

Preparation and Characterization of Palm Kernel Shell/Polypropylene Biocomposites and their Hybrid Composites with Nanosilica

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Hybrid composites are characterized by a variety of properties that are of interest to automotive applications, including strength, mechanical, and thermal properties. In this work, palm kernel shell-filled maleated polypropylene composites and palm kernel shell/nanosilica-filled maleated polypropylene hybrid composites were produced using a Brabender Internal Mixer. The results showed that the usage of the two types of filler in the PP matrix enhanced the tensile strength, elongation at break, and impact strength but reduced the tensile modulus of the PP composites. Thermal studies confirmed that the improved nucleating ability of the hybrid fillers contributed to the superb mechanical properties of the hybrid composites. A lower percentage of water absorption was observed in hybrid composites compared to the palm kernel shell/PP composite system.

Keywords: Palm kernel shell; Nanosilica; Polypropylene; Hybrid; Biocomposites

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INTRODUCTION

Hybrid composites are composites in which two or more reinforcements are utilized in a single matrix in order to obtain diversity in the properties of the composite (Li *et al.* 2006). However, these hybrid composites must be designed judiciously if they are to provide the linear additive properties unavailable in single or binary phase composites and the multiplicative enhancement of the interaction between different constituents (Shonaike and Advani 2003).

Some researchers have done studies on hybrid composites in which a thermoplastic matrix was reinforced with two different fillers. The thermoplastics were mixed with wood flour and recycled glass fiber (Valente *et al.* 2011), short glass fiber and calcite (Fu *et al.* 2002), long glass fiber and calcium carbonate (Hartikainen *et al.* 2005), talc and calcium carbonate (Leong *et al.* 2004), or glass fiber and wollastonite (Joshi and Purnima 2010). So far, little work has been done on hybrid composites that involve nano-size fillers.

Nanoparticles are well known for their size advantage, which gives the matrix a high surface contact area. However, the use of nanoparticles in polymer composites is challenging for material engineers, as the homogenous dispersion of inorganic nano-objects into the polymer matrix is difficult to ensure. This is the natural behavior of nanoparticles, which have a tendency towards agglomeration (Wu *et al.* 2005; Zhou *et al.* 2008) in polymer composites that is even worse than that of microparticles. The

agglomeration of the filler leads to material deterioration, decreasing the performance of the polymer composites in mechanical and thermal properties. However, the ultra-fine phase dimension of nanosilica ensures that there is significant improvement in reinforcement and rigidity of the composites compared to glass and mineral (Lin 2009). The additions of PP-g-MA compatibilizer into the composite in order to reduce agglomeration of filler were demonstrated in a previous report (Orden *et al.* 2010).

Other fillers that have attracted material engineers in recent years are lignocellulosic materials. These materials, comprising lignin, hemicellulose, and cellulose, have become an alternative to conventional fillers such as glass fiber, calcium carbonate, and others. This is due to their environmentally friendly nature, as lignocellulosic materials are derived from plants. Palm kernel shell (PKS) is one of the several lignocellulosic materials that is derived from palm oil plants. PKS is considered agricultural waste (Rasat *et al.* 2011) because only the kernels are extracted from the palm oil that is used for daily cooking. Usually, PKS is burned without recovery of the energy or used to cover the surfaces of the roads in plantation areas (Arami-Niya *et al.* 2012).

Polypropylene plays an important role in composites by protecting the fillers from environmental threats. The usage of polypropylene in the plastic manufacturing industry has increased every year in comparison to other low-cost polyolefins due to its high-temperature resistance, easy processing, and high crystallinity (Peacock and Calhoun 2006).

However, the compatibility of the polymer matrix with the filler should be well-managed in order to achieve the optimum performance of the composite. Since polypropylene is well known for its versatility, it can be modified in many ways to allow it to achieve a wide variety of end-use applications. For example, cost-effective improvements in mechanical properties of polymers have been obtained by adding various fillers and reinforcements. Both mechanical and thermal properties such as tensile strength, flexural strength, heat deflection temperature, and impact strength can be improved with the addition of fibrous materials. Fillers are normally used for reducing the final material cost while enhancing the stiffness and impact strength of the material. However, most fillers or reinforcements and polymer matrices are not compatible with each other. Polymer modification such as a grafting approach can be implemented to overcome this problem (Karian 2003).

There has been limited literature on palm kernel shell-filled thermoplastic composites. Thus, the present research work emphasizes the tensile properties, thermal properties, and water absorption studies of palm kernel shell/nano-SiO₂/polypropylene hybrid composites.

EXPERIMENTAL

Materials

Polypropylene (PP) homopolymer resin grade PX617, which was used as the matrix, was supplied by Titan PP Polymers (PP) Sdn. Bhd. The density of the polymer was specified as 0.9 g/cm³ and the melt flow index (MFI) was 1.7 g/10 min. Fumed nanosilica with an average particle size of 7 nm and density of 2.2 g/cm³ at 25°C, which was used as filler, was obtained from Sigma-Aldrich.

The palm kernel shells, with average density of 1.4485 g/cm^3 , were supplied by Batu Lintang Oil Palm Mill Sdn. Bhd. Compatibilizer, PP-g-MA (polybond 3200) with 5 wt% of maleic anhydride (MA) content was supplied by Uniroyal Polybond Sdn. Bhd.

Preparation of Palm Kernel Shell/Nanosilica-filled Polypropylene Hybrid Composites

The composites were prepared with different compositions consisting of filler loadings between 10 wt% and 40 wt%, as shown in Table 1. The nanosilica and palm kernel shell powder were dried in a vacuum oven for 24 h at 80°C . The palm kernel shell/polypropylene composites were produced at 180°C using a Brabender Plastograph® EC Plus device fitted with mixer W 30 EHT with a rotor speed of 50 rpm. The processing duration was 8 min. To eliminate foreign materials or contaminants that could have been left behind from the previous usages, the chamber was first cleaned with neat polypropylene. Then, polypropylene and PP-g-MA compatibilizer was delivered into the chamber of the Brabender unit; after 3 min of processing time the material had melted. Three minutes were enough time for PP to fully melt before the addition of filler. Then, the well-dried palm kernel shell powder was carefully poured into the chamber, and the mixing was continued up to 8 min of processing time. As for the hybrid composites, the nanosilica and palm kernel shell were pre-mixed first, then carefully poured into the chamber, and the mixing was continued up to 8 min of processing time. After 8 min, the rotors were stopped, and the compounding composites were discharged from the mixer chamber. The selection of 8 min compounding time provided enough time for filler to disperse in PP matrix and decreased the possibility of PKS becoming burnt.

Dumbbell-shaped samples of one-millimeter thickness were prepared using the molding process. For impact and water absorption samples, sheet samples of 3.2-millimeter thickness were prepared. These processes were done using an electrically heated hydraulic press model, GT 7014 A, at 180°C . First, for the tensile test samples, the two metal plates with dumbbell-shaped mold plates were heated to 180°C . For the impact and water absorption tests, the two metal plates with the square-shape mold plates were replaced dumbbell-shaped mold plates. For the smooth surface of the sheet, two thin films were placed between two metal plates inside the compression machine before the loading of the compounding composites. Then, the samples were pre-heated for 8 min. During the pre-heating, the mold was pressed upwards slowly in order to avoid trapping bubbles in the samples when the samples started to melt. After that, the samples were compressed for 2 min to produce a uniform, flat surface. The hot melting samples were quickly transferred to a cold press for 5 min. The samples were stored at ambient temperature for 24 h prior to characterization.

Tensile Test

Tensile tests were carried out on the dumbbell samples using an Instron 5569 tensile testing machine. The crosshead speed of the testing was 50 mm/min, and the gauge length was set according to ASTM D-638. The thickness of the samples was measured using a Vernier caliper. Five samples were tested for each formulation. Tensile strength, elongation at break, and Young's modulus were recorded and calculated by the instrument software.

Impact Test

The notched Izod impact testing was performed using an impact pendulum tester according to ASTM D256. The hammer that was used to strike the samples was 7.5 J, and the experiment was conducted at room temperature. Five measurements were conducted for each sample, and the average of the five samples was used for the mean value.

Water Absorption Test

The palm kernel shell/nanosilica-filled polypropylene hybrid composite samples of the approximate dimensions 76.2 mm × 25.4 mm × 3.2 mm were used for the measurement of water absorption according to ASTM D570-98. The samples were dried at 50 °C for 24 h and immersed in distilled water at room temperature until a constant weight was reached. The specimens were periodically taken out of the water, wiped free of surface moisture with a dry cloth, immediately weighed to the nearest 0.001 g, and replaced in the water. At least three samples for each composition were used. The molar sorption, Q_t , of water by the composites at time t was calculated from,

$$Q_t (\text{mole } \%) = \left(\frac{W_2 - W_1}{18 \times W_1} \right) \times 100\% \quad (1)$$

where W_1 is the weight of the dry sample, W_2 is the weight of the wet specimen, and 18 is the molecular weight of water.

Morphological Study

Studies on the morphology of the tensile surface of the composites were carried out using a scanning electron microscope (SEM). The fracture ends of the specimens were mounted on aluminum stubs and sputter-coated with a thin layer of palladium to discourage electrostatic charging during the examination.

Differential Scanning Calorimetry (DSC)

The crystallization behavior and melting characteristics of the composites were investigated by differential scanning calorimetry (DSC) using a DSC Q10 analyzer in a nitrogen atmosphere of 50 mL/min at the heating rate of 10 °C/min. The crystallinity (X_{com}) of the composite was determined using the following relationship:

$$X_{\text{com}} (\% \text{ Crystallinity}) = \left(\frac{\Delta H_f}{\Delta H_f^\circ} \right) \times 100\% \quad (2)$$

where ΔH_f and ΔH_f° are the enthalpy of fusion of the system and the enthalpy of fusion of perfectly (100%) crystalline PP, respectively. For ΔH_f° (PP), a value of 209 J/g was used for 100% crystalline PP (Fina *et al.* 2010).

RESULTS AND DISCUSSION

Tensile Strength

The effects of filler content on the tensile strength of the binary system (PP/PKS) composites and the tertiary system (PP/Nanosilica/PKS) composites are shown in Fig. 1. It can be seen that for both the binary and tertiary system, at a low filler loading, the

strength increased, whereas at a higher filler loading, the strength decreased slightly. It can also be seen that tensile strength of the PKS-filled polypropylene composites increased with the presence of nanosilica. Nanosilica has a high surface area due to its nano size advantage, which increased the wettability of the filler with the matrix. The improvement of the interaction between filler and matrix resulted in better handling of the external loading towards the matrix and thus improved the overall composites (Leong 2003; Lin 2009).

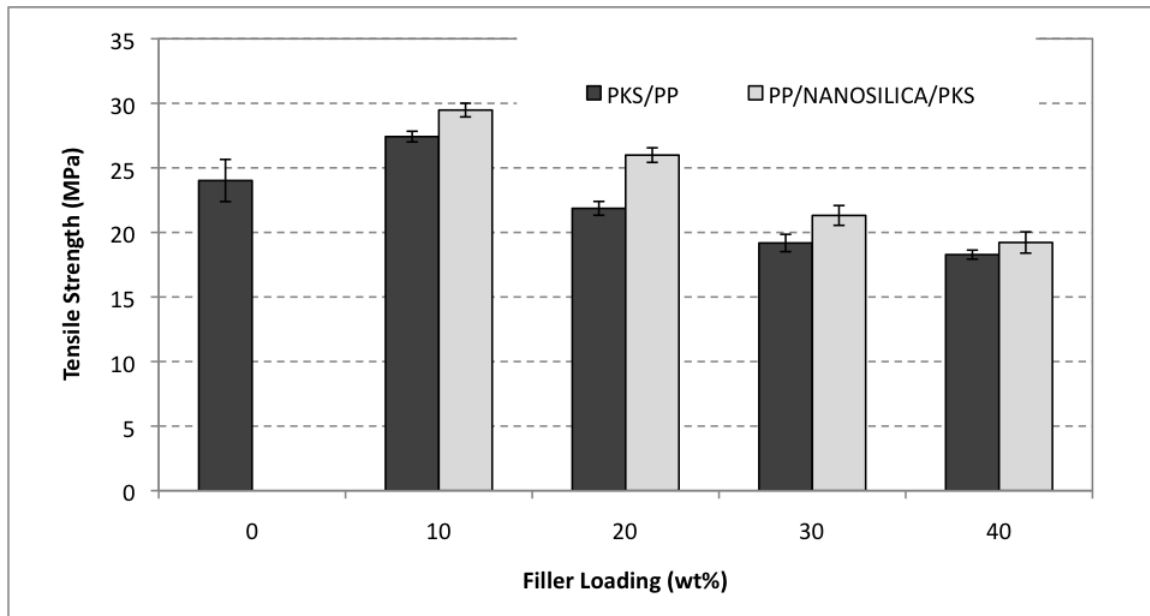


Fig. 1. Tensile strength for binary and tertiary system composites

The PKS and nanosilica particles embedded into the PP were analysed by SEM micrograph as shown in Figs. 2 and 3.

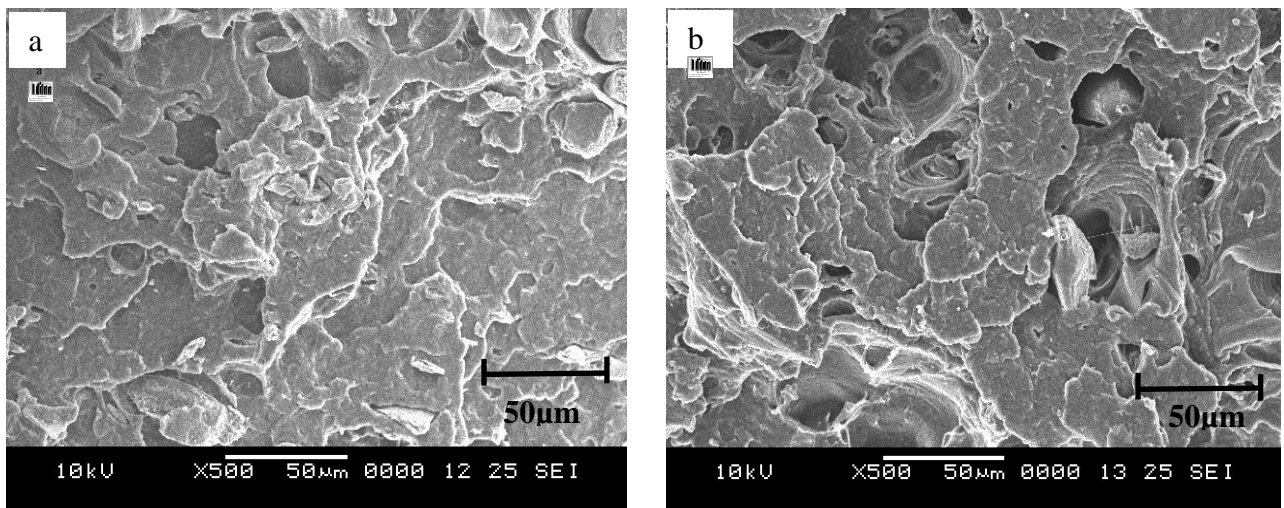


Fig. 2. Tensile fractured surface of 10 wt% filler-filled PP at magnification x500; (a) PKS/Nanosilica/PP composites, (b) PKS/PP composites

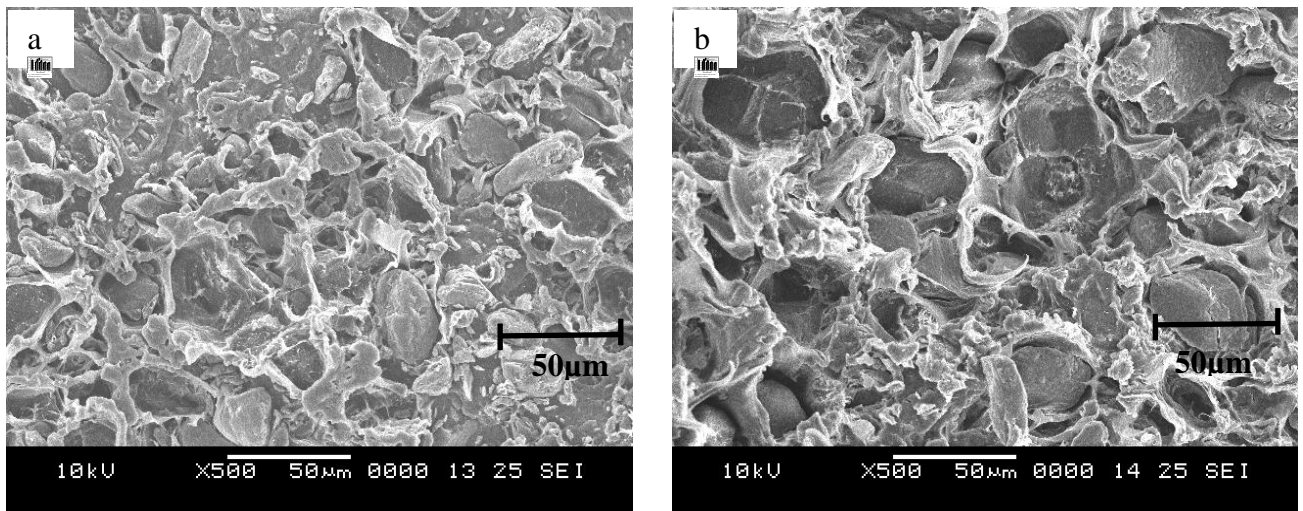


Fig. 3. Tensile fractured surface of 40 wt% filler-filled PP at magnification x500; (a) PKS/Nanosilica/PP composites, (b) PKS/PP composites.

The fractured surface of the tertiary system composites (Fig. 2(a) and Fig. 3(a)) seemed smoother than that of the binary system composites (Fig. 2(b), Fig. 3(b)), as a smaller void was formed in the tertiary system composites compared to the binary system composites. The smoother fractured surface was attributed to better interfacial adhesion of the nanosilica to the PP matrix in comparison to that of the PKS, and the poor interfacial adhesion of the PKS produced larger void spaces. The cavities and voids surrounding the fillers due to breakage at the inter-phase thus reduced the tensile strength of the composites (Chen *et al.* 2009).

Elongation at Break

The effect of filler loading on elongation at break for the binary and tertiary composites is depicted in Fig. 4. The elongation at break of both the binary and tertiary system composites decreased with the increase in filler content. A similar elongation-at-break trend can be observed in Leong's work (Leong 2003).

In the present study it was further observed that the elongation at break of the binary system composites dropped drastically compared to that of the tertiary system composites. This indicated that the nanosilica helped the composites to increase the plastic deformation at high filler loadings.

As nanosilica replaced the amount of PKS in the composites, the brittle composites caused by rigid PKS micro-particles exhibited more ductile behavior, thereby improving the elongation at break. However, both the binary and tertiary system composites showed elongations at break even lower than did the unfilled PP. This may have been due to the agglomeration of PKS, and such agglomerates had a negative effect on the advantageous high surface area of the nanosilica. The agglomeration could be attributed to the insufficient homogeneity and poor filler dispersion in the composites thus, reduced the deformability of the composites (Leong 2003; Lin 2009; Romisuhani 2011).

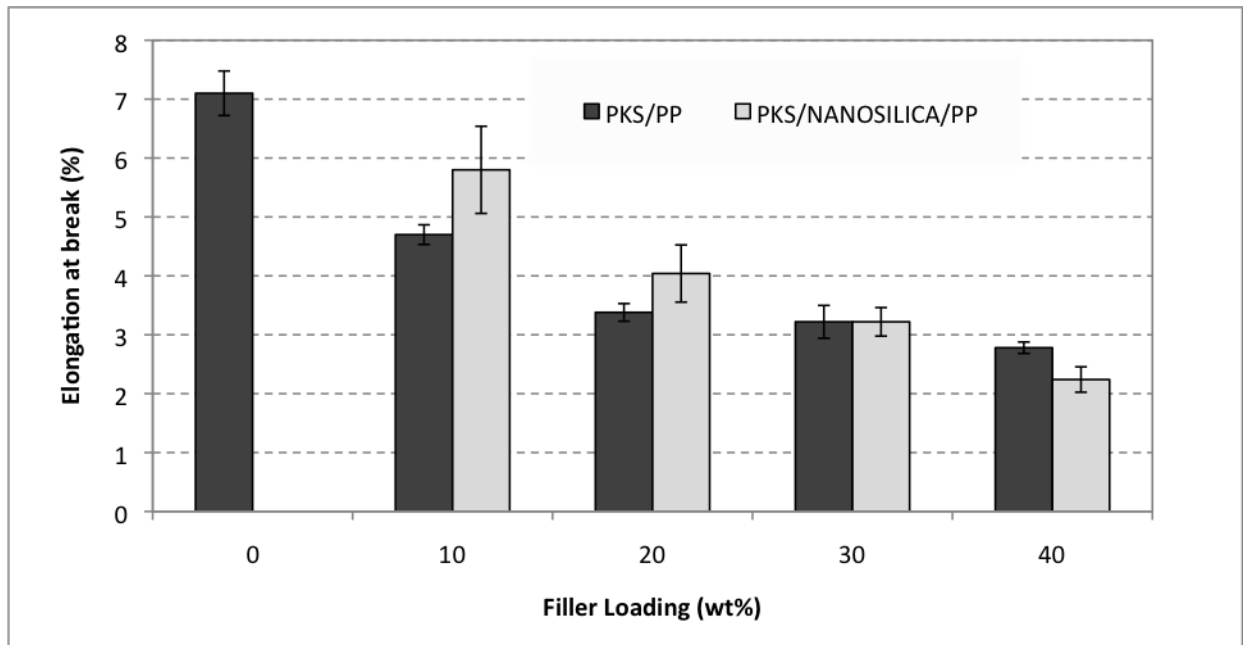


Fig. 4. Elongation at break for binary and tertiary system composites

Young's Modulus

From Figure 5, it can be observed that the increase in filler content increased the Young's modulus of both composite systems. This may be attributed to the rigidity of the fillers that increase the stiffness of the composites.

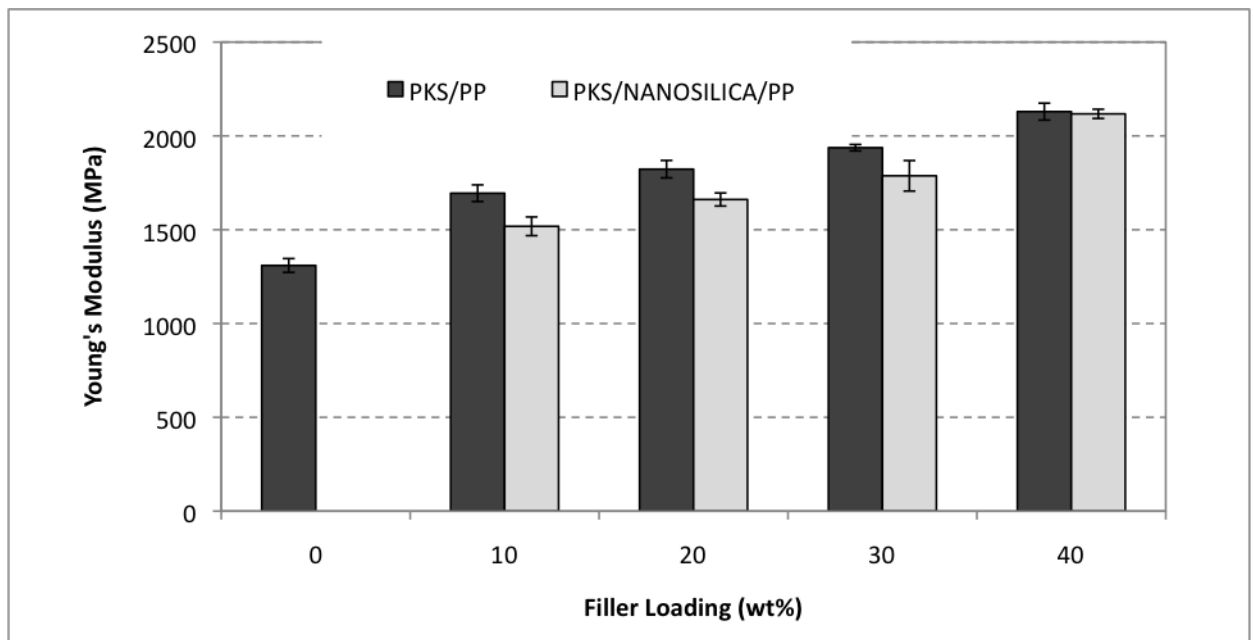


Fig. 5. Young's modulus for binary and tertiary system composites

It can also be seen that the addition of nanosilica to the PKS composites decreased the Young's modulus of the hybrid composites. This was due to the difference in size and shape of the nanosilica and PKS particles. Micro-size filler that had an irregular

morphology gave heterogeneous mechanical properties to the composites, which resulted in high-energy dissipation and a high modulus (Devaprakasam *et al.* 2009). Meanwhile, the nano-size filler in this experiment was spherical in shape and uniform in packing density in the composites, thus giving homogeneous mechanical properties to the composites, which in turn reduced the modulus. For this reason, the replacement of nanosilica on PKS content inside the hybrid composites would result in a decrease in the modulus of the hybrid composites.

Impact Strength

The effects of filler loading on the impact strength of the PKS/PP composites and PKS/nanosilica/PP hybrid composites are shown in Fig. 6. There was a strong enhancement in impact strength with the addition of nanosilica to the hybrid composites. From previous work done by Lin, nanosilica is known for its reinforcement ability and its improvement of the toughness of PP composites at 10 wt% of filler loading. This is because the high surface area of nanosilica enhances the wettability between the filler and matrix, resulting in higher toughness of the composites. However, Lin observed that with the increase in the filler above 10 wt%, the impact strength tended to decrease due to the agglomeration of the filler (Lin 2009). As discussed in the section on elongation at break, the agglomeration of the filler could contribute to a crack propagation in the composites that resulted in a decrease in the toughness of the composites. Bikiaris *et al.* explained that the formation of a boundary layer between the filler surface and the matrix is predicted by the theory of the filler toughening of polymer matrices. They noted that the properties of this layer are different from those of the bulk matrix, because the mobility of macromolecular chains, due to their adhesion to the filler surface, are restricted. The thickness of the boundary layer depends on the adhesion and consequently on the magnitude of the interaction between the filler and the polymer matrix (Bikiaris *et al.* 2005).

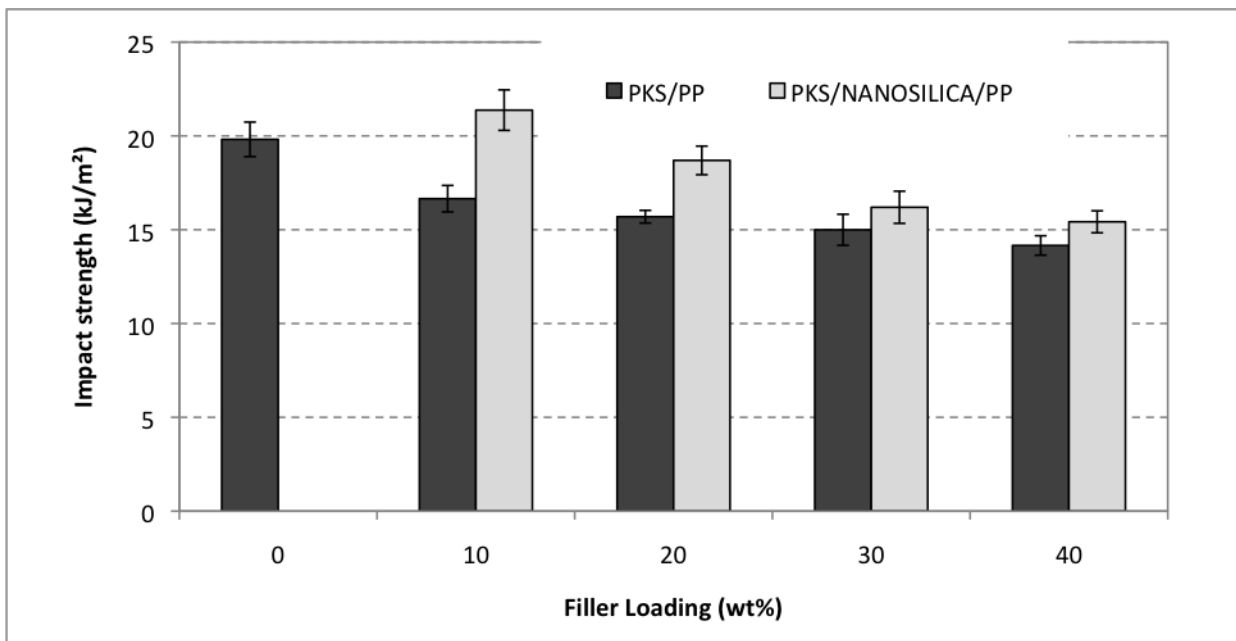


Fig. 6. Impact strength for binary and tertiary system composites

Differential Scanning Calorimetry (DSC)

DSC curves in Fig. 7 show the effects of the binary and tertiary system on the melting of the composites. Table 1 presents the summary of the DSC measurement parameter of the PKS/PP and PKS/Nanosilica/PP composites. From Table 1, it can be observed that the melting point (T_m) of the PKS-filled PP composites was almost the same as in the case of addition of nanosilica into PKS/PP composites. It was also discovered that the heat of fusion (ΔH_f) and the degree of crystallinity (X_c) of the composites increased with the addition of nanosilica to a level even higher than in the case of neat PP. This was because nanosilica acted as a nucleating agent that generated the nucleation sites for PP crystallization. The nanosilica accelerates the crystallization of the PP matrix remarkably. During the absorption of PP chains on the silica surface, the configurational entropy of the entire chain decreased, forming a nucleus of a certain volume within the adsorbed chains and thus enhancing the crystallization of the composites (Wu *et al.* 2005). It can also be observed that the PKS/PP composites had a lower X_c compared to the neat PP in Table 1. This meant that the PKS did not act as a nucleating agent in this composite system. The reason for the reduction of the X_c of the composite should be attributed to the disturbance in the crystalline formation induced by the PKS in the composite during the cooling process (Othman *et al.* 2006).

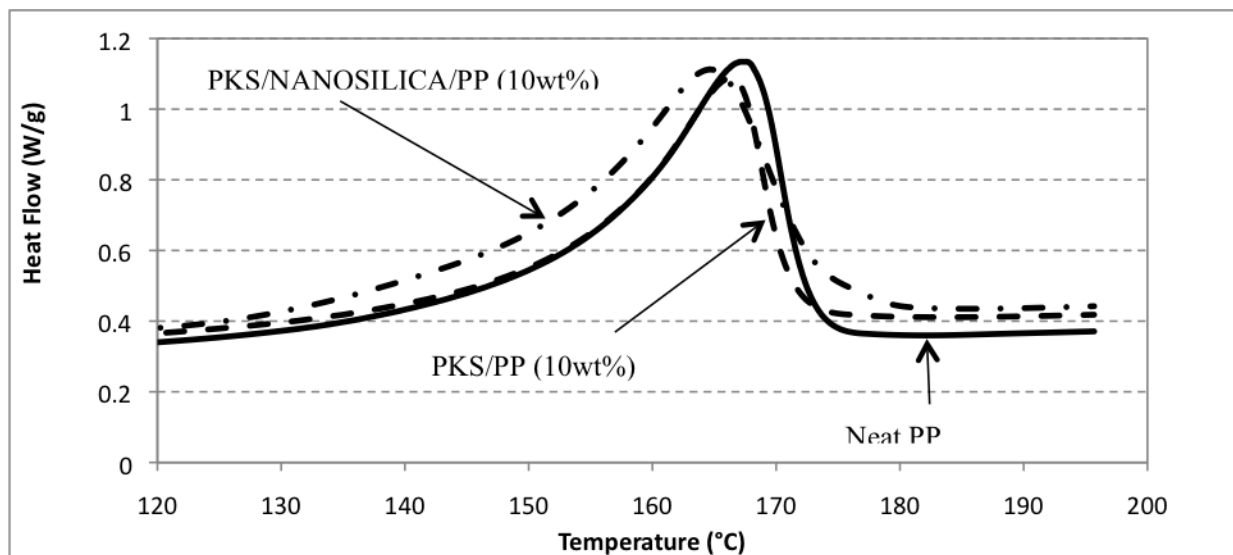


Fig. 7. DSC scan of neat PP, single-filler, and hybrid composites

Table 1. Parameter DSC Analysis of Neat PP, Single-filler, and Hybrid Composites

Composites	T_m (°C)	ΔH_f (J/g)	X_c (% crystallinity)
Neat PP	167.35	77.8	37.22
PKS/PP (10wt%)	167.44	65.41	31.13
PKS/Nanosilica/PP (10wt%)	165.70	83.91	40.15

Water Absorption Characteristics

Figure 8 shows the equilibrium water uptake values, Q_∞ , of the binary and tertiary system composites with different filler loadings. It can be observed that the addition of nanosilica into the PKS/PP composites increased the water resistance of the composites.

The nanosilica reduced the water uptake by 0.04% from the composite with the 40% filler loading, by 0.045% from the composite with the 30% filler loading, by 0.04% from the composite with the 20% filler loading, and by 0.01% from the composite with the 10% filler loading. This could be attributed to the huge interfacial surface area of the SiO₂ nanoparticles, which provided better wettability between the filler and the matrix, thus contributing to the improvement in interfacial adhesion and restricting more water from penetrating into the matrix (Kausch and Michler 2006).

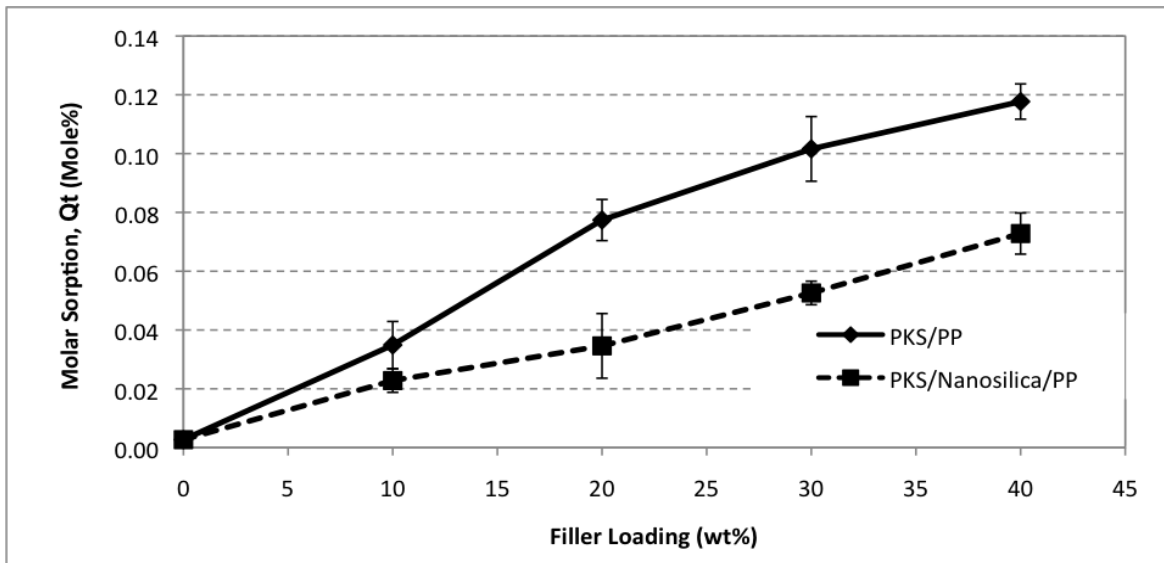


Fig. 8. Effects of filler loading on molar sorption of single-filler and hybrid composites

CONCLUSIONS

1. The incorporation of both PKS and nanosilica into the PP matrix resulted in a composite with higher tensile strength, tensile modulus, and impact strength than the neat PP and binary composites.
2. The addition of inorganic nanosilica into the binary system also reduced the water uptake of the composites.
3. The SEM studies showed smaller void spaces on the surface of the tertiary system composites compared to the binary system composites.
4. The thermal analysis indicated that the crystallinity increased with the addition of nanosilica into the binary system composites.

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