The Effects of Modifying Peanut Shell Powder with Polyvinyl Alcohol on the Properties of Recycled Polypropylene and Peanut Shell Powder Composites

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The effects of the chemical modification of peanut shell powder (PSP) using polyvinyl alcohol (PVOH) were studied. Both modified and unmodified peanut shell powder were used to prepare recycled polypropylene (RPP) and PSP composites. The effects of various PSP loadings (0 to 40% by weight) on the processing, tensile properties, morphology, Fourier transform infrared (FTIR) spectra, and water uptake properties were examined. Results showed that RPP composites with polyvinyl alcohol-modified PSP had higher values of tensile strength, elongation at break, and tensile modulus, but lower water resistance, than RPP composites with unmodified PSP. FTIR analysis revealed slight changes in band positions and intensities, indicating a distinct interaction between hydroxyl groups of the PSP composites and PVOH. RPP composites with PSP modified with PVOH had better interfacial adhesion between the matrix and the filler than RPP composites with unmodified PSP, as shown by scanning electron microscope (SEM) micrographs.

INTRODUCTION

Fillers of various composition are widely used in significant quantities in the plastics industry. Incorporation of filler into the plastic matrix enhances some properties but detracts from other properties. Fillers could influence the compatibility of the components of composites (Siriwardena *et al.* 2001). Natural filler-based composites are one alternative to the use of synthetic filler-based composites for various applications. The growing demand for environmentally friendly materials had led to the replacement of synthetic fillers with natural cellulose-based fillers (Ishak *et al.* 2010). These kinds of composite materials are prepared by combining natural, organic fillers derived from renewable resources with polymers. The polymers can be produced from either petroleum or from renewable resources. The advantages of natural fillers over their inorganic counterparts include large availability, low cost, low density, reasonable strength, reduced energy consumption, and biodegradability (Bledzki and Gassan 1999; Netravali and Chabba 2003).

Although natural fillers offer many advantages, a major disadvantage of cellulosic fillers is their highly polar nature, which makes them incompatible with nonpolar polymers (*i.e.*, PP, PE, and PS). This makes achieving good dispersion and strong interfacial adhesion between the hydrophilic filler and the hydrophobic polymers difficult (Kazayawoko *et al.* 1999). This can lead to poor performance of the final products. Filler

surface modification, or use of adhesion promoters, is the key to solving this problem. Surface characteristics such as wetting, adhesion, surface tension, and porosity can be improved by modifying the filler surface. Many reagents have been used to modify the cell-wall components to improve adhesion with varying degrees of success; some examples of these include acid chlorides, isocyanates, aldehydes, alkyl halides, anhydrides, lactones, and nitriles (Simonsen and Rials 1996). Chemical modifications may activate hydroxyl groups or introduce new moieties that more effectively interlock with the matrix (Sreekala *et al.* 2000). Polyvinyl alcohol (PVOH) is a hydrophilic polymer with a hydroxyl group on each of its repeating units, which permits the development of hydrogen bonds of PVOH with the carboxyl and hydroxyl groups of cellulose fillers.

Peanut is one of the world's important food crops. The production of peanut generates large amounts of waste namely peanut shell. Efforts to find utilization of these waste materials have resulted mostly in low-value or limited applications. In this regard, peanut shell powder (PSP) seems to be an interesting candidate due to its chemical composition. Thus, the use of this lignocellulosic filler is of great interest. In this work, PSP was used as an alternative filler in a recycled polypropylene matrix (Sareena *et al.* 2011). As in the case of wood, the main components of lignocellulose are cellulose, hemicellulose, and lignin. Hydrogen bonds between different layers of polysaccharides make crystalline cellulose resistant to degradation. Cellulose, hemicellulose, and lignin form structures called microfibrils, which are organized into macrofibrils. Such macro-fibrils are responsible for the structural stability of plant walls (Jacob *et al.* 2004). The contents of cellulose (40.5%), hemicellulose (14.7%), and lignin (26.4%) in peanut shells have been determined using Official Methods of Analysis of AOAC (15th Ed.) (Zaaba *et al.* 2013).

Previous studies (Sareena *et al.* 2011) have shown the potential effect of PSP as a natural filler in natural rubber, but no work has been found in the literature for thermo-plastic composites. Therefore, in this study PSP was selected as the filler and it was chemically modified with PVOH in recycled polypropylene (RPP) composites. The tensile properties, FTIR spectra, SEM micrographs, and water absorption characteristics of recycled polypropylene (RPP) composites with modified and unmodified PSP at different filler loadings were compared.

EXPERIMENTAL

Materials

Recycled polypropylene (RPP) with a melt flow index of 30 g/10 min was obtained from Zam Scientific (M) Sdn. Bhd. Peanut shell powder (PSP) was also supplied by Zam Scientific (M) Sdn. Bhd. The peanut shells were subjected to grinding, which yielded an average particle diameter of approximately 66.84 μm. PSP was then dried for 3 h at 70 °C using a vacuum oven before being used for composite fabrication. 99% hydrolyzed polyvinyl alcohol (PVOH) powder, with a molecular weight of 89,000 to 98,000 g/mol and a density of 1.269 g/cm^3, was obtained from Sigma Aldrich.

Modification of PSP with PVOH

PVOH powder (6 wt.%) was mixed with PSP. Ethanol was poured into the mixture. The mixture was then stirred until a homogeneous suspension was formed. The

suspension was heated at 80 ^{o}C for about 15 min to allow the PVOH to dissolve fully and then stored at room temperature for 24 h, until two distinct layers appeared. The upper layer was decanted, and the precipitate (PSP modified with PVOH) was dried in an oven at 70 ^{o}C.

Composite Preparation and Processing

Two types of composites were prepared: RPP with unmodified PSP (RPP/PSP) and RPP with PVOH-modified PSP (RPP/PSP$_{PVOH}$). They were both prepared using an internal mixer (Haake Rheomix Mixer, Model R600/610) at a temperature of 180 °C and speed of 50 rpm to obtain a homogeneous sample. First, the RPP was placed in the mixer and melted for 4 min. Then, the PSP was added. The composites were mixed for another 8 min until the mixing torque stabilized. The total mixing time was 12 min for all samples. The processed samples were then compression molded into a 1-mm-thick sheet by an electrically heated hydraulic press (Kao Tieh Go Tech Compression Machine) at a temperature of 180 °C. Table 1 shows the formulation characteristics for each of the composites.

Table 1. Formulation Characteristics of RPP/PSP and RPP/PSP$_{PVOH}$ Composites

Composite	RPP (wt.%)	PSP (wt.%)	PSP$_{PVOH}$ (wt.%)
RPP	100	-	-
RPP + 10% PSP	90	10	-
RPP + 20% PSP	80	20	-
RPP + 30% PSP	70	30	-
RPP + 40% PSP	60	40	-
RPP + 10% PSP$_{PVOH}$	90	-	10
RPP + 20% PSP$_{PVOH}$	80	-	20
RPP + 30% PSP$_{PVOH}$	70	-	30
RPP + 40% PSP$_{PVOH}$	60	-	40

Measurement of Tensile Properties

Tensile tests were carried out with a Universal Testing Machine (Instron 3366) according to ASTM D638. Dumbbell specimens of 1-mm thickness were cut from the compression molded sheets with a Wallace die cutter. A crosshead speed of 5 mm/min was used, and the tests were performed at 25 ± 3 ^{o}C. Five specimens were used to obtain average values for tensile strength, elongation at break, and Young's modulus.

FTIR Spectroscopy Analysis

The functional groups and chemical characteristics of the composites were obtained by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer System 2000) with a resolution of 4 cm^{-1} in a spectral range of 4000 to 550 cm^{-1} using 32 scans per sample.

Morphology Evaluation

The microstructure of the tensile fractured surfaces of RPP/PSP and RPP/PSP$_{PVOH}$ composites were compared using a scanning electron microscope (SEM, model ZEISS Supra 35 VP). The samples were sputter-coated with a thin layer of carbon as it provides

a good electron-transparent (low atomic number), conductive coating, during the examination. The images were analyzed to investigate the distribution of natural fillers and their interactions within the polymeric matrix.

Water Absorption

Water uptake measurements were carried out according to ASTM D570. Newly prepared samples were dried in an oven at 70 °C for 24 h until a constant weight was attained. The samples were then immersed in distilled water at ambient temperature. After being immersed for a specific amount of time, the samples were removed from the water, gently dried with a clean cloth, and immediately weighed to the nearest 0.001 g. The percentage of water absorption was calculated as follows,

$$WA\ (\%) = [(M_1 - M_o)/M_o]\ X\ 100 \tag{1}$$

where M_o and M_1 are the dried weight and final weight of the sample, respectively.

RESULTS AND DISCUSSION

Processing Properties

The processing torque *vs*. time curves of RPP/PSP$_{PVOH}$ composites for 0, 10, 20, 30, and 40 wt % filler loadings are shown in Fig. 1(a). All curves have three peaks, representing the loading of RPP, loading of filler, and stabilization torque, respectively. RPP was loaded into the mixer at the beginning of the trial. As seen in Fig. 1(a), the initial peak showed high torque due to resistance to shear by solid RPP against the rotors. The torque maxima around the 0.5-min mark showed a decrease with filler loading due to the subsequent decrease in the amount of RPP placed into the mixer (Table 1). At 4 min, the observed peaks were attributable to the addition of filler into the mixing chamber. The torque then began to gradually decrease due to a reduction in viscosity (Cao *et al.* 2011). The stabilization torque could be observed after 8 to 12 min of mixing, when all of the ingredients of the composite had become mixed homogenously.

Figure 1(b) shows the stabilization torque of RPP/PSP and RPP/PSP$_{PVOH}$ composites at different filler loadings. Higher filler loadings led to higher stabilization torque. Similar observations were reported by Siriwardena *et al.* (2001). This is ascribed to agglomeration of filler particles, which leads to higher resistance to flow (*i.e.*, higher torque). This effect became significant as the filler loading approached 40 wt.%. At similar filler loading levels, the stabilization torque of RPP/PSP$_{PVOH}$ composites was higher than that of RPP/PSP composites. The torque became more stable when PSP$_{PVOH}$ particles were homogenized dispersed within the polymer matrix. The chemical similarity of both PSP and PVOH, both having hydroxyl groups, led to hydrogen bond formation and a good degree of adhesion between fillers and matrix. Thus, it required high shear force, resulting in high melt viscosity. Increased viscosity equates to higher resistance to flow of material within the mixing chamber. Consequently, the stabilization torque also increases.

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Tensile Properties

Figure 2(a)-(c) shows the effects of filler loading on the tensile strengths, elongations at break, and tensile moduli of RPP/PSP and RPP/PSP$_{PVOH}$ composites. As can be seen from Fig. 2(a), the RPP/PSP$_{PVOH}$ composites had higher tensile strengths than RPP/PSP composites. The enhancement in the strength is an indication of a good degree of adhesion between fillers and matrix. It could be due to the chemical similarity of both PSP and PVOH, by virtue of both having hydroxyl groups. The existence of such interaction increases the hydrogen bond formation (see later discussion of IR spectra in Fig. 6).

(a)

(b)
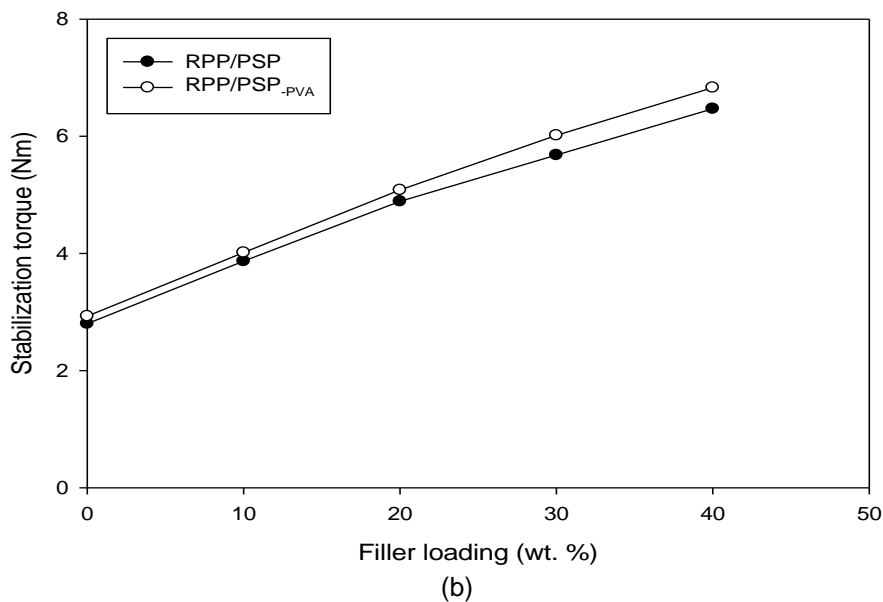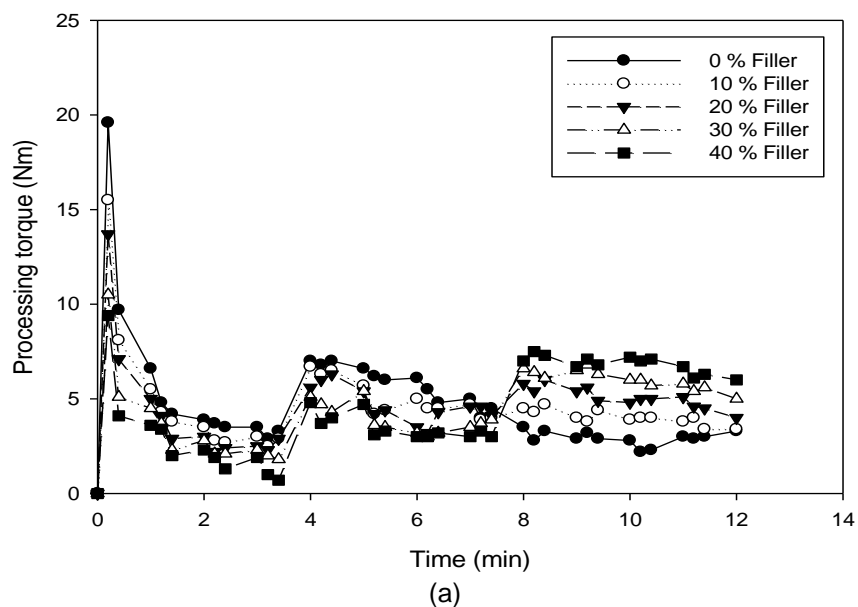
Fig. 1. (a) The processing torque of RPP/PSP$_{PVOH}$ composites throughout the 12-min mixing, and (b) the stabilization torque of RPP/PSP and RPP/PSP$_{PVOH}$ composites at different filler loadings

The tensile strength of the composites decreased as filler loading increased. The reduction of tensile strength could be due to poor adhesion between PSP and the RPP matrix. The irregular shape of the PSP particles could be another cause of the observed tensile strength reduction (Fig. 3). As a result of the PSP particles' irregular shape, their capability to support stress transmitted from the polymer matrix is rather poor (Cao *et al.* 2011). The decreasing trend in tensile strength can also be explained by the agglomeration of filler particles and by the dewetting of the polymer at the interface (Ismail *et al.* 2001). The incorporation of filler in RPP/PSP composites also tended to decrease due to the incompatibility of highly hydrophilic PSP and non-polar hydrophobic RPP. Because of their differing polarities, the interfacial adhesion between PSP and RPP was weak, providing sites for failures to initiate and propagate. This is shown by the SEM micrographs in Figs. 4 and 5.

The effects of filler loading on elongation at break of RPP/PSP and RPP/PSP$_{PVOH}$ composites are shown in Fig. 2(b). An increase of filler loading in the RPP matrix will reduce the toughness of the composites and lead to a lower elongation at break (Jacob *et al.* 2004). The filler hardened the composites, thus decreasing their ductility. At the same filler loading, RPP/PSP$_{PVOH}$ composites had higher elongation at break than RPP/PSP composites. A similar observation was reported by Sreekala *et al.* (2000). In the cited study the lower elongation at break of untreated oil palm fibers could be attributed to the three-dimensionally cross-linked network of cellulose and lignin, which was not present in treated fibers. The treated fibers had a larger elongation at break.

Figure 2(c) shows the effects of filler loading on the tensile modulus of RPP/PSP and RPP/PSP$_{PVOH}$ composites. The incorporation of filler was shown to increase the tensile modulus for both composites. This was due to the inclusion of rigid filler particles in the soft matrix (Cao *et al.* 2011). Abdul Khalil *et al.* (2001) and Ismail *et al.* (2011) reported that the incorporation of starch or cellulosic fiber can improve the stiffness of composite materials. This can be explained by the fact that composite stiffness increases with higher filler content and higher tensile modulus. At the same filler loading, RPP/PSP$_{PVOH}$ composites had higher tensile moduli than RPP/PSP composites. This was due to the strong chemical interaction (hydrogen bonding) between the PSP and PVA, thus increasing the degree of adhesion between fillers and matrix.
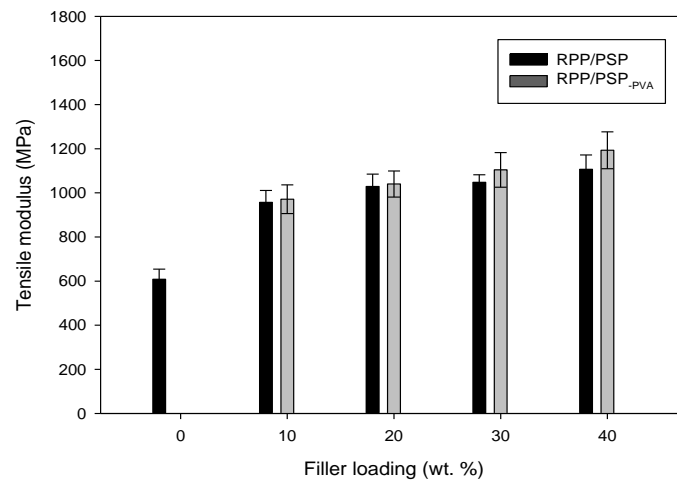
Morphology

Scanning electron microscopy (SEM) was used to examine the tensile-fractured surfaces of RPP/PSP and RPP/PSP$_{PVOH}$ composites. Figures 4 and 5 show SEM micrographs of RPP/PSP and RPP/PSP$_{PVOH}$ composites at 10, 20, and 40 wt.% filler loading. Figure 4(a) shows that at low PSP content, the sample had a rough surface and was deformed in ductile mode. A more porous structure and filler agglomeration were observed for composites with higher filler content, as shown in Figs. 4(b) and (c). The porosity of the structure was due to the low filler to matrix adhesion.
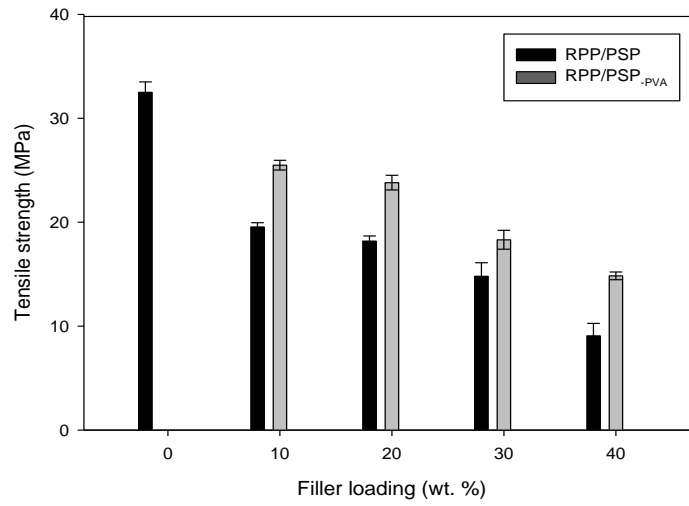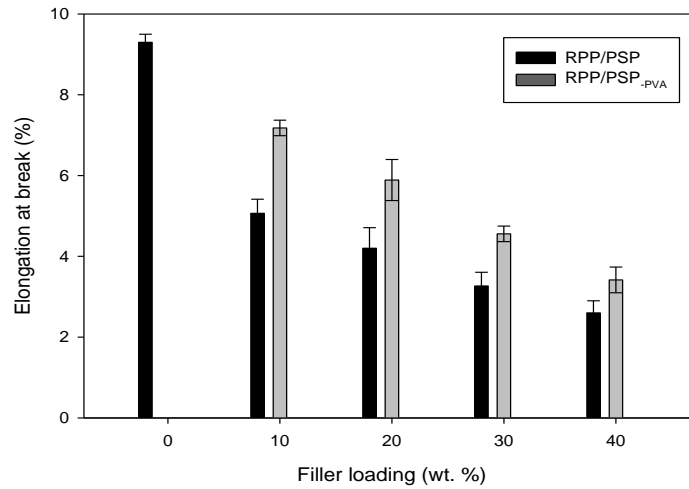
Fig. 2. (a) Tensile strength, (b) elongation at break, and (c) tensile modulus of RPP/PSP and RPP/PSP$_{PVOH}$ composites at different filler loadings
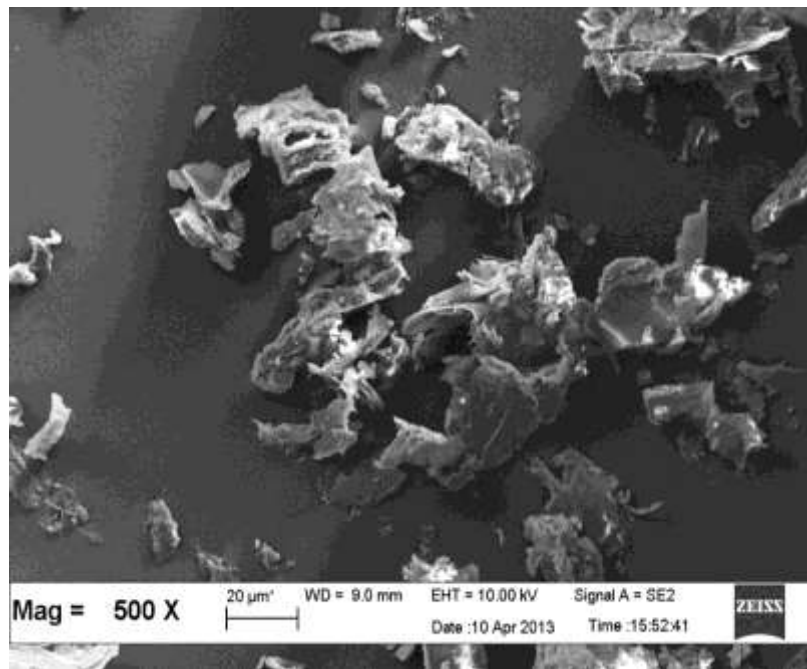
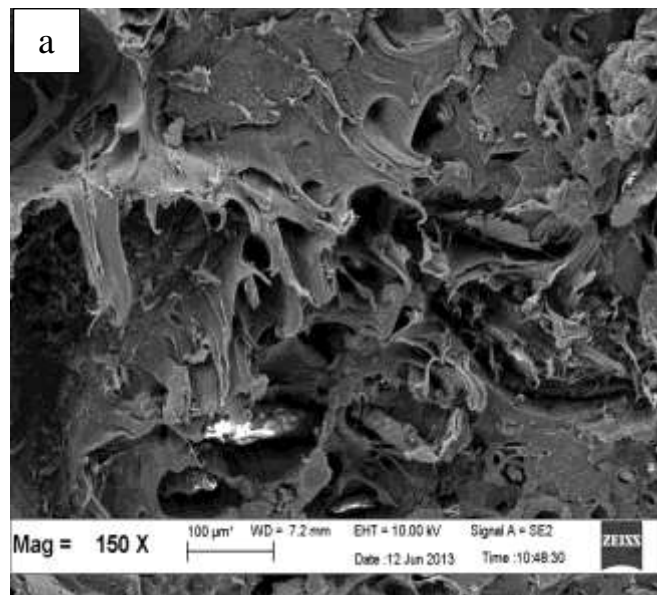**Fig. 3**. SEM micrograph showing irregular morphology of PSP

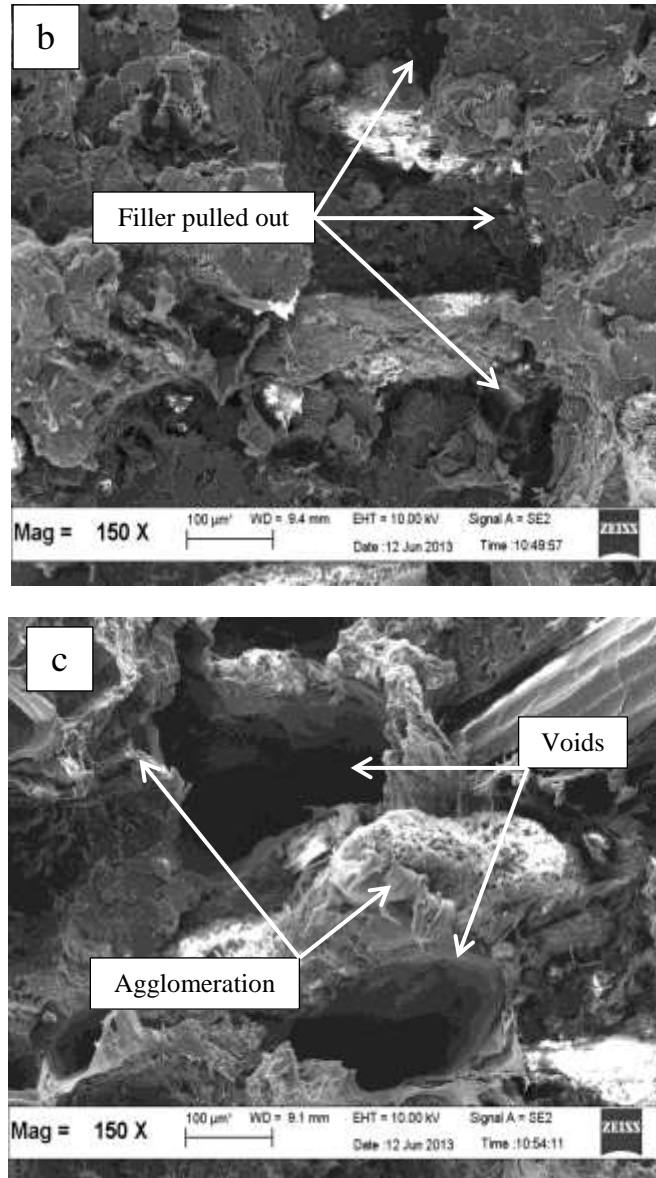**Fig. 4.** SEM micrographs of RPP/PSP composites at (a) 10%, (b) 20%, and (c) 40% filler loading by weight

Fig. 4. SEM micrographs of RPP/PSP composites at (a) 10%, (b) 20%, and (c) 40% filler loading by weight

This low adhesion made removal of fillers from the composites easy, thus reducing tensile strength. The pores or voids are flaws that lead to localized stress concentration during deformation. Finally, premature failure of the composites occurred at higher filler content, indicating lower tensile strength. Similar results were reported by Gauthier *et al.* (1998): as filler loading increases, formation of agglomerates occurs and is detrimental to mechanical properties (Gauthier *et al.* 1998).

For composites with treated PSP, a smoother fracture surface can be seen, as in Fig. 5(a). This indicates that there was better interfacial adhesion between the filler and matrix in the treated PSP composites. In Fig. 5(b), less filler removal and breakage can be observed. These differences are due to the modification of PSP with PVOH, which improves the adhesion of filler to the matrix, thus increasing the tensile strength and elongation at break of RPP/PSP$_{PVOH}$ composites.

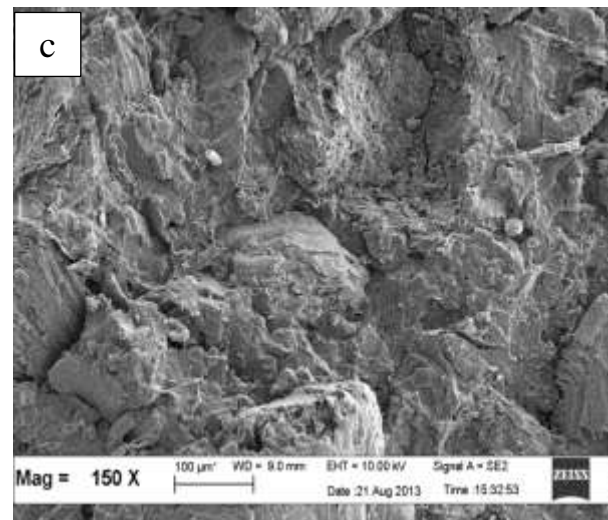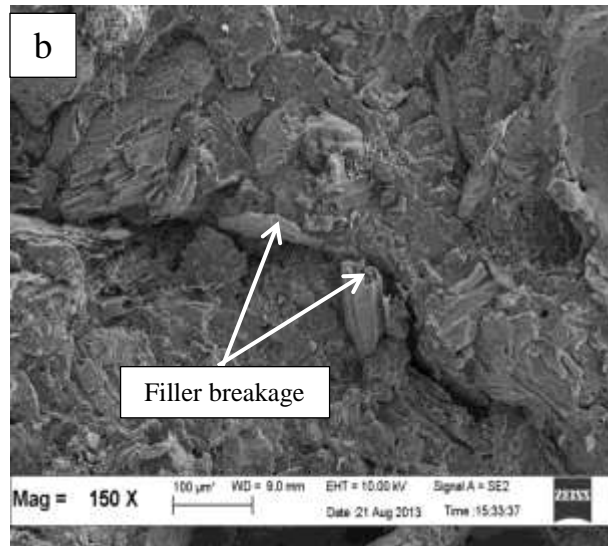Better interfacial
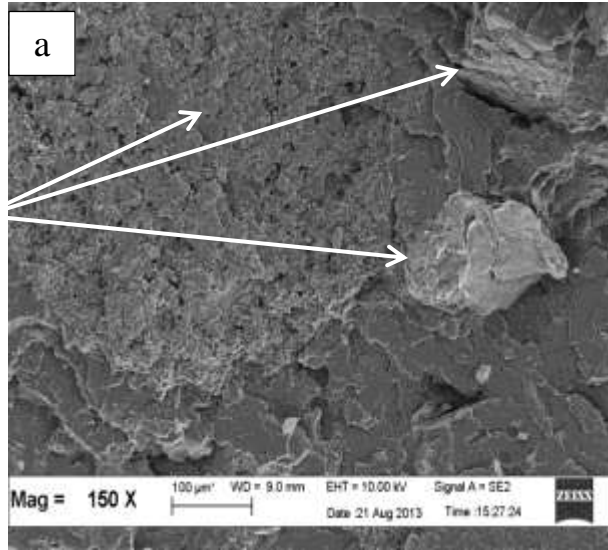adhesion between
PSP$_{PVOH}$ and RPP
matrix

a

Mag = 150 X   100 µm' WD = 9.0 mm   EHT = 10.00 kV   Signal A = SE2   Date :21 Aug 2013   Time :15:27:24

b

Filler breakage

Mag = 150 X   100 µm' WD = 9.0 mm   EHT = 10.00 kV   Signal A = SE2   Date :21 Aug 2013   Time :15:33:37

c

Mag = 150 X   100 µm' WD = 9.0 mm   EHT = 10.00 kV   Signal A = SE2   Date :21 Aug 2013   Time :15:32:53

Fig. 5. SEM micrographs of RPP/PSP$_{PVOH}$ composites at (a) 10%, (b) 20%, and (c) 40% filler loading by weight

IR Spectroscopic Study

FTIR spectroscopy was conducted to determine chemical structural information for the composites and examine the chemical interactions between the filler and matrix. Figures 6(a) and (b) show the IR spectra of RPP/PSP and RPP/PSP$_{PVOH}$ composites, respectively. The spectrum for RPP/PSP$_{PVOH}$ shows some peak changes between 3500 and 3200 cm^{-1}, which are attributed to O-H stretching bands for hydrogen-bonded carboxylic acid. A higher wavenumber for the hydroxyl group absorption indicates that the hydrogen bonding of PSP became stronger when it was modified with PVOH. The peak at 2917 cm^{-1} shows C-H stretching of PSP$_{PVOH}$, while the peaks at 1404 cm^{-1} and 1375 cm^{-1} show CH$_2$ and C-O-H bending, respectively. Another additional shoulder peak was observed at around 1729 cm^{-1}, and this was identified as the peak for an ester group. It is interesting to mention that the peak is due to C=O bonds from ester aliphatic stretching vibrations between hydroxyl groups of PSP and PVOH. Figures 7 show the proposed interactions between RPP, PSP, and PVOH.
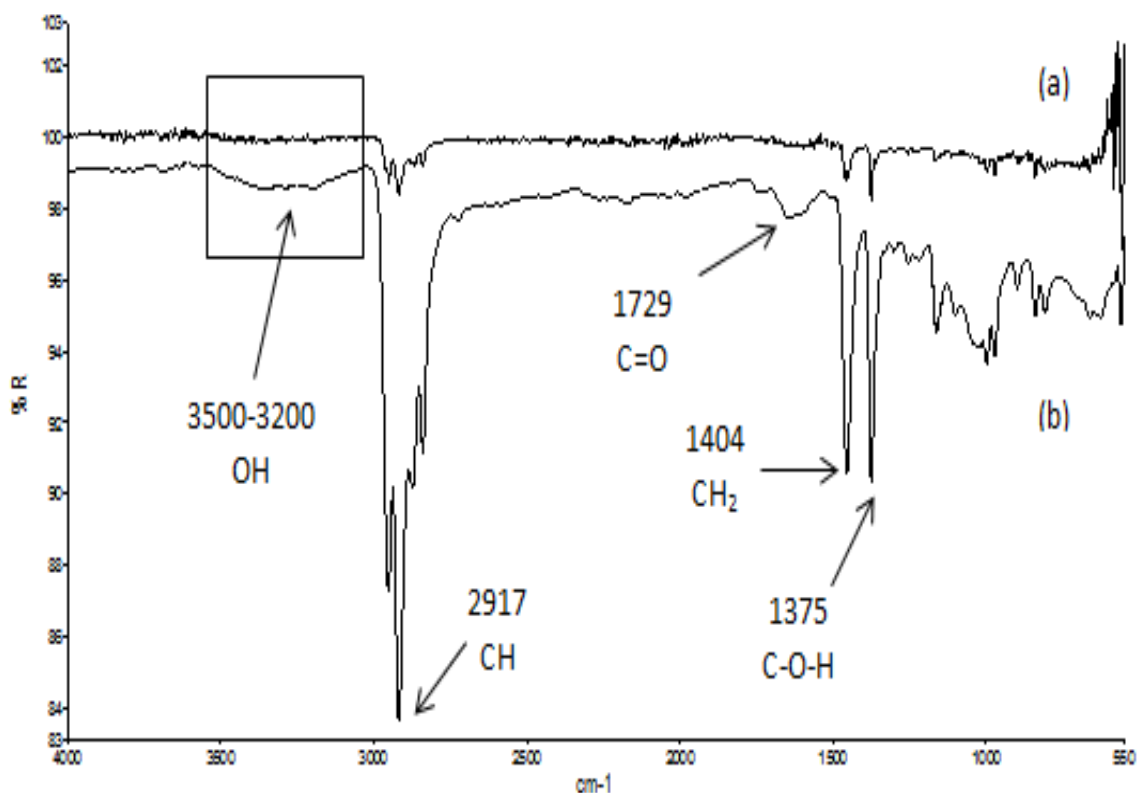

Fig. 6. IR spectra of (a) RPP/PSP and (b) RPP/PSP$_{PVOH}$ composites

Water Absorption

Figure 8 shows the water uptake of RPP/PSP composites at different filler loadings as a function of time. All composites showed a similar pattern of water uptake. The water uptake of RPP/PSP composites increased with immersion time and increasing filler loading. The presence of RPP in the composites can dramatically reduce water absorption due to the hydrophobic characteristics of non-polar RPP. The kinetic

absorption was fast during the initial stage of the absorption process, then gradually slowed before finally reaching a plateau.
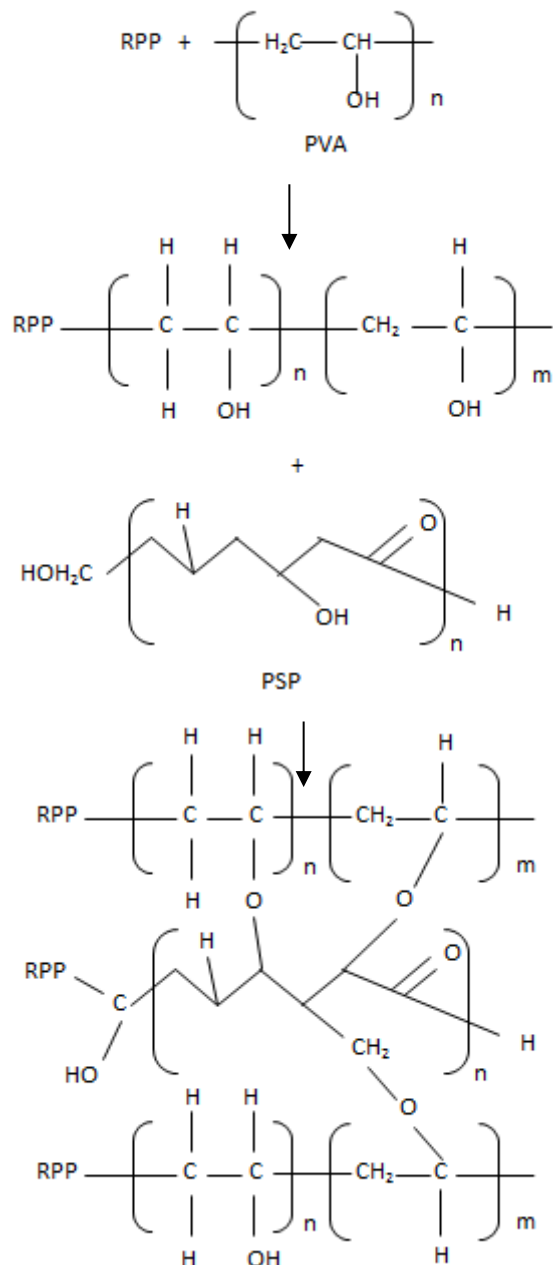

Fig. 7. Proposed interaction of PSP$_{PVOH}$ with RPP matrix

       Natural fillers are permeable to water and have a significant effect on water absorption. Similar results were reported by Najafi *et al.* (2006), in which the percentage of water absorption increased with higher filler content. This is due to the highly hydrophilic nature of lignocellulosic filler. The free hydroxyl groups come in contact with water through hydrogen bonding, resulting in water uptake and weight gain in composites. In addition, higher filler loading resulted in more pores within composites,

thus increasing water accumulation at the interface between the filler and the matrix (Jacob *et al.* 2005).

Figure 9 shows the equilibrium of water absorption for both types of composites after 30 days. The water absorption of RPP/PSP$_{PVOH}$ composites is higher than for the RPP/PSP composites. This is due to the incorporation of PVOH into the RPP/PSP$_{PVOH}$ composites. PVOH is a hydrophilic polymer that absorbs water. The IR spectra in Fig. 4 show an increase in the intensity of -OH stretching bands, which confirms the interaction between PVOH and water.
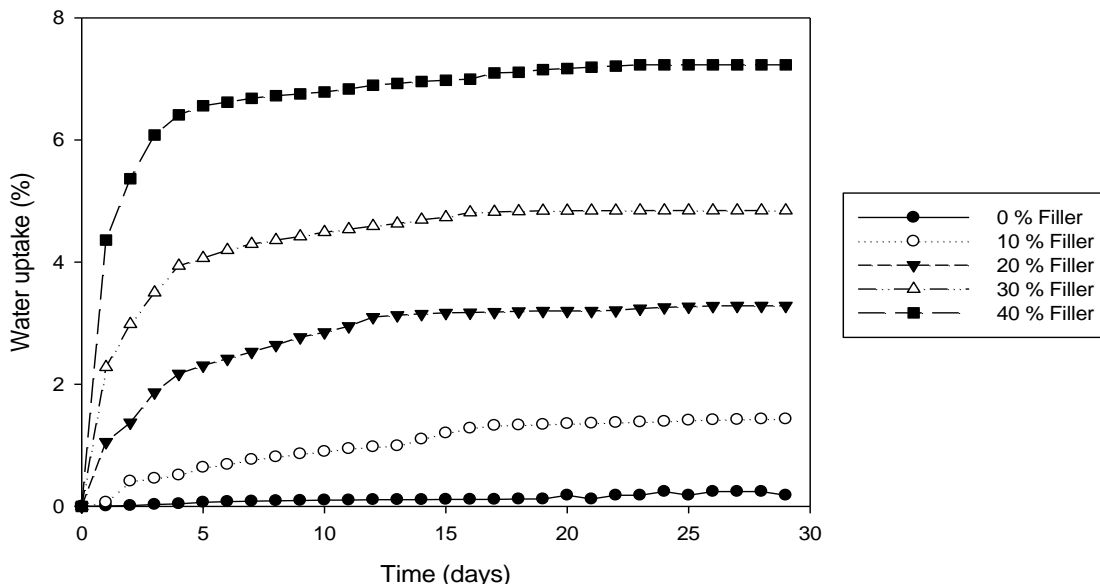

Fig. 8. Water uptake over 30 days of RPP/PSP composites at different filler loading
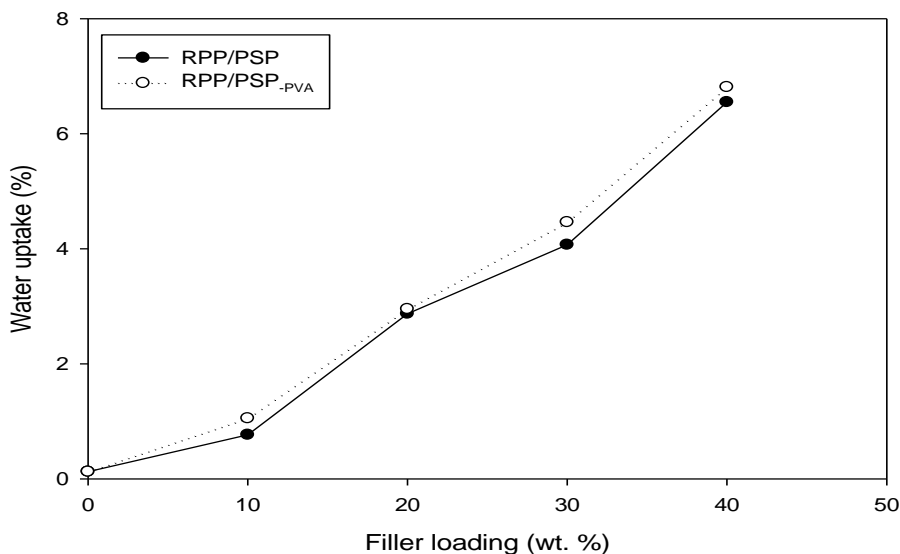

Fig. 9. Equilibrium water uptake of RPP/PSP and RPP/PSP$_{PVOH}$ composites at 30 days

CONCLUSIONS

1. Incorporation of PVOH into RPP/PSP composites increased the stabilization torque, tensile strength, elongation at break, and tensile modulus.

2. Incorporation of PVOH into RPP/PSP composites decreased the water resistance.

3. A smooth fractured surface can be observed in SEM micrographs for composites with treated PSP, indicating a better interfacial adhesion between filler and matrix than for unmodified PSP composites. Composites without PSP treatment had rough surfaces, porous structures, and filler agglomeration and deformed in ductile mode. These observations indicated that low filler-matrix adhesion led to easy removal of fillers from the composites.

4. FTIR analysis revealed slight changes in band positions and intensities, indicating a distinct interaction between the hydroxyl group of PSP and PVOH.

5. The water uptake of RPP/PSP composites increased with immersion time and increasing filler loading. Water absorption of RPP/PSP$_{PVOH}$ composites was higher than that of RPP/PSP composites.

ACKNOWLEDGMENTS

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