

Tensile and Impact Properties of Rice Husk Filled Ethylene-Acrylic Ester Maleic Anhydride Compatibilized Polypropylene Composites

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Rice husk (RH) is an agricultural waste that is gaining importance as fillers for polymers due to its abundant advantages such as light weight, low cost and environmentally friendly. This study investigates the tensile and impact properties of rice husk waste (RH) filled polypropylene (PP) composites with ethylene-acrylic ester maleic anhydride (E-AE-MA) as compatibilizer. The compatibilizer agent is used to improve compatibility between the RH which is hydrophilic and non-polar PP. Tensile test and impact strength test were conducted according to ASTM D638 and ASTM D256 standards. The incorporation of 15 wt% of RH into PP increased the Young's modulus of PP by 28 % but decreased the tensile strength and impact strength by 10 % and 31 % compared to neat PP. The elongation at break was observed to decrease by approximately 4 %. The addition of E-AE-MA at 4 parts per hundred (phr) to the composite increased the impact strength and elongation at break of RH-PP composite by 18 % and 22 % , but decreased the Young's modulus and tensile strength by 18 % and 5 %. The overall results showed that the elongation at break and Young's modulus of the compatibilized RH-PP composite is higher than neat PP, including that E-AE-MA is an effective compatibilizer between RH filler and PP due to its ability to improve adhesion between the two phases.

1. Introduction

The world annual production of paddy rice has reached a peak of 769.9 Mt (FAO, 2018). This represents a total of 169.4 Mt of rice husk at 22 % estimated rice husk percentage (Bisht and Gope, 2015). Rice husk as an agricultural waste has not been fully utilized and is often disposed as industrial solid waste in heaps or in landfills, contributing to environmental pollution. Rice husk (RH) is an agricultural waste which is gaining importance as fillers in polymer industry due to its advantages of being light weight, low cost and environmentally friendly. As a natural fiber, it has an advantage of high abundance with low cost compared to other natural fibers, promising a rich source of raw material for industrial application and scientific research (Ezenkwa et al., 2020). The incorporation of renewable and sustainable resource such as RH in polymer composite fabrication is expected to promote sustainable growth, energy conservation, lower carbon foot print and efficient resource management (Mohanty et al., 2018).

One of the challenges of utilizing RH as reinforcing filler in polymer composites lies on its incompatibility with non-polar matrices. When incorporation into non-polar polymer matrix, the filler particles tend to agglomerate, creating voids within the composite which limit stress transfer from the matrix to filler (Yang et al., 2006). Fiber-matrix incompatibility causes weak interfacial adhesion resulting in decreased composite impact strength, tensile strength and elongation at break (Oliveira et al., 2018). Strong compatibility between the dispersed phase filler and continuous phase matrix is the key to enhanced mechanical properties performance of biocomposites (Low and Rahman, 2017).

Improving RH compatibility with non-polar polymers require fiber surface modification. Surface treatment techniques such as mercerization, ozonolysis, plasma, electron beam irradiation and coupling agents have been employed to achieve RH fiber-matrix compatibility in polymer composites fabrication. Incorporating compatibilizer agents into natural fiber reinforced polymer composite systems has also shown improved fiber-

matrix interfacial adhesion, gaining high prominence in biocomposite fabrication (Ezenkwa et al., 2020). The mechanism of compatibilization in natural fiber reinforced polymer matrix composite results from the formation of ester linkages between the hydroxyl groups of the fiber and the maleic anhydride (MA) groups of the compatibilizer (for MA graft compatibilizers) with further entanglement of hydrophobic end of the compatibilizer with the non-polar matrix, establishing a fiber-matrix interfacial adhesion (Mutjé et al., 2006). According to Basri et al. (2019), a compatibilizer, Joncryl, enhanced the impact strength and elongation at break of banana fiber (BF) reinforced poly-lactic acid (PLA) bio-composite by 19 % and 3.8 % at 10 wt% filler content, but decreased by 5 % in tensile strength compared to uncompatibilized composite. Basri et al. (2019) concluded that Joncryl compatibilizer is incapable of promoting compatibility between the fiber and its matrix polymer, rather, acted as an impact modifier to the composite. Polypropylene grafted maleic anhydride (MAPP) compatibilizer at 4 wt% was found to improve the tensile strength of RH reinforced polypropylene (PP) composite by 10 % at 10 wt% filler content but decreased the elongation at break compared to the uncompatibilized composite (Erdogan and Huner, 2018). Raghu et al. (2018) also observed enhanced tensile strength and impact strength of RH reinforced PP composite by 5 wt% MAPP compatibilizing agent. The observed improved mechanical properties of MAPP compatibilized RH-PP composite systems were attributed to improved fibre-matrix interfacial adhesion by the compatibilizer as well as its base polymer compatibility with PP matrix. Achieving compatibility between the dispersed phase and continuous phase has also been emphasized in polymer blends fabrication. A recent study (Panigrahi et al., 2020) reported that incorporation of E-AE-MA compatibilizer into a blend of non-polar PP and epichlorohydrin rubber (ECR) enhanced dispersion of ECR in PP by 90 % and improved strain at break of the PP/ECR blend by 370 %. Earlier study (Moan et al., 2000) demonstrated that addition of E-AE-MA into polyamide (PA) and polyethylene (PE) matrix blend improved dispersion of PA in PE as evidenced by the morphology of cryo-fractured PE/PA blend. The incorporation of E-AE-MA as a compatibilizer in natural fibre reinforced polyolefin biocomposites was first reported by Panthapulakkal et al. (2005). The study involved RH filled high density polyethylene composite system in which E-AE-MA improved compatibility between RH and HDPE leading to enhanced mechanical properties.

Although many studies have been reported on RH-PP biocomposite system, no study has investigated the effects of E-AE-MA as compatibilizer in RH-PP biocomposite system. The objective of this present study is to investigate the effect of E-AE-MA compatibilizer on RH filled polypropylene matrix interfacial adhesion and its influence on tensile and impact properties of the composite. PP copolymer is known to have good impact property but is decreased with the incorporation of rice husk fillers. It is expected that the incorporation of E-AE-MA as compatibilizer will improve the impact property of RH filled PP biocomposite due to its impact modifying effect.

2. Experimental

2.1 Materials

Polypropylene Copolymer of SM240 grade (Lotte Chemicals, Titan, Malaysia) of melt flow index 25 g/10 min (230 °C /2.16 kg) and density 0.9 g/cm³ was supplied as pellets and used as matrix. The reinforcing filler, raw rice husk was supplied by Padi Bernas Nasional Berhad, Kuala Lumpur, and E-AE-MA of Lotader 4700 grade with melt flow index 7 g/10min (190 °C /2.16 kg) and density 0.94 g/cm³ was obtained from Arkema, France as compatibilizer. Table 1 presents the typical characteristics of E-AE-MA compatibilizer agent.

Table 1: Typical properties of Ethylene-Acrylic Ester-Maleic Anhydride (E-AE-MA)

| Characteristics | Value |
|---------------------------|---------|
| Maleic Anhydride content | 1.3 wt% |
| Melting point | 65 °C |
| Elongation at break | 800 % |
| Tensile strength at break | 5 MPa |

2.2 Composite preparation

The composite RH-PP with E-AE-MA as compatibilizer was fabricated at 15 wt% fixed content of RH and E-AE-MA at 4 phr of the composite, using a counter rotating twin screw extruder of Brabender PL 200 Plastic Coder model at the optimum temperature of 185 °C from feed zone to the die head, with a screw speed of 60 rpm and at pressure 12 bar. The extrudates were cooled to room temperature and pelletized prior to injection molding using an injection molding machine (JSW model NIOOB 11 Muraron-Japan) operating at the temperature range of 180-200 °C. The injection molded standard samples were for tensile and Izod impact

tests. The composites material formulation is shown in Table 2 below. Composite sample with E-AE-MA compatilizer is denoted by PP-RH-MA.

Table 2: Composite formulation

| Sample | PP (wt%) | RH (wt%) | E-AE-MA (phr) |
|----------|----------|----------|---------------|
| PP neat | 100 | - | - |
| PP-RH | 85 | 15 | - |
| PP-RH-MA | 85 | 15 | 4 |

2.3 Characterization

Fourier transform infrared spectroscopy (FTIR) of the uncompatibilized and compatibilized composites were undertaken using Perkin Elmer 1600 Infrared spectroscopy in the regions of 4000 and 750 cm^{-1} . Tensile test involving tensile sample specimens of dimensions 170 \times 9.6 \times 3.3 mm was conducted according to ASTM D638 using a universal material tester Zwick/Roell, ZO20 (Germany) instrument with a 20 KN load cell and at crosshead speed of 50 mm/min. Impact test was conducted according to ASTM D256 using Zwick/Roell HT 25P Pendulum Impact Testing with 11 Joule hammer loads. Scanning Electron Microscopy (SEM) was conducted on the tensile fractured surfaces of the composite specimens using a JEOL JSM IT 300 LV microscope model operating at an accelerating voltage of 10 KV and magnification \times 150.

3. Results and discussion

3.1 FTIR analysis

The IR analysis in Figure 1 below describes the chemical structural differences in uncompatibilized PP-RH and compatibilized PP-RH composites. The IR spectrum of uncompatibilized composite reveals a band at 3,429 cm^{-1} representing hydroxyl (OH) stretching vibration typical of hydrophilic lignocellulosic fiber (Seki, 2009). Upon E-AE-MA addition, the broad shoulder peak of hydroxyl stretching vibration appearing in uncompatibilized composite disappeared in the spectrum of the compatibilized composite. This explains the utilization of available surface hydroxyl groups on RH filler by anhydride groups of the compatibilizer. This interaction between OH groups of the filler and anhydride groups of E-AE-MA enhanced the hydrophobicity of the compatibilized composite. The IR spectra of the composites compatibilized with E-AE-MA further revealed the presence of a weak but sharp peak at 1,735 cm^{-1} . This peak is said to correspond to the formation of carbonyl group (-C=O-) as a result of the interaction between OH groups of the filler and anhydride group of compatibilizer through esterification reaction (Sun et al., 2019).

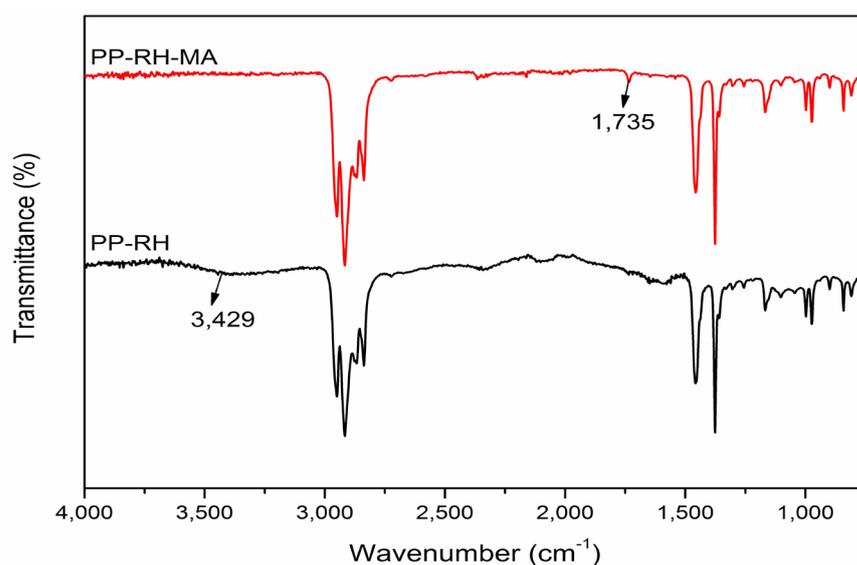


Figure 1: FTIR spectra of uncompatibilized PP-RH and compatibilized PP-RH-MA composites

3.2 Mechanical properties

Table 3 below presents the mechanical properties of uncompatibilized and E-AE-MA compatibilized PP-RH composites. The incorporation of 15 wt% RH into PP matrix is found to decrease the tensile strength of PP by 10 %. Earlier study (Hildago-Salazar and Salinas, 2019) reported that tensile strength of PP matrix decreased at rice husk filler content above 10 wt%. The incompatibility of hydrophilic rice husk filler with non-polar PP matrix results in weak bonding within the constituents of the composite. This depreciates effective stress transfer required to enhance the composite strength (Aridi et al., 2016). Addition of E-AE-MA compatibilizer into the composite also decreased the tensile strength by 5 % compared to the uncompatibilized PP-RH composite. The observed decrease in tensile strength of E-AE-MA compatibilized composite is due to acrylic ester content of the compatibilizer acting as a plasticizer. According to Cadogan and Howick (2000), plasticizers increase the flexibility of a bulk polymer by penetrating between the chains of the polymer on heating, shielding the chains from each other. Saidi et al. (2018) earlier reported a decreasing tensile strength of PVC/rice husk composite due to induced high mobility of polymer chains by plasticizer. The shielding effect of the plasticizer-like compatibilizer hindered effective stress transfer from the matrix to RH filler, decreasing the composite tensile strength.

Table 3: Tensile properties and impact strength of untreated PP-RH and E-AE-MA treated PP-RH composites

| Sample | Tensile Strength (MPa) | Young's modulus (MPa) | Elongation at Break (%) | Impact Strength (J/m) |
|----------|------------------------|-----------------------|-------------------------|-----------------------|
| PP | 21.7±0.5 | 512.0±4.3 | 11.5±2.2 | 79.0±4.8 |
| PP-RH | 19.5±0.4 | 654.6±17.2 | 11.0±2.2 | 54.6±2.7 |
| PP-RH-MA | 18.6±0.1 | 539.8±21.4 | 13.4±2.7 | 64.7±2.6 |

The Young's modulus of the uncompatibilized PP-RH composite increased favorably by 28 % with the incorporation of RH filler compared to PP matrix. Natural fibers have high elastic modulus in relation to pristine PP, which leads to increase in composite stiffness (Luz et al., 2008). Hildago-Salazar and Salinas (2019) also reported increased Young's modulus of untreated PP-RH composite. Compatibilizer E-AE-MA decreased the Young's modulus of PP-RH composite by 18 % compared to uncompatibilized PP-RH composite, whilst maintaining a 5 % increase in stiffness compared to PP. The observed decrease in Young's modulus by E-AE-MA compatibilizer compared to uncompatibilized PP-RH composite is due to the increased flexibility of the composite aided by plasticizer effect of the compatibilizer. A similar decreasing Young's modulus effect of plasticized biocomposite based on microcrystalline cellulose filled polylactic acid has also been reported in Pang et al. (2018).

The elongation at break property of pristine PP is also decreased by 4 % with the incorporation of 15 wt% RH filler. Hildago-Salazar and Salinas (2019) earlier observed a decreased elongation at break of pristine PP with rice husk filler addition, relating it to filler-matrix discontinuities which reduced the extensibility of the biocomposite. The E-AE-MA treatment resulted in an increased elongation at break of 17 % and 22 % compared to pristine PP and uncompatibilized PP-RH composite. This underscores the plasticizer and rubbery nature of the compatibilizer which improved filler-matrix adhesion, as well as increased the ductility of the composite. Improved filler-matrix adhesion and flexibility of the composite by E-AE-MA compatibilizer also favored the impact strength of PP-RH composite in relation to uncompatibilized composite. In this case, an increase of 18 % in impact strength was observed compared to uncompatibilized PP-RH composite. The massive 31 % decrease in impact strength of uncompatibilized PP-RH composite compared to pristine PP at 15 wt% RH filler incorporation was a result of poor filler dispersion in the PP matrix, creating points of stress concentration and stiffening of the composite, which initiated sites for crack propagation (Raghu et al., 2018). Compatibilization by E-AE-MA was effective in enhancing filler-matrix phase continuity due to interfacial bridging effect of the compatibilizer as supported by the micrographs of the compatibilized PP-RH composite shown in Figure 2b below. The action of E-AE-MA in enhancing filler-matrix compatibility is due to the hydroxyl groups of RH fillers reacting with anhydride groups of the compatibilizer establishing ester linkages through esterification reaction, with further entanglement of ethylene non-polar end of the compatibilizer and non-polar PP matrix (Mutjé et al., 2006).

3.3 Morphological analysis

The micrographs of tensile fractured surfaces of the uncompatibilized and compatibilized RH filled PP composites are presented in Figures 2a and 2b. Uncompatibilized PP-RH composite fractured surface in Figure 2a shows traces of large sized filler agglomerates represented by point 1, depicting the tendency of uncompatibilized RH particulates to aggregate due to incompatibility with non-polar PP matrix. Noticeable

gaps existed between the filler and matrix represented by point 2, evidencing poor adhesion (Hildago-Salazar and Salinas, 2019). Such phase discontinuity does not support effective stress transfer from the matrix to filler and resulted in diminished tensile strength of the composite relative to neat PP matrix. Traces of fibre pull-outs (Santiago et al., 2011) can also be seen in the micrograph represented by point 3, evidencing points of weak fibre-matrix adhesion. The effect of E-AE-MA compatibilizer treatment indicates better improved filler-matrix adhesion as shown in Figure 2b. The filler agglomerate sizes were reduced compared to the uncompatibilized PP-RH composite due to improved filler dispersion in the composite system. Fractured points represented by point 4 in Figure 2b were also observed for the E-AE-MA compatibilized PP-RH composite as opposed to fibre pull-out visible in uncompatibilized PP-RH composite due to improved filler-matrix interfacial layer introduced by the compatibilizer.

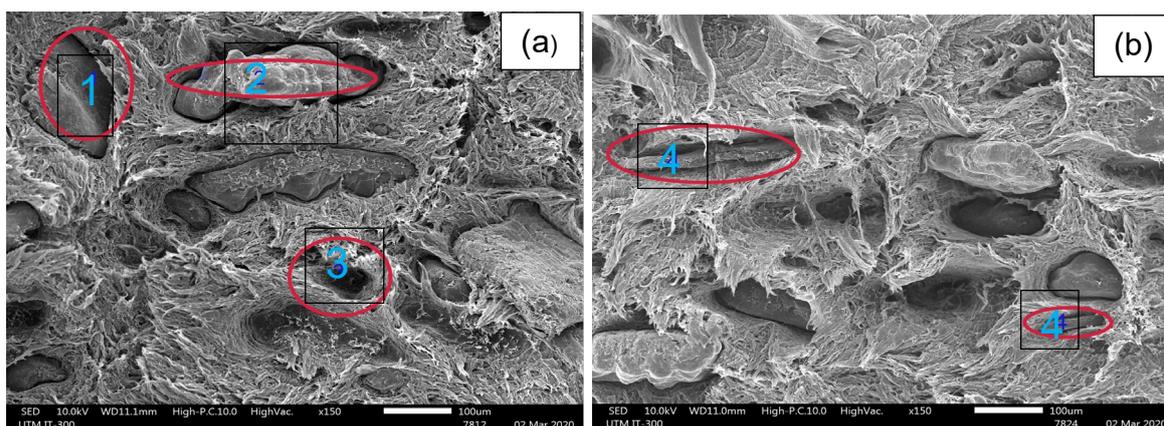


Figure 2: SEM micrographs of (a) uncompatibilized PP-RH and (b) compatibilized PP-RH-MA composites

4. Conclusion

The incorporation of RH into PP matrix enhanced the Young's modulus of the biocomposite 28 % compared to neat PP, but decreased the impact strength, tensile strength and elongation at break by 31 %, 10 % and 4 %. However, the addition of E-AE-MA compatibilizer improved the elongation at break property of PP-RH biocomposite by 22 % and 17 % compared to uncompatibilized and neat PP, and improved the impact strength by 18 % compared to the uncompatibilized PP-RH biocomposite. The tensile strength further decreased by 5 %. The observed improved elongation at break and impact strength indicate the plasticizer and rubbery nature of the compatibilizer which enhanced the ductility of the bio-composite. The inability of E-AE-MA compatibilizer to enhance the tensile strength of the biocomposite is due to its shielding effect, typical of plasticizer agent, which hindered effective stress transfer from the matrix to RH fillers. Although E-AE-MA compatibilizer did not enhance the tensile strength of the bio-composite, improved filler-matrix interfacial adhesion was observed from the SEM micrographs. The FTIR analysis also revealed that E-AE-MA compatibilizer interacted effectively with the RH filler through esterification reaction of the filler surface hydroxyl groups and maleic anhydride groups of compatibilizer, enhancing compatibility with non-polar PP matrix. The observed enhanced impact strength and elongation at break of compatibilized PP-RH biocomposite compared to uncompatibilized biocomposite, whilst maintaining higher Young's modulus than neat PP prove that E-AE-MA is an effective compatibilizer for RH filler and PP.

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