HYBRID COMPOSITES OF POLYPROPYLENE/RICE HUSK/TITANIUM DIOXIDE: THE EFFECTS OF COMPATIBILIZER ON THE MECHANICAL PROPERTIES AND MORPHOLOGY

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ABSTRACT: The rising concern about plastic waste disposal has led to the research to overcome its related environmental problems. Indeed, blending of conventional plastic with degradable materials such as biomass from agro-waste byproduct has drawn a special attention to impart biodegradability. In this work, hybrid composites of polypropylene (PP) and rice husk (RH) containing different percentage of titanium dioxide (TiO_2) (2wt% and 5 wt.%) with and without compatibilizer of maleic anhydride grafted polypropylene (MAPP) were prepared using injection molding method. The ratio of PP/RH and MAPP was fixed at 90/10 and 3 wt%, respectively. The main objective of the study was to analyze the effects of MAPP as a compatibilizer on the mechanical properties and morphology of the PP/RH/TiO_2 composites. The results show that PP/RH/TiO_2-5wt% with MAPP attained the highest results. An enhancement of about 20% and 11% in tensile strength and Young's modulus, respectively was obtained with the inclusion of MAPP. The elongation at break, however, decreases with the inclusion of MAPP. Morphological examinations reveal that the presence of MAPP in hybrid composites improved compatibility between PP and RH leading to good interfacial adhesion.

KEYWORDS: *Hybrid Polypropylene Composites; Rice Husk; Titanium Dioxide; Maleic Anhydride Grafted Polypropylene; Mechanical Properties*

1.0 INTRODUCTION

Over six decades, the use of plastics in daily life grew at significant rate worldwide and plastics have good potential especially in the industrial fields such as packaging materials, building construction, automobile and farming [1-2]. The high volume utilization of plastics has further led to massive global issues such as plastic solid waste [3]. Non-biodegradable nature of plastics has hazardous effects on the environment. This attribute becomes the biggest contributor to plastic solid waste disposal problem [4].

These factors become a driving force to develop low cost, renewable and green materials [5]. One of the alternative methods is to produce modified plastic constituted with natural fiber resources from agricultural byproduct such as rice husk (RH) in order to fulfill all the mentioned factors and to produce materials with partial degradation attributes. RH decomposes into 25-35% cellulose, 26-31% lignin, 18 - 21% hemicellulose, 2-5% soluble, 15-17% silica, and 7.5% moisture content [6]. However, the substitution of RH has since caused poor mechanical properties due to the existence of lignocellulosic fibers which consist of cellulose, hemicellulose, and lignin. The existence of hydroxyl groups associated with carbohydrates of fibers can interfere interfacial bonding with the hydrophobic polymer matric [7].

The important properties of composites such as mechanical properties mainly depend on the interfacial adhesion between polymer matrix and filler [8-9]. The poor mechanical properties of the final products are closely related to poor interfacial adhesion [10–14]. Incorporation of compatibilizers into the composites becomes one of the effective methods to alleviate this drawback. For instance, the common compatibilizer such as maleic anhydride grafted polypropylene (MAPP) is widely used to improve compatibility between hydrophilic natural fibers and the hydrophobic polymer matrix. The previous research indicated that tensile and flexural strengths of wood/polypropylene composites were enhanced with the addition of MAPP [15]. In another work, the use of MAPP in polylactic acid (PLA) and RH composites not only enhanced tensile properties but also was able to make contact surface of polymer/filler smoother and significantly reduce water absorption [16]. Moreover, it has conclusively shown that its inclusion of 1 to 3 wt% into RH-PP has remarkably improved the overall performance of the composites [17]. Hybridization method also becomes an interesting approach to improve mechanical properties by combining two or more filler/fibers [18]. Several works have been carried out to investigate the potential of combination between organic and inorganic fillers as reinforcing agent in composites via hybridization [19]. The incorporation of inorganic fillers such as TiO_2, talc, clay, carbon black, graphene and calcium carbonate into polymer matrix composite improves the properties of composites especially mechanical properties and minimizes the cost [20].

This research investigates hybridized PP composites containing RH fibers and TiO_2 with the objectives to evaluate the effects of MAPP on the mechanical properties and morphology of the composites.

2.0 EXPERIMENTAL

2.1 Materials

PP was bought from Lotte Chemical Titan Malaysia and was used as a matrix in the composite. The density and melt flow index are 0.900 g/cm^3 and 14 g/min, respectively. TiO_2 with the structure of rutile (91.5 wt%) was purchased from Afza Maju Trading has a density of 3.84 to 4.26 g/cm^3. RH was supplied by a local rice factory in Malaysia.

2.2 Alkaline Treatment of Rice Husk

Alkaline treatment was selected to improve adhesion between treated RH and thermoplastics [21]. In this work, a total of 50g of RH was soaked in 500 ml of 1% (w/v) NaOH solution for 24 hours. Hydrochloride acid solution (0.1 M) was poured into NaOH solution to allow neutralization process to occur [22]. RH was then filtered and washed with tap water until pH 7 was obtained. Subsequently, RH was placed into the furnace with temperature of 100˚C for 24 hours. RH was then subjected to grinding process. RH was sieved to obtain RH particles size which was less than 50 μm. The preparation of treated RH is shown in Figure 1.

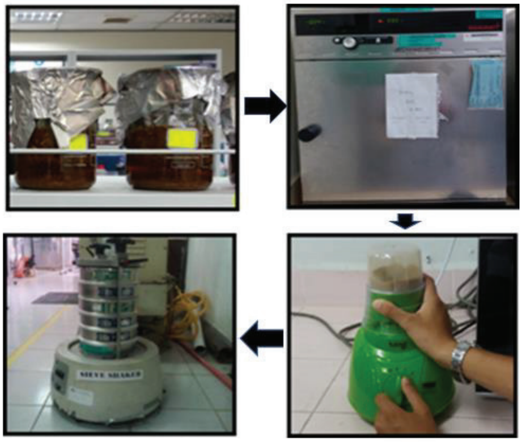


Figure 1: Preparation of treated RH

2.3 Samples Preparation

The first part involved PP and composite sample preparation without the inclusion of MAPP. The mass ratio of PP and RH was kept constant at 90:10 and TiO_2 content was varied at 2 wt% and 5 wt%. PP was firstly loaded into an internal mixer (Brabender) at a temperature of 170˚C and mixing rate at 60 rpm. After PP was fully melted, RH particles were loaded little by little to obtain homogenous mixture followed by TiO_2. The second part was to prepare PP/RH/TiO_2 composites with MAPP. In this part, 3 wt% of MAPP was added into PP/RH/TiO_2 with the same formulation as mentioned before. Finally, the PP/RH/TiO_2 composites with and without MAPP were molded according to ASTM D638 type-V specimen using an injection molding machine (Haake) with the cylinder temperature of 220˚C, mold temperature of 60˚C and 10 seconds of holding time. Table 1 shows the composition of the composites.

Table 1: Composition of composite samples

Polypropylene (PP) (wt%)	Rice husk (RH) (wt%)	Titanium dioxide (TiO_2) (wt%)	Maleic anhydride- grafted polypropylene (wt%)
100	-	-	-
90	10	2	-
90	10	5	-
90	10	2	3
90	10	5	3

2.4 Mechanical Testing

Tensile test was carried out using Instron Universal Testing Machine (Model 3366) according to ASTM D638. The crosshead speed was 10 mm/min at temperature of $25 \pm 3^{\circ}C$. Experiments were carried out with three sample replicates [22].

2.5 Morphological Analysis

The morphology of composite fracture surface was studied using JOEL model scanning electron microscope at an accelerated voltage of 10kV. The sample surfaces were coated with gold before analysis.

3.0 RESULTS AND DISCUSSION

3.1 Mechanical Properties

3.1.1 Tensile Strength

Figure 2 depicts the tensile strength of neat PP and PP/RH/TiO_2 with and without MAPP. As a control sample, neat PP containing no RH, TiO_2, and MAPP showed tensile strength of 40.35 MPa as shown in Table 2. Tensile strength for PP/RH/TiO_2-2wt% composites without MAPP shows a slight increase to 42.9 MPa. This may be due to the inclusion of inorganic filler of TiO_2. It is known that the presence of TiO_2 has significantly enhanced tensile properties because of the better adhesion occurred between PP and TiO_2. Hence, the load is transmitted from PP to TiO_2 [23]. The addition of MAPP into PP/RH/TiO_2-2wt% increases tensile strength up to 47.26 MPa indicating an increase of about 10% as compared to PP/RH/TiO_2-2wt% without MAPP.

Moreover, PP/RH/TiO_2-5wt% composites with MAPP exhibit the highest tensile strength of about 49.96 MPa. It is about 20% improvement in tensile strength as compared to composites without MAPP. Razak et al. [24] stated similar improvement whereby inclusion of MAPP 3 wt% into kenaf and PP composites resulted in the highest value for tensile strength. El Sayed et al. [25] also identified that the adhesion in PP/RH composites was enhanced with the incorporation of MAPP at 3 wt% led to improvement in tensile strength. The reason of this phenomenon lies on the better compatibility between the filler and matrix [26].

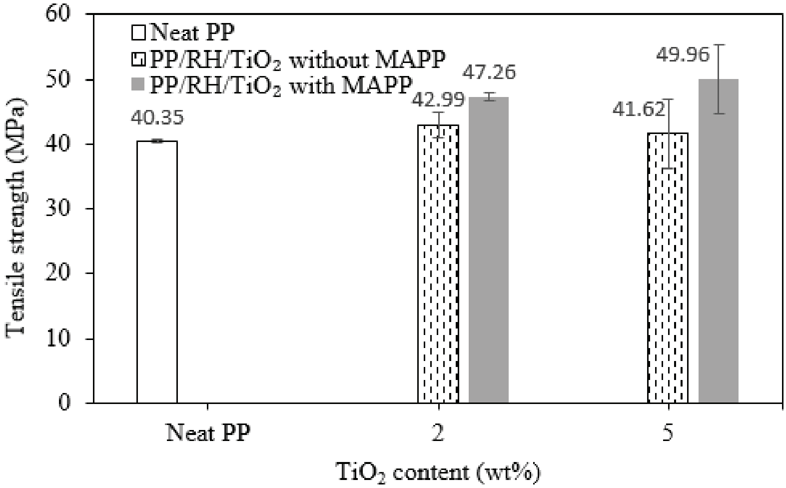


Figure 2: Tensile strength of neat PP, PP/RH/TiO_2 composites with and without MAPP

3.1.2 Young's Modulus

Figure 3 exhibits Young's modulus of neat PP, PP/RH/TiO_2 composites with and without MAPP. Young's modulus of the neat PP was about 2361.05 MPa as shown in Table 2. Generally, Young's modulus for all PP/RH/TiO_2 composites with and without MAPP increase as the contents of TiO_2 increases. PP/RH/TiO_2-2wt% and PP/RH/TiO_2-5wt% composites with MAPP exhibited higher values of Young's modulus than that of composites without MAPP which were about 2276.43 MPa and 2305.86 MPa, respectively. It is about 11% improvement in Young's modulus as compared to composites without MAPP. It is associated with the presence of a compatibilizing agent that has led to an increase in the composite stiffness responsible for the modulus increase [28].

Table 2: Results of tensile strength, Young's modulus and elongation at break of PP and composites

Composite composition (wt%)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
Neat PP	40.35	2361.05	10.28
PP/RH-10wt%/TiO_2-2wt%	42.99	2054.08	7.48
PP/RH-10wt%/TiO_2-5wt%	41.62	2075.18	8.73
PP/RH-10wt%/TiO_2-2wt%/MAPP	47.26	2276.43	6.91
PP/RH-10wt%/TiO_2-5wt%/MAPP	49.96	2305.86	6.71

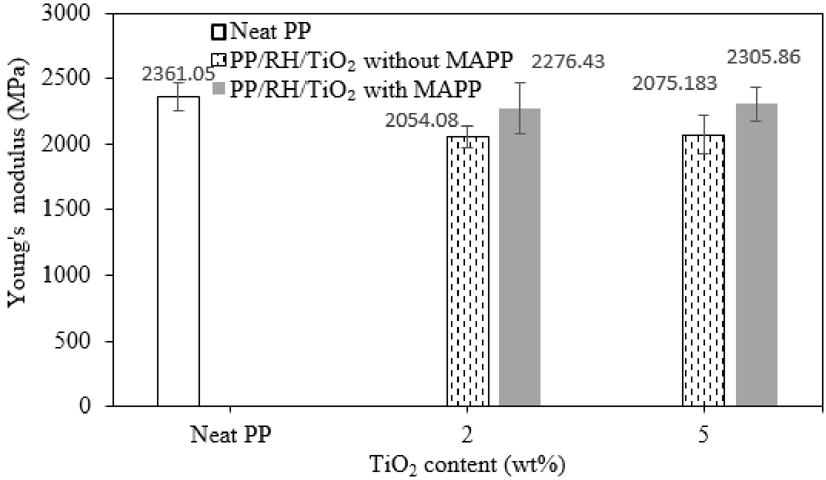


Figure 3: Young's modulus of neat PP, PP/RH/TiO_2 composites with and without MAPP

3.1.3 Elongation at Break

Figure 4 shows elongation at break of composites which denotes the composite flexibility. It can be observed that the elongations at break of PP/RH/TiO_2-2wt% and PP/RH/TiO_2-5wt% composites with MAPP are lower than that of composites without MAPP which are 6.91% and 6.71%, respectively.

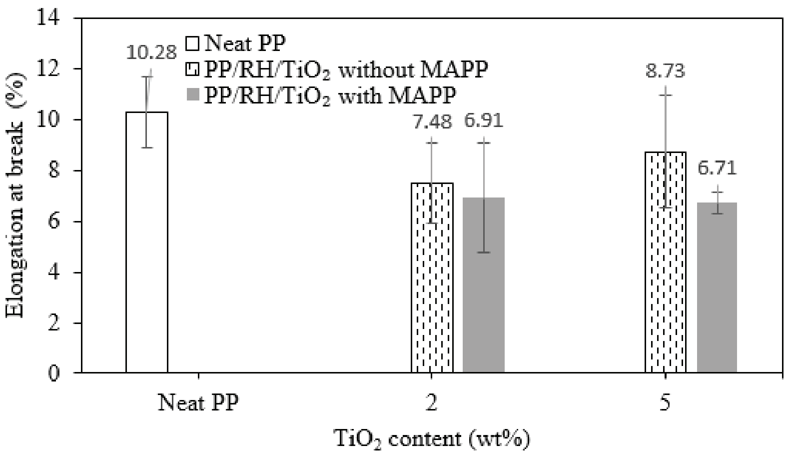
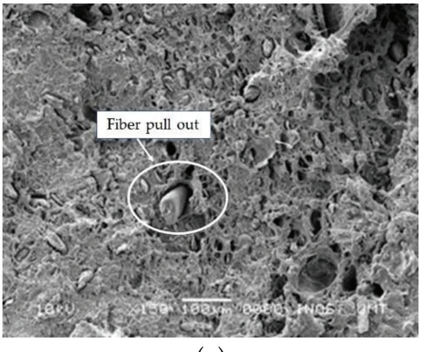


Figure 4: Elongation at break of neat PP, PP/RH/TiO_2 with and without MAPP

A similar trend was also observed when MAPP was used in PP/RH composites. It is because the compatibilizing agent serves to trigger off the interaction between PP and filler surfaces that will make the composites become stiffer. Consequently, the elongation at break value relatively decreases [17]. These results also indicated that MAPP reduces flexibility and elasticity of composites which was similar to that reported in the work of Techawinyutham et al. [27].

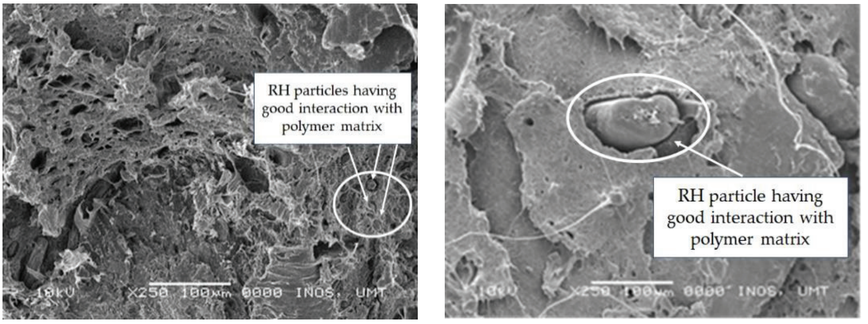
3.2 Morphology

Fillers and polymer matrix interaction can be observed using SEM technique. Thus, micrographs as in Figures 5(a)-(d) show the morphology of PP/RH/TiO_2-2wt% and PP/RH/TiO_2-5wt% with and without MAPP composites tensile fractured surfaces. It is evident that poor interaction between PP and RH particles lead to the occurrence of fiber pull out as denoted in Figure 5 (a) and (b) caused by the presence of void between fillers and polymer matrix. Rosa et al. [28] reported that the fiber pulls out phenomenon happened due to the existence of free space between the particles and the polymer matrix during brittle fracture. Mansor et al. [29] also mentioned that lower immiscibility and insufficient interfacial adhesion between filler and polymer can contribute to mechanical degradation in composite. The incorporation of MAPP in the composites as depicted in Figure 5(c) and (d) has diminished free space between RH particles and polymer matrices and makes the surface more homogeneous as a proof of the better adhesion in the interfacial region. The morphology supports the above findings related to mechanical properties of composites.



(a)

(b)



(c) (d)

Figure 5: SEM images of (a) PP/RH/TiO_2-2wt%, (b) PP/RH/TiO_2-5wt%, (c) PP/RH/TiO_2-2wt%/MAPP and (d) PP/RH/TiO_2-5wt%/MAPP

4.0 CONCLUSION

The investigation of the effects of MAPP as a compatibilizer on the mechanical properties and morphology of hybrid PP/RH/TiO_2 composites was successfully completed and the objectives were achieved. Overall, tensile strength and Young's modulus of composites containing MAPP were improved and higher than that of composites without MAPP. The PP/RH/TiO_2-5wt% composites with MAPP recorded the highest tensile strength of 49.96 MPa and Young's modulus of 2305.86 MPa. However, the elongation at break of the composites generally decreases with the addition of MAPP. The addition of MAPP into PP/RH/TiO_2 composites significantly reduced a free space and promotes compatibility between RH and PP leading to good interfacial adhesion.

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