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

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Several studies conducted around the world have analyzed the possibility of using agro-industrial waste, such as rice husk, which can be combined with polymeric matrices made from pure or recovered polymers, in order to create a new material that can replace or be a substitute for polymeric materials widely used in the market. It is for this reason that this research study seeks to further explore these types of materials, creating a mixture from recovered rice husk (RH), polypropylene (PP) and high-density polyethylene (HDPE), using sulfur-silane as a coupling agent, which improves the materials' interfacial adhesion. Mechanical recycling techniques were used to create the mixture, followed by a subsequent evaluation of it thermal properties with flammability tests and differential scanning calorimetry (DSC) performed.

1. Introduction

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., 2019).

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. The following are among the primary research studies that have mixed polymers from MSW with rice husk particles:

A high-density polyethylene (HDPE) with polypropylene (PP) mixture was characterized, which facilitated the production of stakes to be used in the agricultural sector. With a particle size of flour, this mixture did not use a coupling agent. Certain mechanical and chemical properties were characterized, revealing that the mixture increased its compressive strength, but its tensile properties decreased. Furthermore, it had a sound ratio of mass to volume and was highly resistant to the chemical agents used (Baller & Castiblanco, 2016)

High-density polyethylene (HDPE) and polyethylene terephthalate (PET) (both polymers originating from a recycling process) ended up being a good polymer blend that exhibited optimal properties in the physical, mechanical and thermal tests to which it was subjected. Moreover, this study indicates that this behavior is due, in some part, to using a high percentage of HDPE in the mixture (Cheng et al.,2015).

The interfacial adhesion between polypropylene and fiberglass (FG) is strong. However, increasing the FG content to a certain percentage within the mixture causes cracking in the resulting material, making it susceptible to breakage (Arun et al.,2014).

In some cases, only one polymer is used for these mixtures. The uses of low- (LDPE), medium- (MDPE) and high-density (HDPE) polyethylene have been analyzed. The latter has the best mechanical, thermal and morphological properties for these types of mixtures (Jayaraman et al.,2013; Tong et al., 2014).Another polymer that has been individually analyzed for these types of mixtures is PP. Increasing the PP content percentage in a mixture increases its mechanical, thermal and morphological properties (Rosa et al.,2009) Lastly, polyvinyl chloride polymer (PVC) has been used within these types of mixtures, which improves their thermal and mechanical properties (Xu et al.,2008).

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One of the variables taken into account in this type of research has been the type of risk husk used. In this case, black rice husks were compared with white rice husks, with the latter yielding the best properties for these types of mixtures (Fuad et al.,1995). Moreover, research studies have analyzed the particle size of rice husks to be used in mixtures as a variable, in which the husk used had the particle sizes of flour, powder and ash (Jayaraman et al.,2013; Tong et al., 2014; Bera & Kale,2008). Flour is the most commonly used particle size, as it prevents the husks from binding together, which hinders stress transfer between the polymer and the husks.

Therefore, the polymer matrix formed by high-density polyethylene and polypropylene was selected for this study as these two polymers have the best mechanical, thermal and morphological properties within the mixture. As an agro-industrial waste, flour-particle-sized rice husk is included in this matrix, in order to optimize the abovementioned properties.

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) (Cheng et al.,2015), Struktol (Aridi et al., 2016), and aminopropyltrimethoxysilane (APS) (Santiagoo et al., 2011). The latter two have a silane component, which is in the same chemical group as the coupling agent used in this research project; sulfur-silane.

In accordance with the above, it is evident that mixtures between polymers and rice husk particles are an optimal alternative for the use of urban plastic waste, which has a low value in the recycling chain. Making it possible to use of rice husks reduces the environmental impacts generated by the inadequate management and disposal of this agro-industrial waste. Consequently, this research study aims to obtain and evaluate the mechanical and morphological properties of two types of plastic waste, polypropylene (PP) and high-density polyethylene (HDPE), mixed with rice husk particles, with sulfur-silane used as a coupling agent.

With respect to the HDPE/PP with rice husk particle mixtures obtained and analyzed in this research study, all performed well in the tests to which they were subjected, which included: flammability tests and differential scanning calorimetry. However, the mixture that stood out with the best behavior according to thermal properties was the 80%HDPE/PP–20%RH mixture. That said, every mixture can provide optimal qualities depending on its potential use. Another aspect to note regarding the mixture was the sound performance of the sulfur-silane coupling agent, which facilitated interfacial adhesion in all the mixtures of rice husk particles with the high-density polyethylene and polypropylene matrix. The good thermal properties obtained makes future research on this mixture and its uses technically viable, which could have applications in the construction and automotive sectors. In this manner, it is possible to generate options to use these types of waste, thus enabling their inclusion in the recycling chain.

2. Materials and Methods

The materials used to develop this study were high-density polyethylene and polypropylene, as these are both recovered from uncontaminated household waste, in addition to rice husks as an agro-industrial waste. RT-69 sulfur-silane was used as a coupling agent because it contains y-chloropropyltriethoxysilane, an ingredient similar to the silica present in the composition of rice husks, which supports their bonding with the polymer. A compatibilizing agent was not used. Two experimental variables were used for the purposes of this study. The first was the rice husk percentage content, and the second was the content of the polymer mixture. This was done in order to evaluate the influence of the husk particles on the properties of different compositions. Table 1 shows the mixtures' compositions for their subsequent characterization. These compositions were chosen based on the literature review.

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.

Procedure

Specimen preparation: Each phase developed to produce the specimens is presented below.

Grinding: The first step to create the specimens is to convert the rice husks into flour. This process takes place in a blade mill over 8 'h' with approximately 12 kilograms (kg) of husks added. The mesh size for this mill was 0.9 millimeters (mm) in order to obtain husk particles larger than 0.35 mm.

Sieving: The resulting material from the grinding process was sieved in order to produce particles smaller than 1.12 mm. In this step, 212 micron (µm) and 355 µm sieves were used, which were placed in the upper and lower parts of the specimen. This process generated 1700 grams (gr) – 2 kg of rice husk particles. The HDPE pellets had to be sieved separately with 1-2 mm mesh in order to prevent problems with the material entering the extruder.

Drying: Following the sieving process, the rice husk particles were placed in an oven at 100ºC for 24 'h' and then stored in hermetically sealed bags to prevent an increase in humidity.

Mixing the polymers: Several steps were carried out in an extruder to prepare the mixture. First, the HDPE and PP pellets were added in a 75:25 ratio, which was followed by the extrusion process. A twin screw extruder was used in order to extract the polymer mixture. This process maintained a melting temperature of 210ºC, with the following temperature profile for the extruder: 180ºC (feed zone), 185ºC – 190ºC (transition zone), and 150ºC (final zone). At the same time, 14.3 megapascals (Mpa) of pressure and 57.9 Newton/meter (N/m) of torque were applied at a speed of 90 revolutions per 'min' (rpm).

Pelleting: Four thread mixtures were obtained from the previous step, which were dried by immersing them in water and subsequently stored. Following the pelleting, the threads were then introduced into a blade mill to obtain the pellets. This process was carried out at room temperature.

Weighing the materials: In this step, a digital scale was used and the three materials were weighed at the same time. First, the coupling agent was added to dampen the husks, which were then added to the mixture, followed by the addition of the pellets from the polymer mixture.

Mixing the materials: This step was carried out in an internal mixer at an average speed of 60 rpm, at a melting temperature of 190ºC, with an average duration of 5 'min' per mixture.

Grinding the material mixture: Small agglomerates of material were obtained from the material mixtures made in the previous step, which were ground in a blade mill with the resulting product sieved through a 4 mm mesh.

Specimen preparation: The material was placed in a 0.1 mm thick aluminum mold, which was then taken to a molding press and preheated for 12 'min'. The plates were placed 14 mm apart to ensure that the mold was heated properly. When the material entered the melting phase, it was heated to 190ºC, with an initial pressure of 15 Bars, ultimately reaching a final pressure of 110 bars. After the material was fused, it was left to cool at room temperature for 12 'min' until it reached a temperature of 37°C. Lastly, the material was separated from the mold and cut into specimens in accordance with each standard for the tests to be carried out. A summary of the Materials and Methods is presented in Figure 1.

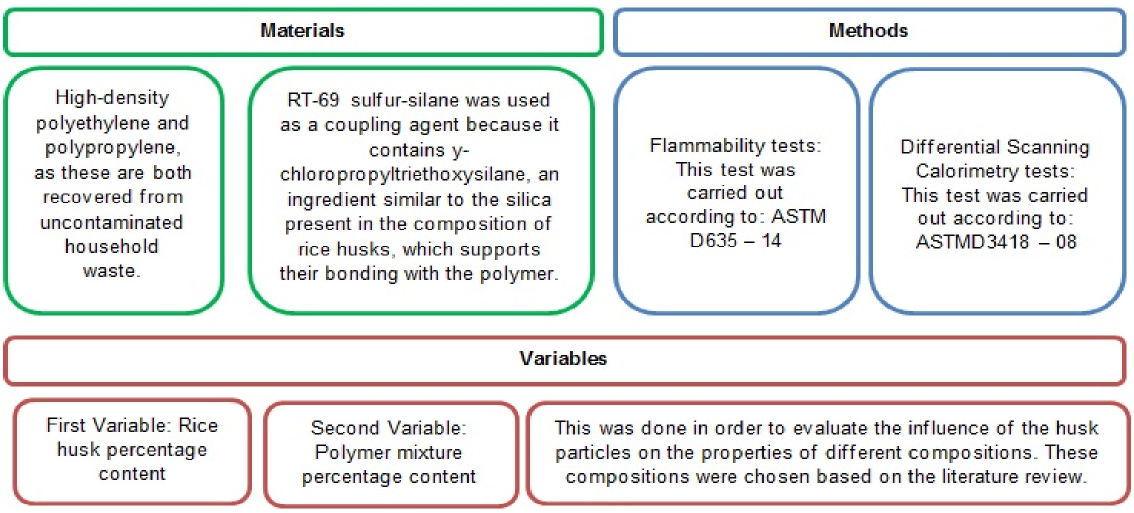

Figure 1. Materials and Methods

3. Results and Discussion

2.1 Thermal characterization

Flammability: This test was developed based on the technical reference standard, ASTM D635 – 14: Standard Test Methods for Rate of Burning and/or Extent and Time of Burning of Plastics in Horizontal Position; in this test, the specimen is placed horizontally, which is then marked at 25 mm and 100 mm (ASTM, 2014). This method to test a sample's response to fire sets out to compare its relative linear burning velocity or extension, and burning time, or both, of plastic bars, molds or cut pieces, with the samples tested in a horizontal position. Table 2 shows the experimental values obtained in the flammability test.

Table 2. Flammability Test Results

Sample	Time to reach 100 mm or self-extinguish	Distance not burned; between 25-100 (mm)	Distance burnt; between 25-100 (mm)	Combustion speed (mm/min)	Observation
75% HDPE / 25% PP	222.55 ± 17.04	0	75	23.208 ± 1.638	Was dripping
80% HDPE/PP - 20% RH	187.59 ± 25.72	0	75	26.133 ± 3.286	Was dripping
60% HDPE/PP - 40% RH	256.97 ± 76.33	0	75	19.775 ± 5.123	No dripping occurred
40% HDPE/PP - 60% RH	231.27 ± 21.26	0	75	21.265 ± 2.009	No dripping occurred
20% HDPE/PP - 80% RH	292.38 ± 50.26	0	75	16.953 ± 2.641	No dripping occurred

Uncertainty (95% reliability)

The results obtained from this test were similar among the mixtures, with the addition of husk particles slightly improving the property. As for the necessary time to reach 100 mm or self-extinguish, approximately 238.152 seconds were required, while the average combustion velocity was 21.462 mm/min, indicating that this type of material tends to be consumed rapidly by fire. With respect to the distance burnt, it is evident that the specimens were consumed by fire, as in every mixture, there was no space that had not been burnt in the first 25 mm, and in the 25 – 100 mm section, all the material was consumed by fire. After removing the ignition source, there were no signs of combustion or flames. One property within the mixture that the rice husk particles did impact was dripping; as more were added, dripping was reduced or eliminated.
Differential scanning calorimetry (DSC): The standard, ASTMD3418 – 08: Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry, was used as a reference in this step. In this test, aluminium was used as a sample carrier material and indium as a calibration material, the initial scanning temperature was -90°C, which was steadily increased in order to find its glass transition temperature and melting temperature (ASTM,2008). This technique is based on measuring the difference of heat flow between a studied sample and a reference sample. One of the thermal properties that can be measured through this test are a material's melting and glass transition temperatures. The former is related to the degree of crystallinity present in a composite, while the second is related to the movement of polymer chains, in which the greater the mobility, the more ductile and less resistant the composite, while composites with less mobility tend to be rigid. Table 3 shows the results obtained in the DSC test.

Table 3. DSC Test Results

Sample	Melting temperature (°C)	Glass transition temperature (°C)
75% HDPE/ 25% PP	131.55	-
80% HDPE/PP - 20% RH	131.85	201.5
60% HDPE/PP - 40% RH	130.83 – 229.94	172.85
40% HDPE/PP - 60% RH	130.37 – 225.17	175.49
20% HDPE/PP - 80% RH	127.9 – 214.27	165.25

Uncertainty (95% reliability)

Based on the results obtained in this test, adding husk particles increased the melting temperature range, which can be attributed to the fact that rice husks have some degree of thermal resistance to melting in the mixture, making it degrade at higher temperatures. These results confirm that thermal stability and flammability resistance properties improve as the content of husk increases (Cheng et al.,2016). A more specific case of this husk with PP blends also confirms that the addition of husk increases the thermal stability of the polymeric matrix (Hidalgo-Salazar & Salinas, 2019). The optimum composition regarding this thermal property was 60% HDPE/PP–40% RH, as it reached a temperature range of 130.83ºC - 229.94ºC.
DSC analysis is an important technique in the study of thermal properties such as specific heat, glass transition temperature, melting point, crystallinity and the thermal stability of composite materials (Ghijsels, A., and Waals, 1980 cited in Kumar et al., 2013). As such, this test was performed to determine the glass transition temperature, which demonstrated that adding husks to the mixtures causes this property to rise in the composites. However, as husks are added to the mixture, this temperature decreases. The 80% HDPE/PP – 20% RH mixture had the best performance with a glass transition temperature of 201.5ºC. This property demonstrates that the polymer does not have a glass transition temperature because it is very rigid, with limited mobility within its polymer chains.

4. Conclusions

As for the flammability property, it was found that these types of materials can be completely consumed by fire due to their low fire-resistance. However, when analyzing the self-extinguishing time, it was found that rice husks increased the mixtures' fire-resistance in addition to reducing dripping due to the protective role played by the husk particles on the polymer matrix.
The results obtained from the DSC test demonstrated that there is no visible change in the initial melting temperature. It can be seen that by increasing the rice husk content in the mixture, melting does not occur at a temperature if not in a specific temperature range. This may be due to the increasing amount of this component within the mixture where said temperature tends to the value for rice husk. The mixture that achieved the best result for glass transition temperature tests was the 40% HDPE/PP–60% RH mixture and the best mixture for the melting temperature property was 80% HDPE/PP–20% RH.

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