777.683	0.331 \pm 0.070

Uncertainty (99.7% reliability)

Breaking strain: Table 2 makes it clear that adding rice husk particles increases the mixtures' breaking strain. The largest increase was in the mixture with 60% husk, which had a breaking strain of 14.957 Mpa. The smallest increase was in the mixture with 80% husk, with a breaking strain of 6.216 Mpa, which could be attributed to its high husk content.

In this study, the mixture with the best performance in the traction modulus property was 20% HDPE/PP–80% RH, which was compared to the results obtained in other studies, such as the 44% PP–24% RH mixture (Jayaraman et al., 2013). The later had a high score in this test, resulting in a difference of approximately 1017 MPa. This indicates that the reference mixture has a greater capacity to withstand the stress and deformation to which it can be subjected.

Tensile modulus: As for tensile modulus, Table 2 shows that adding 20% rice husk nearly doubles this property within the mixture. However, further additions of husk particles reduced the tensile modulus in the mixture. Despite the foregoing, the best performing mixtures contained 20% and 80% husk particles, reaching tensile moduli of 2701.693 Mpa and 2774.481 Mpa, respectively.

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Elongation at break: With respect to elongation at break, Table 2 shows a directly proportional relationship between the mixture's elongation and the addition of husk particles; as more husk particles are added, the greater the elongation reached by the mixture. This behavior holds true until the mixture reaches 40% HDPE/PP–60%RH, which had the greatest elongation at break (7.614%). However when rice husk reaches 80% of the mixture, this property drops to 0.331%. An analysis of the elongation of the polymer matrix (75% HDPE/25% PP) with respect to the first addition of husk particles, demonstrates that rice husks significantly reduce this property in the mixture.

When comparing the best performing mixture in this study, with respect to elongation at break, the 40% HDPE/PP–60% RH mixture, with results obtained by other research studies, it is evident that it has a smaller elongation, due to its higher rice husk content, making the material more rigid and consequently, lowering its elongation capacity.

Flexural tests: This type of test is performed to analyze the deformation caused by exerting force on the center of a specimen which is clamped at its ends (ASTM, 2010). Determining these properties is done on reinforced and non-reinforced materials, including high modulus composite materials and electrical insulating materials in the form of rectangular bars molded or cut from sheets or plates. These test methods are applicable to both rigid and semi-rigid materials (ASTM, 2010). The values obtained in the flexural test are presented in Table 3.

Table 3. Results of the flexural test

Sample	Flexural strength (Mpa)	Flexural modulus (Mpa)
75% HDPE / 25% PP	32.6 ± 1.382	990.097 ± 47.241
80% HDPE/PP - 20% RH	34.133 ± 3.141	1411.615 ± 71.648
60% HDPE/PP - 40% RH	30.19 ± 1.702	1884.664 ± 141.794
40% HDPE/PP - 60% RH	23.968 ± 2.431	2176.614 ± 218.546
20% HDPE/PP - 80% RH	19.552 ± 1.266	3145.028 ± 568.810

Uncertainty (95% reliability)

Flexural strength: According to Table 3, with respect to the flexural strength property, there is an inverse relationship between the composite's flexural strength and the addition of husk particles. Each time husk particles are added, the property reduces by approximately 5 Mpa with respect to the prior addition. The 80% HDPE/PP–20% RH mixture had the greatest flexural strength, reaching 34.133 Mpa.

For this property, the 70% HDPE–30% RH and 70% PP–30% RH mixtures analyzed in other studies had similar values to those obtained for the 80% HDPE/PP–20% RH mixture in this study, with values of 33.719 Mpa and 31 Mpa, respectively (Tong et al., 2014) and (Bera et al., 2008). The closeness of the data suggests that chemically pre-treating the husks does not significantly affect the flexural strength of the mixture, and the consistency of high HDPE content within the mixtures results in similar performances for this property.

Flexural modulus: Regarding the flexural modulus, Table 3 reveals that adding husk particles to the mixture causes this mechanical property to increase by an average of 395.5 Mpa each addition. The 20% HDPE/PP–80% RH mixture had the highest flexural modulus value (3145.028 Mpa), while the mixture with the lowest flexural modulus value had 20% RH (1411.165 Mpa).

When analyzing the flexural modulus, the values recorded by the 95% PP–5% RH mixtures [945 Mpa (Bera et al., 2008)] and 80% HDPE–20% RH mixtures [1158,766 Mpa (Tong et al., 2014)] show considerably lower moduli than the value obtained by the 20% HDPE/PP–80% RH mixture (3145.028 Mpa) developed in this study. This is due to the latter's high husk content, enabling it to have better performance in the flexural modulus property as a result of its greater resistance to stress and deformation to which it can be subjected.

Impact test: There are different types of impact tests; free-fall drop, Izod impact and pendulum impact. This study employed the pendulum impact test. The objective of this type of test is to determine the energy necessary to break a material (ASTM, 2018). Table 4 presents the values obtained in this test.

Table 4. Impact Test Results

Sample	Impact strength (J/m)	Type of failure	Percentage of failure type (%)
75% HDPE / 25% PP	163.16 ± 79.64	H and C	H= 20% and C= 80%
80% HDPE/PP - 20% RH	46.62 ± 5.90	H and C	H= 40% and C= 60%
60% HDPE/PP - 40% RH	31.76 ± 2.46	C	C= 100%
40% HDPE/PP - 60% RH	19.43 ± 1.79	C	C= 100%
20% HDPE/PP - 80% RH	11.18 ± 2.40	C	C= 100%

Uncertainty (95% reliability)

Impact strength: To determine the type of failure, seven specimens for each mixture were tested to analyze the material's breakage pattern. According to the results in Table 4, two types of failures were obtained. The first was type H, representing the occurrence of an incomplete break; meaning that one of the parts of the sample could not be held horizontally, while the other part was held vertically (hinge with an inner bending angle less than 90°) (ASTM, 2018). The second was type C, which represented the occurrence of a complete failure, in which the sample separated into two or more pieces. As rice husk particles are added to the mixture, the probability increases that when subjected to impact, the sample will separate into two or more pieces. This property shows that as the husk proportion present in the mixture is reduced, the greater the mixture's impact strength. Therefore, the 80% HDPE/PP–20% RH mixture was the strongest (46.62 J/m). However, this mixture is not even half as strong as the polymer matrix (75% HDPE–25% PP).

The most similar values to those of the 80% HDPE/PP–20% RH mixture, were obtained by PP–Black Rice Husk mixture (Fuad et al., 1995). This is due to both having the same type of rice extracted from the husks. However, there is a greater decrease in impact strength in the 80% HDPE/PP–20% RH mixture, which may be attributable to the presence of HDPE.

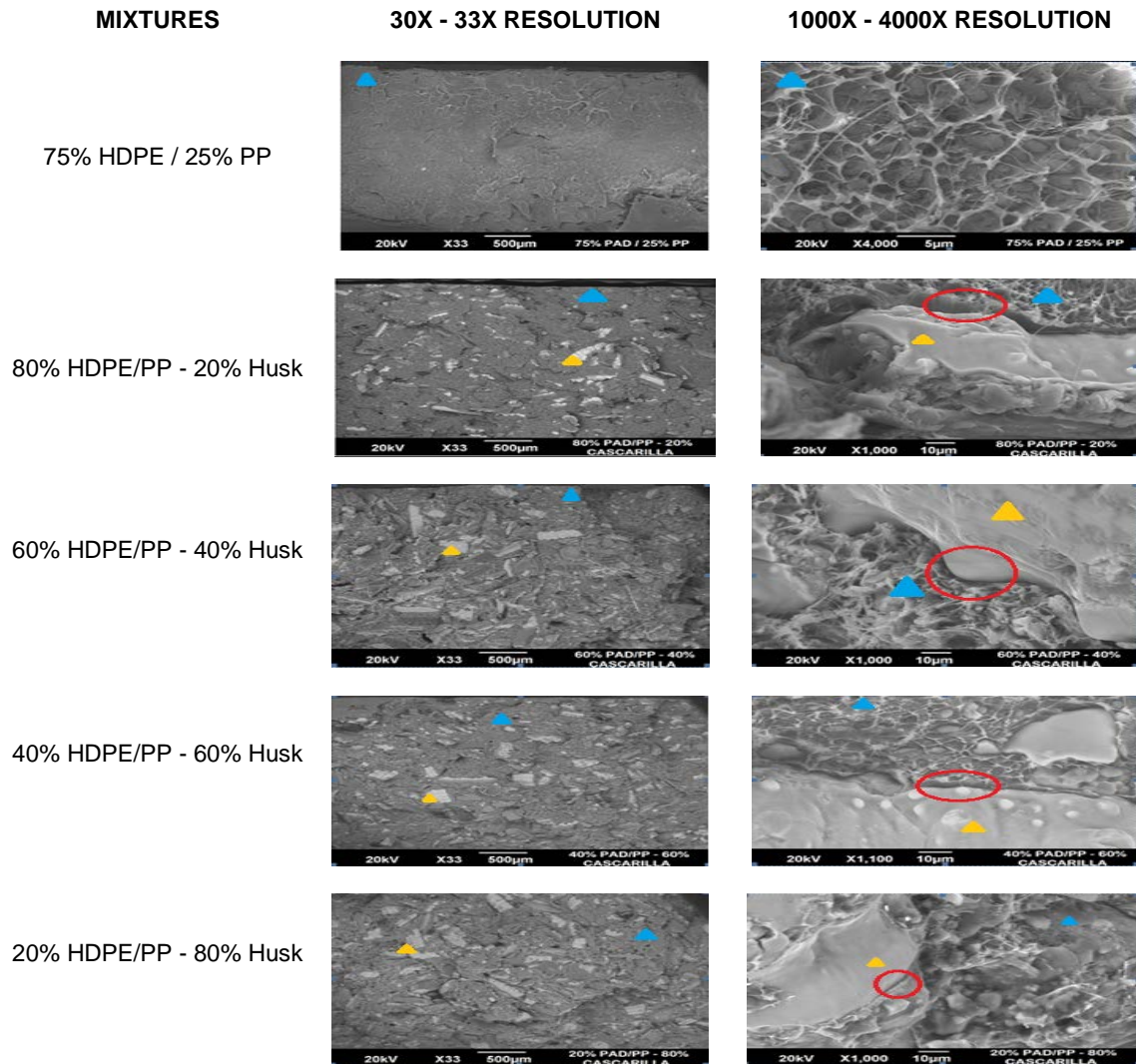
3.2 Morphological characterization

Scanning Electron Microscopy (SEM) is a surface analysis technique, which consists of focusing a narrow electron beam on a sample in order to obtain its morphological, topographical and compositional information, through the production of high resolution images. Figure 2 presents the images obtained for each mixture in 30X – 33X and 1000X – 4000X resolutions.

In the 33x and 4000x images of the 75% HDPE/25% PP mixture, a harmonization between the polymers can be seen, which achieved a good stress transfer throughout the polymer mixture. There was no presence of cracks on the surface of this mixture's specimens.

In the images of the 80% HDPE/PP–20% husk mixture, it is evident that the matrix formed by the polymers was highly compatible within the mixture, and coupled well with the rice husk particles, which enabled good interfacial adhesion throughout the mixture. However, there is a small separation between the husk particles and the matrix as indicated by the red circle. A similar situation occurs with the 60% HDPE/PP–40% RH, 40% HDPE/PP–60% RH and 20% HDPE/PP–80% RH mixtures in the images presented in Figure 2.

It can be seen that by increasing the rice husk content to 40%, 60% and 80%, the positive coupling of the materials in the mixture is maintained, favoring solid interfacial adhesion and stress transfer between them. At the same time, it is evident that the small separation between materials continues to be present without any variation in their magnitude when increasing the mixture's husk content. This phenomenon is indicated with a red circle in the images.



Shapes: 1. Blue triangle, Polymer matrix. 2. Yellow triangle, Rice Husks. 3. Red Circle, Bonding materials.

Figure 2. Results from the morphology test.

4. Conclusions

When compared with the other mixtures, the 80%HDPE/PP – 20% RH mixture had the best results in the majority of the tests. There was an increase in the tensile modulus and flexural modulus properties with the addition of rice husks as they facilitate the transfer of stress. As such, these mixtures can be subjected to a greater amount of stress and deformation.

Increasing the rice husk content caused a decrease in certain mechanical properties, such as tensile strength, flexural strength, impact strength and elongation at break. This is due to rice husks increasing the mixtures' rigidity, resulting in mechanical limitations when subjected to force. At the same time, this rigidity affects the mobility of polymer chains, causing the glass transition temperature to decrease.

In the morphological tests carried out on these types of mixtures, good interfacial adhesion and optimum stress transfer between the added materials in the different proportions established were evident. This increased the mechanical and morphological properties of the mixtures. Despite the presence of small separations or cracks between the materials, they did not interfere with the mixtures' performances in the different tests. When comparing the mechanical results obtained in the experimental phase of this study with literature, it can be concluded that the RH mixtures with HDPE and PP can be used in the automotive sector (fans and gasoline containers), agricultural sector (irrigation systems and tubing), as well as in the construction sector (sheets and shower and bath screens). Nevertheless, additional studies are needed to confirm these applications.

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