

Effects of polypropylene methyl polyhedral oligomeric silsesquioxanes and polypropylene-grafted maleic anhydride compatibilizers on the properties of palm kernel shell reinforced polypropylene biocomposites

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Abstract

The effects of the polypropylene-grafted maleic anhydride (PP-g-MAH) and polypropylene methyl polyhedral oligomeric silsesquioxane (PP-POSS) compatibilizers on the mechanical, thermal and physical properties of palm kernel shell (PKS) reinforced polypropylene (PP) were investigated. The production of PP/PKS biocomposites was performed by melt mixing using Brabender Internal Mixer. Mechanical test results showed that the biocomposites with PP-g-MAH have better tensile strength compared to biocomposites with or without PP-POSS. The results also showed an increase in the tensile strength and elongation at break when compatibilizers were added. Polypropylene-grafted maleic anhydride improved the Young's modulus of the biocomposites, but PP-POSS reduced it. Moreover, adding compatibilizers in biocomposites reduced the water absorption of the biocomposites. The compatibilizers improved the nucleating ability of filler in the composites. The PP-g-MAH compatibilizer provided better performance in improving nucleating ability to biocomposites compared to PP-POSS.

Keywords: *biocomposites, palm kernel shell, polypropylene-methyl-polyhedral oligomeric silsesquioxane, mechanical properties, thermal behavior.*

1. Introduction

Producing environmental-friendly materials due to ecological issues has increasingly captured the attention of the world in government sectors and in the scientific community. The awareness of ecological issues led many government leaders of the countries in the world to introduce green technology to people. Converting wastes to functioning materials through green technology is an approach to solve one of the major ecological issues on wastes. Malaysia, who has become one of the biggest palm oil producer in the world, produces tons of wastes which include empty fruit bunches (EFB), palm kernel shells (PKS), pericap and palm oil effluent. These wastes worsen the disposal problem^[1]. Transforming wastes, such as palm kernel shells, into a useful and low-cost biocomposite material would reduce the problem^[2].

Moreover, scientists have shown their enthusiasm in doing research related to natural fillers reinforced biocomposites to produce environmental-friendly materials. In order to reduce the production of petroleum-based thermoplastic, natural fillers from waste have been broadly used. However, thermoplastics are required to undergo surface modification to remove the hydroxyl groups on the surfaces of natural fillers. These hydroxyl groups can be attracted to water

molecules that will reduce the mechanical properties of the thermoplastic composites. Therefore, elimination of hydroxyl group should be done in order to make hydrophilic fillers compatible with hydrophobic thermoplastic^[3].

Many polymer modifications have been implemented by researchers to overcome this compatibility problem such as the use of Polypropylene-grafted-Maleic Anhydride (PP-g-MAH)^[4-6], Polypropylene-grafted-Acrylic Acid (PP-g-AA)^[7], Polypropylene methyl Polyhedral Oligomeric Silsesquioxanes (PP-POSS)^[8,9], isocyanate group^[10,11], Poly(ethylene-co-glycidyl methacrylate) (PEGMA)^[12] as compatibilizers. Among the compatibilizers, Polypropylene-grafted-Maleic Anhydride (PP-g-MAH) compatibilizer is the most effective compatibilizer for lignocellulosic filler and matrix at the interface^[13]. Furthermore, the use of PP-g-MAH in lignocellulosics filler filled PP composites has been studied by^[14] which accentuated the interest of using rice husk flour and wood flour in PP composites. They found that PP-g-MAH improved the dynamic mechanical thermal properties of the composites. Thus, Polypropylene-grafted-Maleic Anhydride (PP-g-MAH) compatibilizer was used in this study to improve the properties of polymer composites.

In line with the objective to reduce the PKS wastes and petroleum-based thermoplastics, neat PP, uncompatibilized and compatibilized PP/PKS composites were produced on lignocellulosic filler in this study. The compatibilizers, PP-g-MAH and Polypropylene methyl Polyhedral Oligomeric Silsesquioxanes (PP-POSS), were used to investigate the effects on the mechanical, thermal and water absorption properties of these biocomposites.

2. Experimental Procedures

2.1 Materials

In this study, Polypropylene (PP) homopolymer resin grade PX617 with density of 0.9 g/cm³ and Melt Flow Index (MFI) of 1.7 g/10 min at 230 °C was purchased from Titan PP Polymers (PP) Sdn. Bhd. The palm kernel shells, that have an average density of 1.4485 g/cm³, were provided by Batu Lintang Oil Palm Mill Sdn. Bhd, Kedah. The compatibilizers, namely, PP-g-MA (polybond 3200) with 5 wt% of maleic anhydride (MA) content, and PP-POSS with 10 wt% of methyl POSS, were supplied by Uniroyal Polybond Sdn. Bhd. and Sigma-Aldrich (M) Sdn. Bhd, respectively.

2.2 Preparation of palm kernel shell

The palm kernel shells (PKS) were first removed from coir and then grounded using a grinder followed by sieving (63 µm) to obtain fine and uniform particle size. After that, the PKS were dried in the oven for 24 hours at 80 °C.

2.3 Preparation of palm kernel shell reinforced polypropylene composites

The PKS and PP matrix were mixed using a Brabender internal mixer fitted with cam blades. The melt mixing was carried out at 180 °C with a rotor speed of 60 rpm. The polypropylene matrix was preheated in the mixing chamber of the internal mixer for 4 minutes. Then, the PKS powder was carefully inserted into the mixer within 30 seconds. The mixing process of PKS powder and PP was continued for 6 minutes. Afterwards, the compounded specimens were discharged from the mixing instrument. In preparing the composites with compatibilizer (PP-g-MA or PP-POSS), the compatibilizer was mixed first with the PP matrix before the preheating process. After discharging the specimens from the mixing instrument, the compounded specimens were sheeted with 1 mm thickness using hot press process at temperature of 180 °C for 10 minutes.

2.4 Mechanical test

2.4.1 Tensile test

All the samples were cut into dog-bone shape using Wallace die cutter. The test was carried out using an Instron 5569 tensile testing machine. The crosshead speed of testing is 50 mm/min and the gauge length was set at 50 mm according to ASTM D-638, at room temperature. At least five samples were tested for each formulation. Tensile strength, elongation at break and Young's modulus were recorded and calculated by the instrument software.

2.4.2 Un-notched impact test

The impact tests were performed according to ASTM D256 using an impact pendulum tester with 7.5 J of impact energy. All the samples were cut into rectangular shape. At least five samples of each material were tested.

2.5 Morphological study

The fractured surface of the tensile area was analyzed using a model JSM-6460 LA JEOL scanning electron microscope (SEM). The fracture ends of samples were sputtered with a thin layer of palladium to avoid electrical charge during the analysis.

2.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis from -50 °C to 200 °C were performed on a Pyris Diamond Thermogravimetric Differential Thermal Analyzer at a heating rate of 10 °C/min in nitrogen atmosphere.

2.7 Differential scanning calorimeter (DSC) analysis

The thermal behavior of the polypropylene and biocomposites were examined using a differential scanning calorimeter (DSC) TA instrument analyzer at standard heating/cooling rate of 10 °C/min in nitrogen atmosphere. The temperature range used was -60 °C to 200 °C. First, the samples of about 5 mg were placed in the DSC aluminum pan and heated from -60 °C to 200 °C and hold for 2 minutes. Then, the samples were cooled to -60 °C and hold for 2 minutes. Afterwards, the cooled samples were heated back to 200 °C. Results obtained were analyzed using the Origin Pro software.

2.8 Water absorption test

The samples were cut into rectangular shape at an approximate dimension of 76.2 × 25.4 × 3.2 mm. The tests were conducted according to ASTM D570-98. The samples were dried at 50 °C for 24 hours and immersed in distilled water at room temperature until a constant weight was reached. The samples were periodically taken out from the water, wiped the surface moisture with a dried white cloth to remove water at the surface of samples, weighed to the nearest 0.001g immediately and replaced in the water. At least three samples for each composition were used and the results were averaged to obtain a mean value.

3. Results and Discussion

3.1 Mechanical test

Fillers are known to play an important role in the mechanical properties of thermoplastic composites. Results showed in Figure 1 that the tensile strength of the PKS reinforced PP biocomposite decreased with the increasing of filler content.

It can be explained by the different nature of PP matrix with the PKS filler. PP characterized by non-polar nature whereas PKS filler has polar group. This gives poor interfacial interaction between PP and PKS thus, lead to the poor strength of the composite. Poor dispersion of PKS inside PP matrix also contributed to the strength deterioration

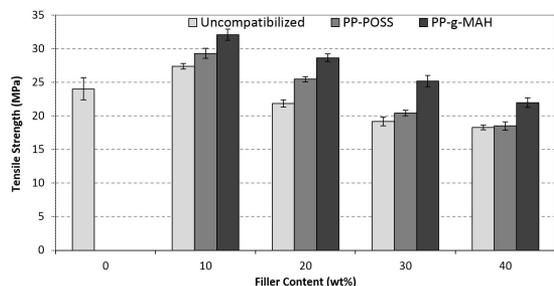


Figure 1. Effect of filler content and compatibilizers on tensile strengths of PKS reinforced PP biocomposites.

of the composites^[15]. Nevertheless, PKS reinforced PP biocomposites appeared to have higher tensile strength with the addition of PP-g-MAH and PP-POSS. Encapsulation of PKS particles by the PP-g-MAH compatibilizer occurs in the PKS reinforced PP biocomposites because of the strong polar interaction between PKS particles and PP-g-MAH compatibilizer which lead to the formation of compatibilizer phase between PKS and PP matrix^[16]. Well-known cage like structure POSS were proposed to trap PKS particles and lubricate dispersion of PKS in PP matrix^[17,18]. PP-g-MAH shows better tensile strength compared to PP-POSS. This is because PP-g-MAH forms chemical bonding with the PKS filler while PP-POSS only has physical bonding with the PKS filler^[13,19].

The Young's modulus of the PKS reinforced PP biocomposites increases with the increasing amount of filler content (as shown in Figure 2). It occurs due to the replacement of polymer matrix by stiffer particulate filler, which improves the overall composites modulus. The increase of the modulus is also due to the fact that the deformation and mobilization of matrix were restricted by the present of particulate filler that introducing a mechanical restraint^[20,21]. Incorporating PP-g-MAH compatibilizer into the PKS reinforced PP biocomposites shows not much improvement of Young's modulus at low filler content. However, the modulus significantly increased at 30 wt% and 40 wt% of filler content by about 300 MPa compared to PKS reinforced PP biocomposites without PP-g-MAH compatibilizer^[22]. Explained that, the increment of modulus of composite is due to the PP-g-MAH that solved the incompatibility problem between hydrophilic filler and hydrophobic polymer. The esterification function of copolymer bonding formed bridge between PKS filler and PP matrix while the hydroxyl group at the PKS formed hydrogen bonds with carboxyl group of PP-g-MAH. The modulus of PP composites decreased slightly when PP-POSS was added. It means that PP-POSS is a plasticizer toward the PP matrix reducing the rigidity of the PP composites^[17,23].

Figure 3 shows the effect of compatibilizers on elongation at break of PKS reinforced PP biocomposites. With the increasing of PKS content, elongation at break of PKS reinforced PP biocomposites decreased. The possible reason for this kind of behavior may be attributed to the fact that the restricted deformation of the PKS is generally greater than PP matrix, which restricted the deformation of overall composites. According to Leong et al.^[20], the nature of PKS of having a high rigidity may change the mode of failure

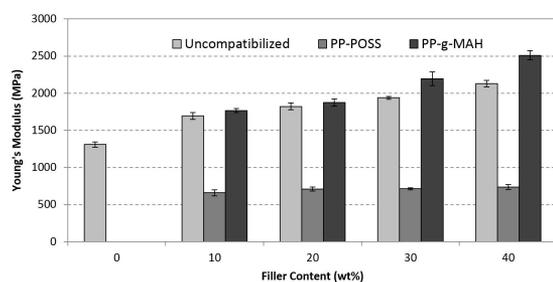


Figure 2. Effect of filler content and compatibilizers on Young's modulus of PKS reinforced PP biocomposites.

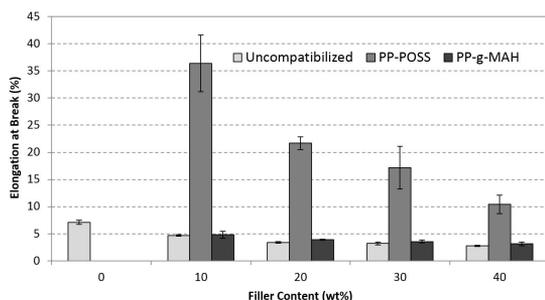


Figure 3. Effect of filler content and compatibilizers on elongation at break of PKS reinforced PP biocomposites.

of the PP matrix from ductile to almost brittle behavior. From Figure 3, the addition of PP-g-MAH and PP-POSS improved the elongation at break of PKS reinforced PP biocomposites. This may be due to the homogeneous structure that was developed by good interfacial adhesion between PP matrix and PKS which allowed the composites to have more deformation before break^[5]. Polypropylene-methyl-Polyhedral Oligomeric Silsesquioxanes (PP-POSS) shows a significant increase of elongation at break may be due to POSS, which could plasticize the molecular chain of PP matrix thus increasing the flexibility of the PP matrix^[8].

Moreover, the impact strength has direct correlation to the adhesion of the filler to the PP matrix. The result shows that PKS particles content and PP-g-MAH compatibilizer improved the impact strength. Figure 4 illustrates the impact strengths of the PKS reinforced PP biocomposites with different filler loading and with and without PP-g-MAH compatibilizer. It is clearly seen that at higher PKS content in PKS reinforced PP biocomposites, there is drastic decreased in impact strength of the composites.

Due to the hydrophilic particulate filler, it tends to agglomerate which initiates the crack propagation, and reduce the ability of the PKS reinforced PP biocomposite to absorb the impact energy through plastic deformation^[24]. It can also be explained that irregular shape of PKS (Figure 5) resulted to the inconsistent stress transfer from PP matrix to the PKS filler^[25,26]. However, the impregnation of PP-g-MAH into the PKS reinforced PP biocomposites assists the impact strength of the composites. This is because PP-g-MAH improves the wettability between PKS and PP, consequently improve the interfacial bonding in the composites and increase the impact strength^[27]. From Figure 4 also, it can be observed

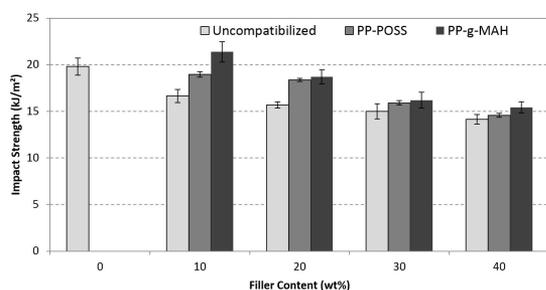


Figure 4. Effect of filler content and compatibilizers on un-notched impact strength of PKS reinforced PP biocomposites.

that PP-g-MAH gives the PKS reinforced PP biocomposites better impact strength compared to PP-POSS^[28]. Explained that filler was not well dispersed in PKS reinforced PP biocomposites by using PP-POSS compatibilizer while PP-g-MAH provide better dispersion of PKS in PP matrix.

3.2 Morphological study

The SEM micrograph of tensile fracture surfaces of PKS is shown in Figure 5, and the PKS reinforced PP biocomposites with 10 wt% and 40 wt% of filler content are illustrated in Figure 6. In Figure 6a, a few PKS particles are seen compare to tensile fracture surface of Figure 6b. In composite system without compatibilizer, it also can be seen that number of holes of Figure 6b is higher than Figure 6a and large amount of voids due to detachment of PKS particles can be seen in Figure 6b. This is due to the poor bonded interfacial area between matrix and filler causes brittle deformation of the composites^[29]. Figures 6c-f show tensile fracture surface of PKS reinforced PP biocomposites with compatibilizers. Figures 6c-f show less voids compare to Figures 6a and 6b. PP-g-MAH and PP-POSS compatibilizers help the matrix to encapsulate filler by introducing interfacial bond between the two elements^[30]. From Figure 6a, it can be seen that the pull of PP matrix which supported high elongation at break of tensile result^[31].

3.3 Water absorption

The water absorption of the PKS reinforced PP biocomposites is dependent on the nature of natural filler since the PP exhibit hydrophobic behavior. Figure 7 shows the equilibrium water uptake values, Q_{∞} , of the biocomposites versus different filler content with compatibilizers.

Figure 7 shows that increasing the PKS content in PP matrix will increase the water uptake by the composites. This is due to the hydrophilic PKS that contains hydroxyl group, which bonds with water molecules through hydrogen bonding^[32]. As more filler is added to the PP matrix, more hydrogen bonding formed between hydroxyl group and water molecules, thus increasing the water absorption of the composites^[33].

On the contrary, results showed that the water uptake by PKS reinforced PP biocomposites decreased with the addition of compatibilizers. This can be explained by the polymer modification by PP-g-MAH compatibilizer. Maleic anhydride group of PP-g-MAH forms a hydrogen bond with

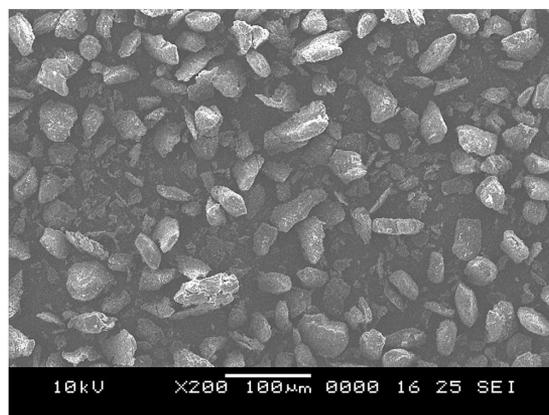


Figure 5. SEM images of Palm kernel shell powder.

some free hydroxyl group of PKS, which reduces the water absorption and it increases the resistance of composites towards water molecules. Polypropylene-grafted-Maleic Anhydride (PP-g-MAH) also enhanced the interaction between the PP and PKS improving the adhesion. However, there are still cracks and voids in the composites causing easy penetration and storage of water through voids^[34]. Both compatibilizers led to the reduction of water uptake by the composites. Between the two compatibilizers, the addition of PP-g-MAH shows better water resistant than PP-POSS based on Figure 7. This may be due to less hydrogen bonding because of PP-g-MA layer formed on the filler surface thus, constraint the water from coming into contact with the OH groups in the filler while physical bonding formed by PP-POSS and PKS still allowed water penetrate through into the PKS filler^[35].

3.4 Differential scanning calorimeter (DSC)

Table 1 shows the DSC measurements of neat PP and its biocomposites with compatibilizers containing 10 wt% and 40 wt% of PKS content. The melting point and crystallization temperature were obtained from the main peak of the endothermic and exothermic curves, respectively. On the other hand, glass transition temperature was acquired from the slope of endothermic stepwise change. From Table 1, it can be seen that the melting point temperature decreased with the addition of PKS content^[36] reported similar results in his study of flax, hemp and sisal fibers filled polypropylene composites. Table 1 shows that the heat of fusion and crystallinity of PKS reinforced PP biocomposites decreased at a higher filler content. It means that the PKS did not act as a nucleating agent in this system^[27]. This may be due to the fact that high PKS content tends to form agglomeration, thus there will be less available nucleation site of PP to crystallize at the interfaces and reduce the crystallinity of the composites. However, impregnation of PP-g-MAH compatibilizer into PKS reinforced PP biocomposites showed higher heat of fusion and crystallinity of the biocomposites. This is due to the chemical bond formed between the PKS and PP matrix which does not physically constrain the mobilization of the polymer chain. Hence, the addition of MA group from PP-g-MAH compatibilizer improved the

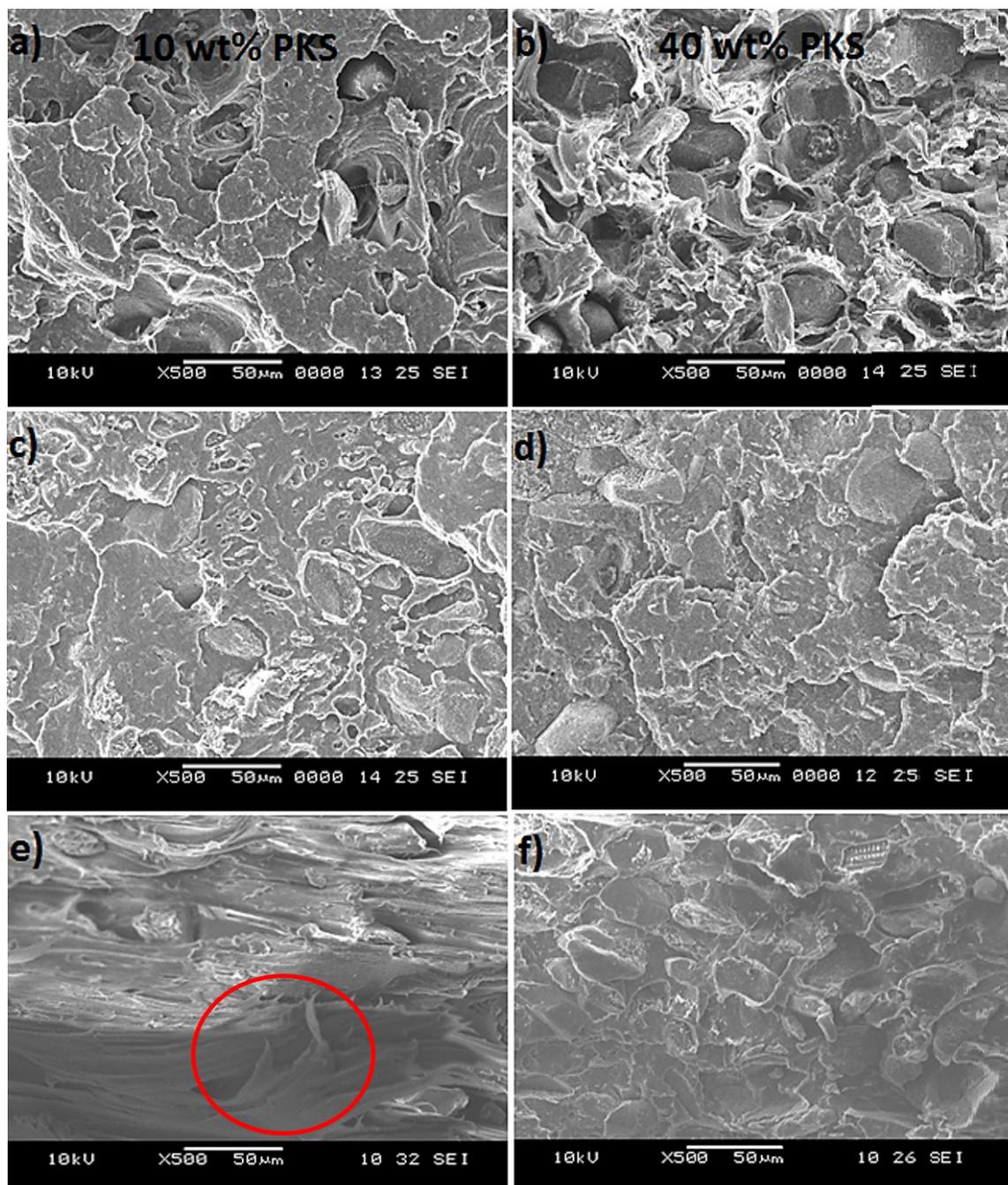


Figure 6. Tensile fractured surface of uncompatibilized PKS reinforced PP biocomposites and compatibilized PKS reinforced PP biocomposites at magnification X500 (a) 10 wt% PKS (Uncompatibilized); (b) 40 wt% PKS (uncompatibilized); (c) 10 wt% PKS (PP-g-MAH); (d) 40 wt% PKS (PP-g-MAH); (e) 10 wt% PKS (PP-POSS); (f) 40 wt% PKS (PP-POSS).

Table 1. DSC parameter analysis of neat PP, uncompatibilized biocomposites (10 wt% and 40 wt% filler) and compatibilized biocomposites (10 wt% filler).

Composites	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_f (J/g)	X_c (% crystallinity)
Neat PP	-3.10	139.92	165.31	85.19	40.76
Uncompatibilized (10wt%)	-2.50	138.68	165.09	84.75	40.55
Uncompatibilized (40wt%)	-2.30	134.88	163.63	54.23	25.95
PP-POSS (10wt%)	-5.70	139.42	165.08	81.26	38.88
PP-g-MAH (10wt%)	-7.20	138.06	165.02	92.10	44.07

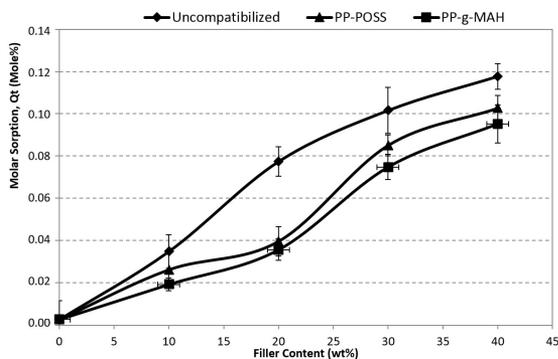


Figure 7. Effect of filler content and compatibilizers on water absorption of PKS reinforced PP biocomposites.

chemical bond between filler and matrix by enhanced the interfacial adhesion PKS to the PP matrix^[14].

Table 1 also shows that the crystallization temperature, T_c , decreased from 139.92 °C for neat PP to 134.88 °C for biocomposites with 40 wt% of PKS. This supports the crystallinity and heat of fusion result of the composites and neat PP whereby PKS reduced the formation of spherulite in the composites. It is suggested that there is a poor interaction between PKS filler with Polypropylene matrix^[37]. Nonetheless, PP-g-MAH and PP-POSS compatibilizer assist the PKS to act as nucleation sites for spherulites formation, thus maintaining the value of T_c . The addition of PKS content into PP matrix shows a slight increase in glass transition temperature, T_g . This proves that chemical bonding do not occurs at the interface between PKS filler and PP matrix. Only physical bonding occurs where PKS filler was encapsulated by PP matrix^[14]. By further examining the data listed in Table 1, it can be found that the compatibilized PP composites with either PP-g-MAH and PP-POSS have lower T_g . This could be due to the chemical bonding between the filler and matrix where compatibilizers aid in the adhesion of filler toward the matrix thus, acting as a plasticizing agent in composites system^[38].

3.5 Thermogravimetric analysis (TGA)

Thermal stability of the PKS plays an important role to foresee its implementation into PP matrix. Figure 8 shows the thermal behavior of the biocomposites using TGA.

Figure 8 illustrates that the 10 wt% of PKS in PP matrix has higher thermal stability compared to 40 wt% of PKS. It validates that there is a poor adhesion between the palm kernel shell and polypropylene at higher filler content, which means that it becomes less a stable structure towards heat^[39]. On the hand, biocomposites with the presence of PP-g-MAH show remarkable thermal stability than the other composites tested in this study. This indicates strong adhesion of the hydrogen bonds and covalent linkages between the hydroxyl group of PKS and the maleated anhydride group of PP-g-MAH^[27]. The biocomposites with the presence of PP-POSS compatibilizer in this study has lower thermal stability compared to PP-g-MAH. This suggested that the lengthy alkyl chains and silicon cage of PP-POSS could create a softer shell. This softer shell may limit the stress transfer from PP matrix to PKS^[40].

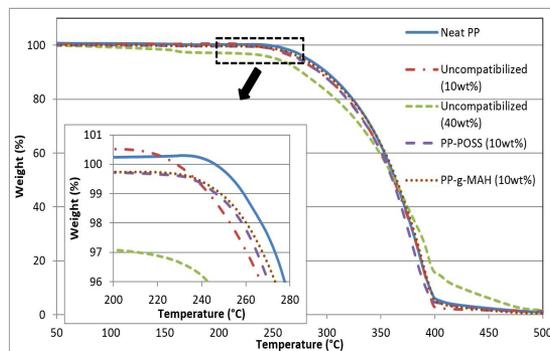


Figure 8. TG curves of PKS reinforced PP biocomposites at different filler loading and with compatibilizers.

4. Conclusions

The Polypropylene (PP) was reinforced using palm kernel shells (PKS). Increasing the amount of PKS on the filler significantly increases the Young's modulus; increases the water uptake; increases the tensile strength at 10 wt% PKS but deteriorates above 10 wt% of PKS; slightly increases the glass transition point temperature; decreases the elongation at break, impact strength, crystallinity, heat of fusion, crystallization temperature, melting point, thermal stability; and producing more holes or voids on the surfaces of the biocomposites. All these effects can be attributed to the presence of the hydroxyl groups in the surface of PKS resulting to poor adhesion of PKS to the PP matrix and attraction to water molecules.

Adding compatibilizers such as PP-g-MAH and PP-POSS generally increased the adhesion between the PKS and PP matrix by removing the hydroxyl groups on the PKS surface producing less voids and cracks compared to the uncompatibilized biocomposite. Some of their effects differ due to their molecular composition. Using PP-g-MAH as the compatibilizer produced the following results: highest increase of tensile strength, impact strength, Young's modulus, heat of fusion and crystallinity; slight increase in elongation at break; highest decrease of water uptake improving water resistance; highest thermal stability among the biocomposites in this study; highest decrease in glass transition temperature, crystallization temperature; and slight decrease in melting point.

On the other hand, using PP-POSS as the compatibilizer produced the following results: highest and significant increase in elongation at break; an increase in tensile strength, impact strength and crystallization temperature; significant decrease in Young's modulus; decrease in water uptake, crystallinity, heat of fusion and glass transition temperature; slight decrease in melting point; and lower thermal stability than using PP-g-MAH as the compatibilizer.

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