Effect of Peanut Shell Powder Content on the Properties of Recycled Polypropylene (RPP)/ Peanut Shell Powder (PSP) Composites

Nor Fasihah Zaaba, Hanafi Ismail,* and Mariatti Jaafar

Green composites are gradually replacing general plastics to achieve the aim of environment sustainability. In the present study, both compatibilized and uncompatibilized recycled polypropylene (RPP) and peanut shell powder (PSP) composites were prepared. The effect of various PSP loadings (0 to 40% by weight) on the processing, tensile properties, morphology, Fourier transform infrared (FTIR) analysis, and water uptake properties were examined. The results showed that the incorporation of PSP caused an increase in stabilization torque, tensile modulus, and water absorption, but lowered the tensile strength and elongation at break of the RPP/PSP composites.Compatibilized RPP/PSP composites with poly(ethylene-co-acrylic acid) (PEAA) significantly enhanced the tensile properties while decreasing the water absorption of RPP/PSP composites. FTIR analysis revealed a slight change in band positions and intensities, indicating a distinct interaction between the chains of polymers. SEM micrographs showed the interaction between PSP and the matrix.

Keywords: Poly(ethylene-co-acrylic acid); Peanut shell powder; Recycled polypropylene

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INTRODUCTION

Plastics or composites used in major industrial applications come from the petrochemical industry. The widespread utilization of plastic materials has created severe environmental, economic, and social problems. It is becoming increasingly difficult to find disposal sites for plastic-based materials (Pun et al. 2003; Wang et al. 2003; Ambrose et al. 2002). The disposal of plastics, especially those used in packaging, poses a serious challenge to waste management (Fernandes et al. 2004). In recent years, environmental problems have led to research and industry attention to incorporating organic fillers with recycled thermoplastics.

Polymeric materials such as thermoplastics are very versatile in terms of day-to-day applications. However, the preparation of such thermoplastics is impossible without additives or foreign materials to assist in processing and improving their properties. For example, there may be reinforcing fillers, lubricants, stabilizers, oxidation inhibitors, pigments, and plasticizers incorporated into a thermoplastic to make it a better and more usable product. Polypropylene (PP), due to its intrinsic properties such as high melting temperature, low density, and high chemical resistance, finds use in a wide range of applications (Jaziri et al. 2007). Easy incorporation of high loadings of fillers and reinforcing agents and the ability to produce blends with other polymers, including rubbers, makes polypropylene (PP) versatile (Stehling et al. 1981; Galli et al. 1984).
Polypropylene was the first synthetic stereoregular polymer to achieve industrial importance (Ahmed 1982), and it is presently the fastest growing fiber for technical end-uses where high tensile strength coupled with low cost are essential features; it has shown consistent growth of about 5% per annum in the last 10 years (O’Day 2000). Recycled polypropylene (RPP) could be used as a raw material for the life cycle of a new product. This reuse highlights the difference between end of life and end of use. Due to this recycling, the life time of the polymer is expanded, leading to the preservation of non-renewable resources and limitation of waste production (Corbiere-Nicollier et al. 2001).

One interesting approach to improve the mechanical properties and impart degradability is the use of natural fillers to reinforce recycled polypropylene/peanut shell powder (RPP/PSP) blends. Peanut (Arachis hypogaea L.) is the pod or legume belonging to the family Leguminosae. On a worldwide scale, peanut is grown primarily for its seed oil and is also an important protein food resource in developing and developed countries (Bertiolia et al. 2011; Emekli-Alturfan et al. 2008). Peanut shells are abundant and inexpensive byproducts of peanut processing operations. Most of this agricultural byproduct is set on fire or arbitrarily discarded, except for the small quantity that is manufactured into medium-density fiberboard, agglutinant, plastic stuffing, etc. (Ak gul and Tozluoglu 2008). Peanut shells contains many functional components that have been demonstrated to be safe to humans (Gao et al. 2011). The reinforcing properties of peanut shells have never been tested on a thermoplastic before. It is of great economic importance to explore the high-value utilization of peanut shells.

Peanut shell powder is a lignocellulosic filler. The main components of lignocellulose are cellulose, hemicellulose, and lignin. Hydrogen bonds between different layers of polysaccharides contribute to the resistance of crystalline cellulose to degradation. Cellulose, hemicellulose, and lignin form structures called microfibrils, which are organized into macrofibrils that mediate structural stability in the plant wall (Rubin 2008). For peanut shells, the contents of cellulose (40.5%), hemicellulose (14.7%), and lignin (26.4%) have been determined using Official Methods of Analysis of AOAC (15th ed.) (Lopez Ravilli et al. 2012).

Poly(ethylene-co-acrylic acid) [PEAA] is a carboxylated ethylene copolymer. It is synthesized via the high-pressure, free radical copolymerization of ethylene and acrylic acid (Wakabayashi and Register 2005). Nuclear magnetic resonance (NMR) studies have been used to verify that the hydrogen opposing the acrylic acid group is also subject to backbiting during polymerization, lending itself to branching as well (Wakabayashi and Register 2005; McCord et al. 1997). The properties of PEAA copolymers depend strongly on the constituent monomers, ethylene, and acrylic acid. Ethylene is a common monomer found in many olefinic polymers. Furthermore, its ordered, symmetric structure allows it to crystallize under appropriate conditions. Composed of only carbon and hydrogen, polyethylene is hydrophobic in nature. Although acrylic acid also has a backbone of carbon and hydrogen, the pendant carboxylic acid group enables this polymer to interact with water.

The purpose of the present study is to evaluate the potential use of peanut shell powder (PSP)-filled recycled polypropylene (RPP). The effects of different amounts of PSP incorporated in RPP/PSP composites were investigated. Compatibilized and uncompatibilized composites with PEAA were compared. This work focuses on the mechanical, morphological, and water uptake properties of these composites.
EXPERIMENTAL

Materials
Recycled polypropylene was obtained from Zam Scientific (M) Sdn. Bhd. with a melt flow index of 30 g/10 min. Peanut shell powder (PSP) was supplied by Zam Scientific (M) Sdn. Bhd. The peanut shells were subjected to a grinding process, which yielded an average particle size of approximately 66.84 μm. PSP was then dried for 3 h at 70 °C using a vacuum oven before being used in subsequent composite fabrication. Poly(ethylene-co-acrylic acid) [PEAA] was obtained from Sigma Aldrich with 5 wt.% acrylic acid.

Methods
Sample preparation and Processing
PSP was melt-blended with RPP using an internal mixer (Haake Rheomix Mixer, Model R600/610) at a temperature of 180 °C at speeds of 50 rpm to obtain a homogeneous sample. The RPP was first charged into the mixer and melted for 4 min. The PSP and PEAA were added at fourth minute, respectively. The blend was allowed to mix for another 6 min to obtain the stabilization torque. The total mixing time was 10 min for all samples. The processed samples were then compression molded in an electrically heated hydraulic press (Kao Tieh Go Tech Compression Machine) at a temperature of 180 °C into a 1-mm-thick sheet. Table 1 shows the formulation of the composites with and without compatibilizer.

Table 1. Formulation of RPP/PSP Composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (weight proportion)</th>
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<tr>
<td></td>
<td>RPP (wt. %)</td>
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<tr>
<td>RPP</td>
<td>100</td>
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<tr>
<td>RPP + 10 % PSP</td>
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<td>RPP + 20 % PSP</td>
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<td>RPP + 30 % PSP</td>
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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 test was performed at a temperature of 25 ± 3 °C. Five specimens were used to obtain average values for tensile strength, elongation at break, and Young’s modulus.

FTIR spectroscopy analysis
Functional groups and chemical characteristics of RPP/PSP composites were obtained by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer System 2000) with a resolution of 4 cm⁻¹ in the range 4000 to 550 cm⁻¹ using 32 scans per sample.
Morphology evaluation

Scanning electron micrographs of the tensile fractured surfaces of RPP/PSP composites were obtained using a scanning electron microscope (SEM, model ZEISS Supra 35 VP). The samples were sputter coated with a thin layer of carbon to avoid electrostatic charging during the examination. The image results were analyzed to investigate the distribution of natural fillers in the polymeric matrix and their interactions.

Water absorption

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

$$WA(\%) = \left[\frac{(M_1 - M_0)}{M_0}\right] \times 100,$$

where $M_0$ and $M_1$ are the dried and final weights of the sample, respectively.

RESULTS AND DISCUSSION

Processing Properties

The melt processing characteristics of the RPP/PSP composites were studied with processing torque-time curves. Figure 1(a) shows the processing torque of the melt-mixed blends with PSP loadings of 0 to 40 wt.%. A similar pattern of processing torque curves was observed for all composites. There were three increments of torque due to the different material loadings. It can be seen that an initial torque from 1 to 3 min corresponded to the initiation of rotor charging of solid material, which is RPP into mixing chamber. For the 0% PSP blend, the torque was higher compared to the 10% and 40% PSP composites from 0 to 5 min. This is due to the greater amount of RPP dosage introduced into the mixing chamber. Hence, torque decreased with an increase in PSP loading due to the reduction of the charged weight of RPP. After loading, the blend started to melt under shear and temperature. Completion of melting was achieved after 3 min of mixing. At this time, the torque begins to decrease gradually due to a reduction in viscosity (Cao et al. 2011). In addition, an increase in torque could be observed between 4 and 6 min of mixing, corresponding to the introduction of peanut shell powder to the blend. After 8 min, the processing torque stabilizes, demonstrating that a good level of mixing was achieved.

At the end of mixing, the stabilization torque for different PSP loadings was obtained (Fig. 1b). It can be seen that the stabilization torque increased as PSP loading increased. The PSP addition increased the viscosity and stabilization torque (Ismail et al. 2001b). Filler particle agglomeration occurs at higher filler loadings and leads to higher equilibrium torque (Siriwardena et al. 2002). The compatibilized composites exhibited higher stabilization torques than the uncompatibilized samples in all the examined composites. The addition of compatibilizers improved the filler-matrix interfacial bonding through interaction between the pendant carboxylic acid group from acrylic acid and the hydroxyl groups from PSP, which resulted in increase the blend viscosity and higher
stabilization torque in the compatibilized composites. IR spectra in Fig. 4 show the C=O bonds, further confirming the ester aliphatic stretching vibrations between the hydroxyl groups of PSP and PEAA. Upon completion of filler dispersion, the torque started to decrease gradually, which might be due to a reduction in viscosity of composites.

![Graph showing processing torque](image)

**Fig. 1.** (a) The processing torque of compatibilized RPP/PSP composites, and (b) the stabilization torque of RPP/PSP composites with and without compatibilizer at different PSP loadings

**Tensile Properties**

Figure 2(a)-(b) shows the effect of PSP loading on tensile strength, elongation at break, and tensile modulus of RPP/PSP composites with and without compatibilizer. As
the amount of PSP increased, the tensile strength of the RPP/PSP composites decreased. The reduction of tensile strength might be due to poor adhesion between PSP and the RPP matrix. The irregular shape of the PSP may be another cause of the tensile strength reduction (Fig. 3). As a result, the 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 dewetting of the polymer at the interphase (Ismail et al. 2001a). Apart from that, the incorporation of PSP in RPP/PSP composites also tended to decrease due to the incompatibility of highly hydrophilic PSP and non-polar hydrophobic RPP. Because of their different polarities, there was a weak interfacial adhesion between PSP and RPP, thus providing sites for failures to initiate and propagate. A reduction in the effective surface area of the filler phase yields inefficient stress transfer from the matrix (Fabunmi et al. 2007). Consequently, the tensile strength was not improved. The drop in tensile strength became more dramatic at a PSP loading of 40 wt.%. This is because the filler-filler interaction became more prominent than the filler-matrix interaction with increasing PSP content. The applied force could not transfer efficiently from the polymer matrix to the filler. This is justified by the SEM micrograph in Fig. 5. The addition of PEAA as a compatibilizer resulted in higher tensile strength for RPP/PSP composites. The results can be explained in term of the better adhesion at the filler-matrix interface due to the presence of a compatibilizer, as shown later in the morphology study. The interfacial adhesion may be improved through the formation of hydrogen bonding between acrylic acid from PEAA and the hydroxyl groups on the PSP surfaces. Good interfacial bonding can reduce the interfacial stress concentration and may prevent filler-filler contact.

Figure 2(b) depicts the elongation at break of RPP/PSP composites with different PSP loadings. The incorporation of PSP into RPP resulted in a reduction of elongation at break. This can be attributed to the decrease in polymer chain mobility or deformability of a rigid interface between the filler and the matrix. In addition, the irregular morphology of PSP, as shown in Fig. 3, caused the obstruction of stress propagation from the matrix to the filler. This hindered the filler orientation during the tensile test and resulted in the deterioration of the elongation of the composites (Cao et al. 2011). At the same filler loading, the compatibilized composites showed higher elongation at break than the uncompatibilized composites did. This is due to better dispersion and adhesion between the filler and the matrix, which enhances the stress transfer from the matrix to the filler phase. The SEM micrograph in Fig. 6 shows the evident of less pulling out of the filler and filler agglomeration of compatibilized composites. Therefore, the flexibility of composites increased.

The incorporation of PSP was found to increase the tensile modulus of RPP/PSP composites, as shown in Fig. 2(c). When PSP increased from 0 to 40 wt. %, the moduli also increased, from 608.30 to 820.70 MPa. The addition of PSP was expected to increase the modulus because of 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 based on the fact that composite stiffness increases with higher filler content and higher tensile modulus. However, at similar filler loadings, compatibilized composites exhibited lower tensile moduli than uncompatibilized did. Again, this might be due to better interactions between RPP and PSP with the presence of PEAA. PEAA, the incorporation of a comonomer such as acrylic acid into polyethylene, has been known to reduce its crystallinity (Cantero et al. 2003; Wakabayashi and Register 2005).
Although the acrylic acid units are relatively small, they cannot be incorporated into the regular structure of the crystallite regions. They are forced out of the crystal packing and aggregate in the amorphous matrix surrounding the crystals. All other things being held constant, a reduction in crystallinity should result in a reduction in the stiffness of the material (Wakabayashi and Register 2005). Therefore, the addition of PEAA into the composites causes a decrease in the rigidity of RPP and leads to a reduction in tensile modulus for all compatibilized composites.
Fig. 2. (a) Tensile strength, (b) elongation at break, and (c) tensile modulus of RPP/PSP composites with and without compatibilizer at different PSP loadings.

Fig. 3. SEM micrograph of the irregular morphology of peanut shell powder.
IR Spectroscopic Study

Infrared spectra of RPP/PSP composites with different PSP loadings are presented in Fig. 4. The observed peaks correspond to the functional groups of RPP and PSP. From Fig. 4(a), it can be seen that the RPP/PSP composites exhibited IR main peak positions of 2915 cm\(^{-1}\), 1469 cm\(^{-1}\), and 717 cm\(^{-1}\), representing C-H stretching, \(-\text{CH}_3\) bending, and \(-\text{CH}_2\) vibration, respectively. For compatibilized RPP/PSP composites, as shown in Fig. 4(b), an additional shoulder peak was observed at around 1729 cm\(^{-1}\) and is identified as the peak of an ester group (Kahar et al. 2012). It is interesting to mention that this peak is due to C=O bonds from ester aliphatic stretching vibrations between the hydroxyl groups of PSP and PEAA. There was also a remarkable decrease in the intensity of OH stretching bands at 3200 to 3600 cm\(^{-1}\) in the spectrum, which further confirmed the interaction between PEAA and hydroxyl groups on the surface through hydrogen bonds. Similar results were reported by Cantero et al. (2003) in their study of the effect of fiber treatment on wettability and mechanical behavior of flax/polypropylene composites.

Morphology

Scanning electron microscopy (SEM) was used to examine the tensile fractured surfaces of RPP/PSP composites. Figures 5 and 6 show SEM micrographs of uncompatibilized and compatibilized RPP/PSP composites at (a) 10\%, (b) 20\%, and (c) 40\% (by weight) PSP loadings. From Fig. 5(a), it can be seen that at low PSP loading, the sample had a rough surface and deformed in ductile mode. As PSP loading increased, the presence of filler was more visible. It can be observed from Fig. 5(b) and (c) that filler was embedded in the matrix and arranged in a disoriented manner, and most of the PSP was in direct contact with other PSP particles. As filler loading increases, formation of agglomerates is inevitably detrimental to mechanical properties (Gauthier et al. 1998).

Fig. 4. IR spectra of RPP/PSP composites (a) uncompatibilized and (b) compatibilized with PEAA
**Fig. 5.** SEM micrographs of uncompatibilized RPP/PSP composites at (a) 10%, (b) 20%, and (c) 40% (by weight) PSP loadings
Some of the fillers were pulled out or remained loosely within the RPP matrix. Furthermore, Fig. 5(c) reveals poor adhesion of the filler to the matrix, as is evident from the voids between the matrix and filler particles. These voids act as stress concentration points and contribute to the decrement of mechanical properties (Gauthier et al. 1998). Consequently, lower tensile strength and elongation at break were obtained for composites with higher filler loadings.

Figure 6 shows SEM micrographs of compatibilized RPP/PSP composites at (a) 10%, (b) 20%, and (c) 40% (by weight) PSP loadings. Obviously, from Fig. 6(a), (b), and (c), less pulling out of the filler and filler agglomeration can be observed. These correlate to the incorporation of PEAA, which improves the adhesion of the filler to the matrix. Additionally, a higher toughening effect can be observed compared to the uncompatibilized blends (Cao et al. 2011). These findings are evidence of the good interfacial adhesion between the filler and the matrix, which leads to improved tensile strength and elongation at break. This also shows that PEAA is an effective compatibilizer for these composites.

**Water Absorption**

Figure 7 shows the water uptake of uncompatibilized RPP/PSP composites at different PSP loadings. All blends showed a similar pattern of water uptake. The water uptake of RPP/PSP composites increased with the immersion time and increasing PSP loading. The presence of RPP in the composites can dramatically restrain the water absorption and reduce the water sensitivity due to the hydrophobic characteristics of non-polar RPP.

The kinetic absorption was fast within the initial stage of the absorption process, followed by a gradual increase and finally a plateau. Natural fillers are permeable to water and have a significant effect on water absorption. Najafi et al. (2006) reported that the percentage of water adsorption increased with higher filler content. This is due to the highly hydrophilic nature of lignocellulosic filler. The free –OH groups come in contact with water through hydrogen bonding, which results in water uptake and weight gain in composites. In addition, higher PSP loading also resulted in more entrapped voids and thus an increase in water accumulating at the interface between the filler and the matrix (Jacob et al. 2005).

Figure 8 presents the variation of water uptake at 30 days with PSP content for uncompatibilized and compatibilized RPP/PSP composites. The water absorption was dependent on the availability of free –OH groups on the surface of the filler. The equilibrium water uptake at 30 days for compatibilized composites was lower than that of uncompatibilized composites. In compatibilized composites, the number of –OH groups can be reduced via the esterification between acrylic acid in PEAA and the –OH groups of PSP.

IR spectra on Figure 4 show the reduction in the intensity of OH stretching bands, which further confirmed the interaction between PEAA and hydroxyl groups of PSP. Therefore, the absorption of water could become restricted. Moreover, there were fewer voids in compatibilized composites due to the improvement of interfacial filler/matrix adhesion, which led to the limitation of the penetration of water molecules into composites (Cao et al. 2011).
Fig. 6. SEM micrographs of compatibilized RPP/PSP composites at (a) 10%, (b) 20%, and (c) 40% (by weight) PSP loadings
Fig. 7. Water uptake of uncompatibilized RPP/PSP composites at different PSP loadings.

Fig. 8. Equilibrium water uptake of RPP/PSP composites at 30 days with and without compatibilizer.

CONCLUSIONS

1. The effect of peanut shell powder content on the properties of RPP/PSP composites was investigated with a comparison between uncompatibilized and compatibilized composites. The incorporation of PSP into RPP/PSP composites increased the stabilization torque, tensile modulus, and water absorption of the RPP/PSP...
composites. However, the tensile strength and elongation at break showed the opposite effect.

2. FTIR analysis showed the occurrences of bonding between functional groups, indicating a distinct interaction between the chains of polymers.

3. In addition, the presence of PSP increased the percentage of water uptake at equilibrium of RPP/PSP composites.

4. The observed SEM micrographs showed evidence of interactions between PSP and the matrix.

5. With the presence of PEAA as a compatibilizer, the stabilization torque, tensile strength, and elongation at break increased, while the tensile modulus and water absorption of RPP/PSP composites decreased. FTIR and SEM results showed evidence of good adhesion between PSP and the matrix.

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