Recycled Polypropylene/Peanut Shell Powder Composites: Pre-Treatment of Lignin Using Alkaline Peroxide

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This study investigated the performance of recycled polypropylene (RPP)/peanut shell powder (PSP) composites with untreated PSP and treated PSP with alkaline peroxide. The RPP/PSP and RPP/PSP-H_2O_2 composites were prepared by melt mixing and compression molding at different PSP loadings (10 wt.% to 40 wt.%). The samples were characterized by processing properties, tensile properties, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and water absorption behavior. The treated PSP enhanced the stabilization torque, tensile strength, elongation at break, tensile modulus, and water absorption of RPP/PSP-H_2O_2 composites. FTIR spectra and SEM showed that the elimination of lignin content strongly influenced the fractured surface and chemical characteristics of the RPP/PSP-H_2O_2 composites.

Keywords: Lignocellulosic; Alkaline peroxide; Peanut shell powder; Recycled polypropylene; Lignin removal

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INTRODUCTION

Natural lignocellulosic fillers have garnered attention as bio-friendly reinforcement for polymer composites. Ecological concerns have resulted in tailoring new composites that focus on an eco-product or on sustainable development. Natural fillers are made of biodegradable polymers and are considered environmentally safe (Rozman *et al.* 2003; Averous and Le Digabel 2006). Lignocellulosic thermoplastic composites have been made using various types of organic fillers including kenaf fibers, bamboo fibers, sago starch, rice starch, and corn starch (Ismail *et al.* 2002). The polar hydroxyl groups on the surface of lignocellulosic fillers, which are contributed mainly by cellulose and lignin, have been utilized to create a well-bonded interface with a non-polar polymer matrix, such as high-density polyethylene (HDPE) and polypropylene (PP) (Rozman *et al.* 2006). Hence, good compatibility between the filler and matrix are required to produce non-polar thermoplastic composites with excellent final properties. This compatibility is usually achieved by the chemical modification of the filler surface, incorporation of a coupling agent, delignition, bleaching, or chlorination (Rozman *et al.* 2003; Pracella *et al.* 2006; Habibi *et al.* 2008; Supri *et al.* 2013).

Normally, the application of chlorine in conservative bleaching procedures yields massive quantities of chlorinated organic compounds, which result in serious environmental issues. Thus, chlorine-free bleaching processes have become increasingly important. Hydrogen peroxide is the most popular agent for bleaching chemical, lignin-retaining, mechanical, and recycled pulp. The hydrogen peroxide bleaching process principally leads to the loss of chromophoric groups in lignin instead of pulp delignification (Qin *et al.* 1999). Although hydrogen decays due to its instability and catalysis, bleaching efficiency is enhanced by using NaOH to activate residual hydrogen peroxide (Zhao *et al.* 2012).

Polysaccharides within secondary cell walls are surrounded by a lignin matrix that restricts their accessibility. The physiological role of lignins in plant cell walls is related to its resistance to degradation. Lignin shields susceptible carbohydrates from attack by pathogens, offers structural firmness to the cell wall, and creates a hydrophobic barrier to water diffusion over cells that drive fluid transport. While the role of lignin in cell wall resistance is recognized, the causes of this resistance are not fully understood. Lignin resistance is associated with its abundance (Van Soest 1994; Chen and Dixon 2007; Studer *et al.* 2011), position within the cell wall (Yang and Wyman 2004), properties such as hydrophobicity (Nakagame *et al.* 2011), and ability to bind enzymes (Rahikainen *et al.* 2011).

Peanut shell powder (PSP) has been examined as a natural filler in rubber composites (Sareena *et al.* 2011) but never in thermo-plastic composites. The cellulose (40.5%), hemicellulose (14.7%), and lignin (26.4%) contents of peanut shells have been determined previously (López Rivilli *et al.* 2012; Zaaba *et al.* 2013). In this study, lignocellulosic PSP fillers were pre-treated with hydrogen peroxide to eliminate lignin prior to produce recycled polypropylene (RPP) composites. The processing properties, tensile properties, Fourier transform infrared (FTIR) spectra, scanning electron microscope (SEM) images, and water absorption characteristics of recycled polypropylene (RPP) composites containing treated and untreated PSP at different filler loadings were compared.

EXPERIMENTAL

Materials

Recycled polypropylene (RPP) with melt flow index of 30 g/10 min, density of 0.896 g/cm^3, and tensile modulus of 900 MPa was purchased from Zarm Scientific and Supplies, Penang, Malaysia. Peanut shell powder (PSP) was also supplied by Zarm Scientific and Supplies, Penang, Malaysia. Prior to composite fabrication, the peanut shells were ground to an average particle diameter of 66.84 μm and dried for 3 h at 70 °C using a vacuum oven. Sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), and acetic acid were obtained from Sigma Aldrich, Kuala Lumpur, Malaysia.

Pre-treatment of PSP by Alkaline Peroxide

PSP was soaked in distilled water at a temperature of 65 °C to 80 °C for at least 12 h to eliminate the impurities and large particles. A total of 20 g of PSP was placed in a 500-mL flask containing 15 w/v% of NaOH. The flask was maintained at 75 °C in a water bath with shaking at 40 rpm for 3 h to remove lignin. Next, the PSP was washed several times with distilled water and treated with 2 w/v% of H_2O_2 at 45 °C and 40 rpm for 8 h. Continued reaction will remove more of the lignin content and activate the OH groups of the cellulose. The PSP was washed with distilled water and treated with 10 w/v% of acetic acid at room temperature for 30 min to neutralize the excess NaOH. Washing with distilled water was repeated until the cellulose residue was free from acid. Finally, the treated PSP was dried in an oven overnight at 70 °C.

Composite Preparation and Processing

Two types of composites were prepared: RPP with untreated PSP (RPP/PSP) and RPP with H_2O_2-treated PSP (RPP/PSP-H_2O_2). Both composites were prepared using an internal mixer (model R600/610 Rheomixmixer, Haake, Karlsruhe, Germany) at 180 °C and 50 rpm to obtain a homogeneous sample. The RPP was placed in the mixer and melted for 4 min before 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 compression molded into a 1-mm thick sheet by an electrically heated hydraulic press (Kao Tieh Go Tech Compression Machine, Taichung, Taiwan) at temperature of 180 °C. Table 1 shows the formulation ofeach of the composites.

Table 1. Formulation of RPP/PSP and RPP/PSP-H_2O_2 Composites

Composite	RPP (wt.%)	PSP (wt.%)	PSP-H_2O_2 (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-H_2O_2	90	-	10
RPP + 20% PSP-H_2O_2	80	-	20
RPP + 30% PSP-H_2O_2	70	-	30
RPP + 40% PSP-H_2O_2	60	-	40

Measurement of Tensile Properties

Tensile tests were carried out using a universal testing machine (model 3366, Instron, Canton, Mass, USA) according to ASTM D638 (1994) (Obasi *et al.* 2013). 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 °C. Five specimens were used to obtain the average values for tensile strength, elongation at break, and tensile modulus.

Fourier Transform Infrared (FTIR) Spectroscopy Analysis

The functional groups and chemical characteristics of the composites were obtained by FTIR with a Perkin Elmer System 2000 (Selangor, Malaysia) at a resolution of 4 cm^{-1} in a spectral range of 4,000 to 550 cm^{-1}, using 32 scans per sample.

Morphology Evaluation

The microstructure of the tensile fractured surfaces of the RPP/PSP and RPP/PSP-H_2O_2 composites were compared using a ZEISS Supra 35 VP SEM (Oberkochen, Germany). The samples were first sputter-coated with a thin layer of carbon, which provides an electron-transparent (low atomic number), conductive coating. The distribution of natural fillers and their interactions within the polymeric matrix were analyzed in the captured images.

Water Absorption

Water uptake measurements were carried out according to ASTM D570-98 (2010). 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 23 to 26°C. After being immersed for 0 to 30 days, 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 (*WA*) was calculated using Eq. 1,

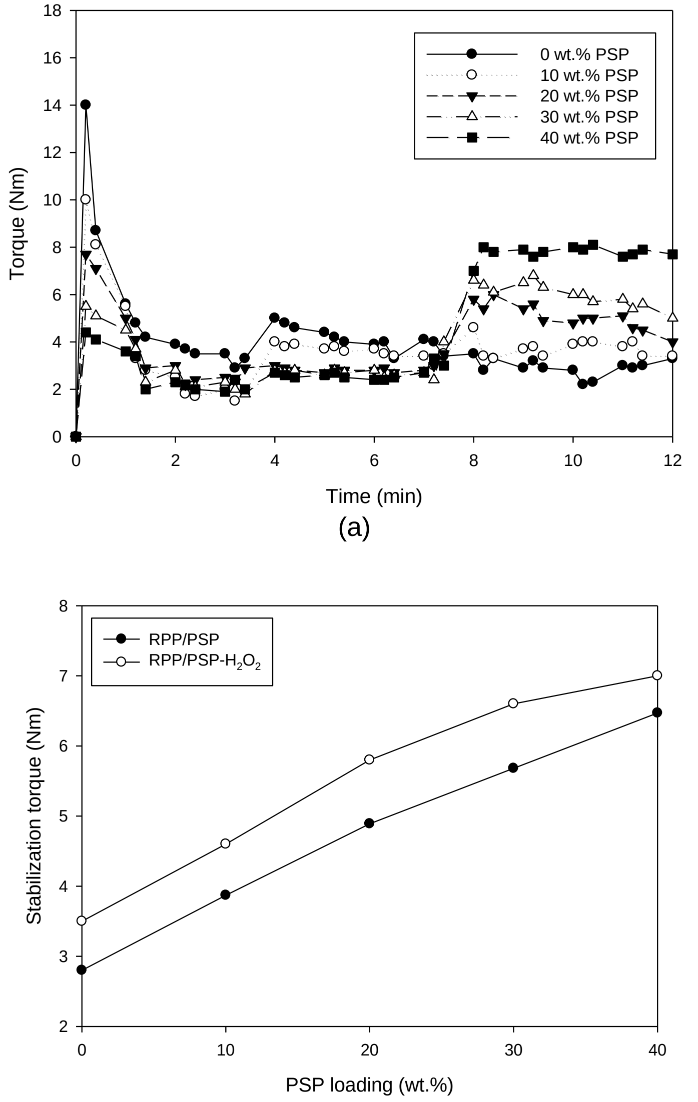
$$WA\ (\%) = [(M_1\text{-}M_o)/M_o] \times 100 \qquad (1)$$

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

RESULTS AND DISCUSSION

Processing Properties

Figure 1(a) illustrates the convenience mixing torque of the RPP/PSP composites at various mixing times and at a set temperate of 180 °C.



(a)

(b)

Fig. 1. (a) The processing torque of RPP/PSP-H_2O_2composites during the 12 min of mixing, and (b) the stabilization torque of RPP/PSP and RPP/PSP-H_2O_2 composites at different filler loadings

Normally, peak torque and stabilization torque elucidate the processing behaviour of the composites. Different peaks were obtained for all cases, which were related to different amounts of RPP and PSP that were charged into the mixing chamber. The first peak at around 0.2 min for all compounds illustrates the shear force during mixing before RPP was melted. The reduction of the mixing torque showed the reduced viscosity as the RPP melted. The following peak at around 4 min corresponded to the introduction of PSP. This peak was correlated with the abrupt increase in viscosity and the resistance of the PSP in melted RPP. Subsequently, the torque diminished until it stabilized at 12 min, which was comparable to the outcome with PP/bentonite composites (Othman *et al.* 2006).

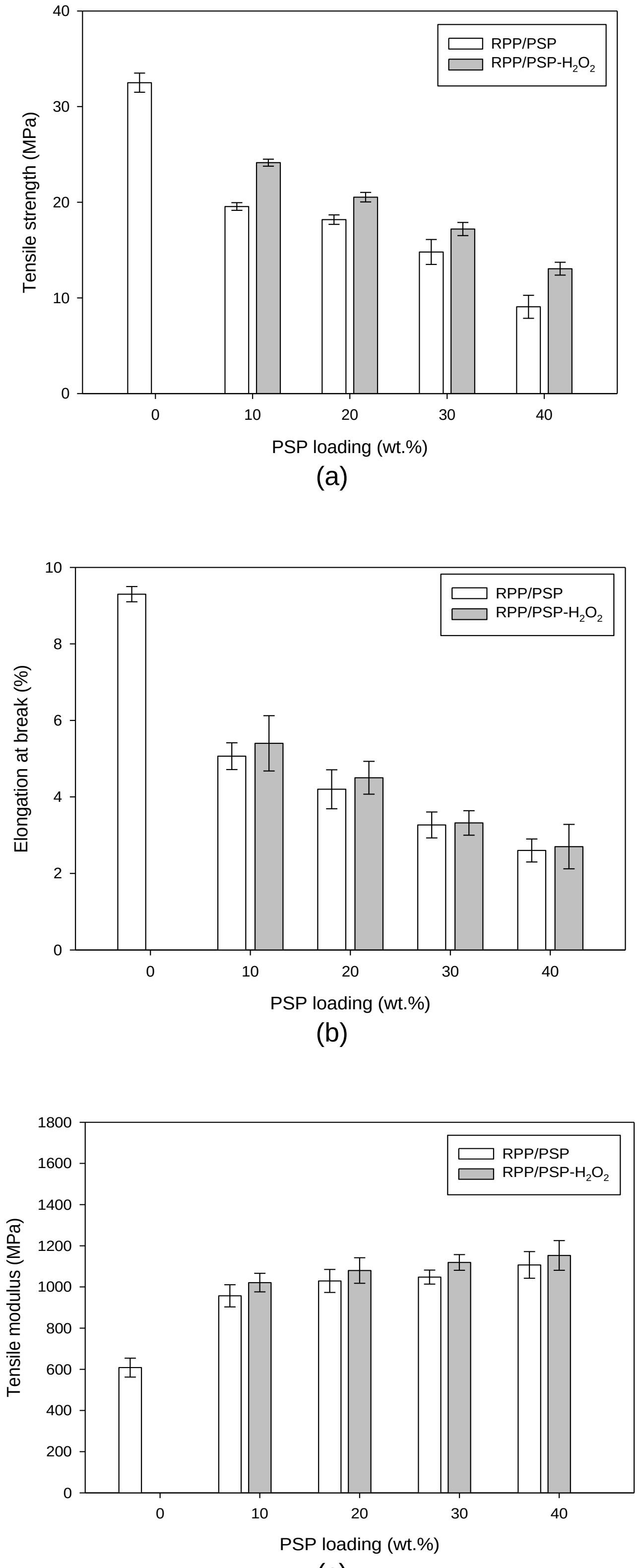
The stabilization torque for the different PSP loadings was obtained at the end of the time of mixing (Fig. 1b). The stabilization torque increased with increasing PSP loading. The PSP addition increased the viscosity and the stabilization torque (Ismail and Salmah 2001). Filler particle agglomeration occurs at higher filler loadings and leads to a higher equilibrium torque (Siriwardena *et al.* 2002). When comparing both composites, the treated composites presented a higher stabilization torque than the untreated composites. The PSP pre-treatment allowed better interfacial interaction with the RPP matrix; this interaction occurred between the carboxylic acid group that formed from the peroxide solution and the hydroxyl groups from the PSP. This interaction caused an increase in blend viscosity and a higher stabilization torque in the treated composites. These results were corroborated by FTIR analysis (described below).

Tensile Properties

The tensile strength, elongation at break, and tensile modulus of the RPP/PSP and RPP/PSP-H_2O_2 composites were evaluated at different filler loadings (Fig. 2). With increased PSP loading, tensile strength and elongation at break decreased for both composites. The stress transferring along the applied force is interrupted by the incorporation of fillers into the polymer matrix (Pracella *et al.* 2006). Moreover, the lack of interfacial interaction between fillers and the matrix exaggerated the problem. The irregular shape of the PSP fillers (Fig. 3) does not allow them to support the stresses transferred from the polymer, which weakens the composites (Cao *et al.* 2011).

The agglomeration of filler particles and drying of the polymer at the interphase also reduces the tensile strength and elongation at break (Ismail *et al.* 2001). The high hydrophilicity of PSP limited its incorporation into non-polar, hydrophobic RPP. The difference in polarities weakened the interfacial adhesion between PSP and RPP, thus providing sites for failures to initiate and propagate.

Likewise, the treated composites showed a higher tensile strength and elongation at break than untreated composites. Alkaline peroxide treatment increases the aspect ratio and decreases the filler diameter. During the alkaline treatment of jute fibers, the elimination of lignin and hemicellulose has an effect on the tensile characteristics of the fillers (Ray *et al.* 2001). The middle lamella assembly of the ultimate cell becomes more flexible and homogeneous as lignin is eliminated. This effect is due to the slow elimination of microvoids, whereas the ultimate cells themselves are exaggerated slightly, thus increasing the elongation at break of the composites. Moreover, the interfibrillar region is likely to be less dense and less stiff after the elimination of hemicellulose, allowing the fillers to relocate themselves along the path of tensile deformation. Better arrangements between the fillers improve load sharing as natural fillers are strained, leading to higher tensile strength in the fillers.



(a)

(b)

(c)

Fig. 2. (a) Tensile strength, (b) elongation at break, and (c) tensile modulus of RPP/PSP and RPP/PSP-H_2O_2 composites at different filler loadings

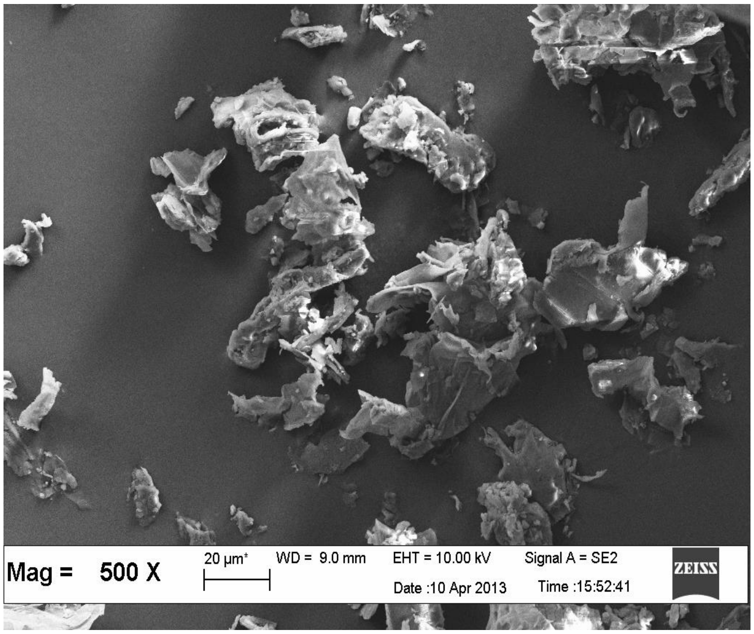


Fig. 3. SEM micrograph of the irregular morphology of peanut shell powder

Pre-treatment of the PSP resulted in a slightly higher tensile modulus compared with untreated PSP. The tensile modulus clearly increased with increased PSP loading (Fig. 2c). The change in tensile modulus can be clarified by the stiffening effect of the PSP. The inclusion of rigid filler particles in the soft matrix improves the stiffness of composite materials (Abdul Khalil *et al.* 2001; Cao *et al.* 2011; Ismail *et al.* 2011). The treated composites had a slightly higher tensile modulus than the untreated composites. There are few factors that could have affected the tensile modulus of treated composites, such as aspect ratio and degree of molecular orientation. In this case, the higher tensile modulus of the treated PSP might have been due to the well-oriented cellulosic fillers, which could increase stiffness and result in a higher tensile modulus.

Infrared Spectroscopy

FTIR spectra of the RPP/PSP and RPP/PSP-H_2O_2 composites showed mostly the O-H and aliphatic C-H stretching frequencies in the region from 4000 to 1900 cm^{-1} (Fig. 4). The results discussed below were confined to the residual region, from 100 cm^{-1} to 500 cm^{-1}. The first band was centred between 2909.2 cm^{-1} and 2932.31 cm^{-1}, predominantly arising from the C-H stretching in aromatic methoxyl groups. There was anotable absence of the absorbance peak at 1740 cm^{-1}, which is due to the ester carbonyl vibration in acetyl, feruloyl, p-coumaroyl, *etc*. groups in lignin and hemicelluloses (Sun *et al.* 2002). The stretching peaks at about 1654 cm^{-1} originated from conjugated C-C stretching, indicating that there is an ester bond between hydroxycinnamic acids and lignin, while at 1461 cm^{-1}, the band represented C-H stretching in CH_2 and CH_3. Alkaline peroxide treatment did not have any dramatic effect on lignin structure, except for an increase in carboxylic acid content and a decrease in phenolic hydroxyl content, which was indicated by a relative increase in carbonyl group stretching from 1256 to 1133 cm^{-1}. The introduction of carboxyl groups into lignin is important because this functional group is hydrophilic and facilitates dissolution in water (Sun *et al.* 2003).

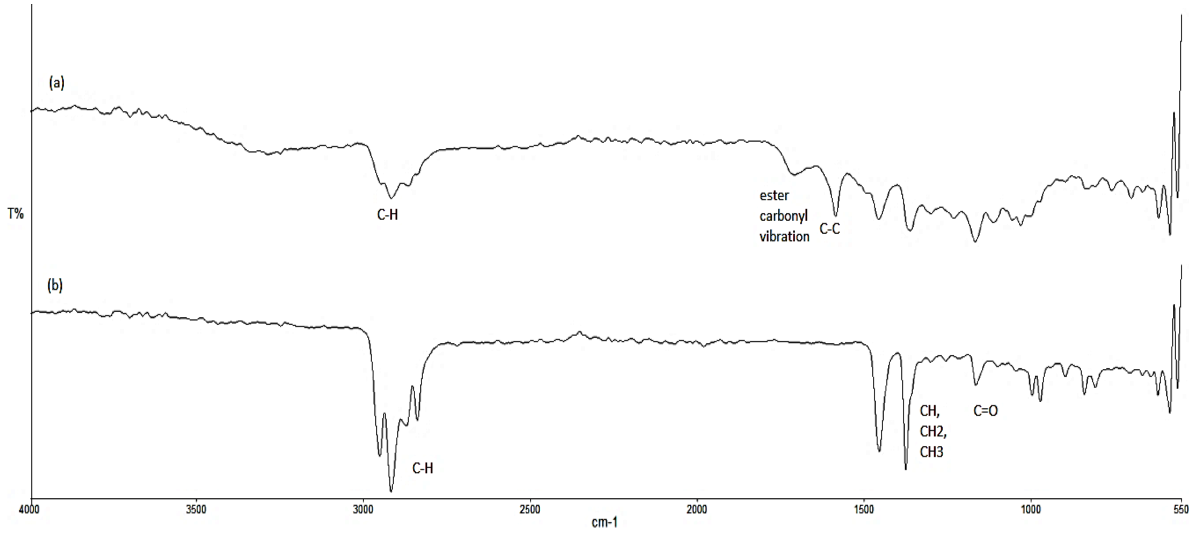


Fig. 4. IR spectra of (a) RPP/PSP and (b) RPP/PSP-H_2O_2 composites

Morphology

Scanning electron microscopy was used to examine the tensile-fractured surfaces of the RPP/PSP and RPP/PSP-H_2O_2 composites at 10 and 40 wt.% filler loadings (Fig. 5, 6). Figure 5a shows the rough surface of untreated composites. A more porous structure and filler agglomeration were observed for composites at higher filler loadings (Fig. 5b). The porosity of the structure was due to the low adhesion of filler and matrix, which reduced tensile strength by allowing the fillers to be removed easily from the composites. The pores or voids are flaws concentrate stress locally during deformation. Hence, premature failure of the composites occurred at higher filler content, indicating lower tensile strength. High filler loading can result in agglomeration, which is detrimental to the mechanical properties (Gauthier *et al.* 1998, Siriwardena *et al.* 2002).

For composites with treated PSP, a smoother fracture surface was observed (Fig. 6a). Thus, alkaline peroxide pre-treatment had an effect on filler-matrix adhesion. Better interfacial adhesion between the treated PSP filler and the RPP matrix can be seen clearly in Fig. 6b. The interfacial adhesion might have been improved by the elimination of lignin during pre-treatment. The elimination of the lignin breaks down the filler bundles, thus exposing more hydroxyl and carbonyl groups on the surface.

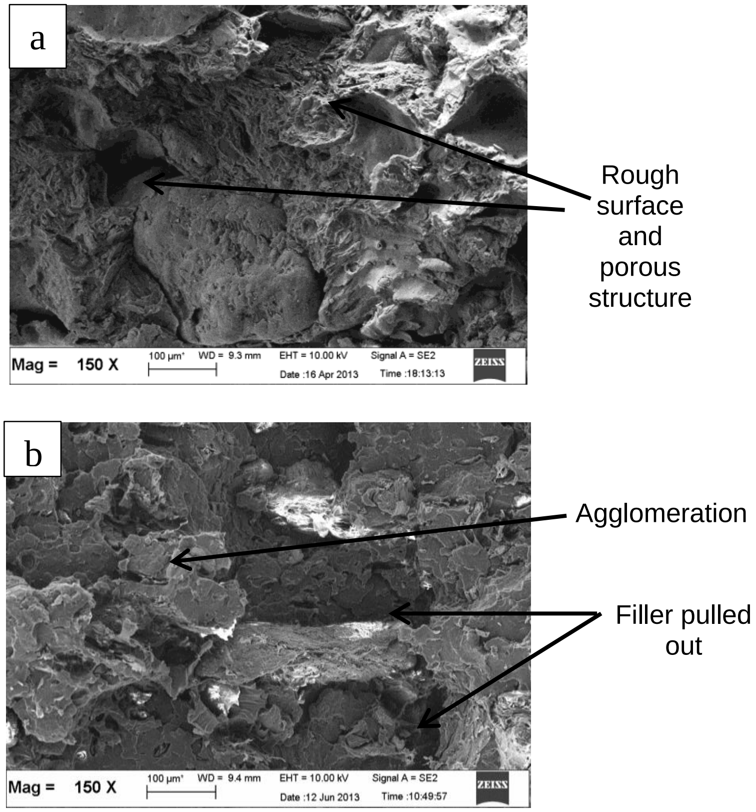


Fig. 5. SEM micrographs of RPP/PSP composites at (a) 10% and (b) 40% filler loading

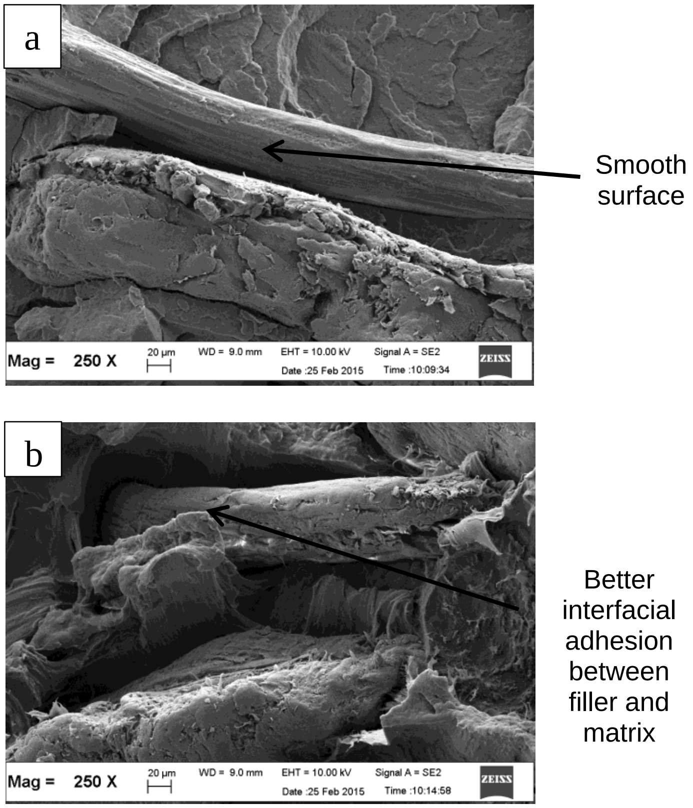


Fig. 6. SEM micrographs of RPP/PSP-H_2O_2 composites at (a) 10% and (b) 40% filler loading

Water Absorption

The water absorption characterization of RPP/PSP and RPP/PSP-H_2O_2 composites indicated how stable the composites were in water (Fig. 7). All composites displayed a similar pattern of absorption. In the first stage, samples absorbed water very rapidly; next, there was a gradual increase and a final plateau. Water absorption for all composites clearly increased with increased PSP loading. Natural fillers are permeable to water and have an effect on water absorption. Najafi *et al.* (2006) reported that water absorption increased with higher filler content. This result maybe due to the highly hydrophilic nature of the lignocellulosic filler. The free hydroxyl groups come in contact with water through hydrogen bonding, resulting in water uptake by composites. Moreover, higher filler loading creates more pores within composites, thus increasing water accumulation at the interface between the filler and the matrix (Jacob *et al.* 2005).

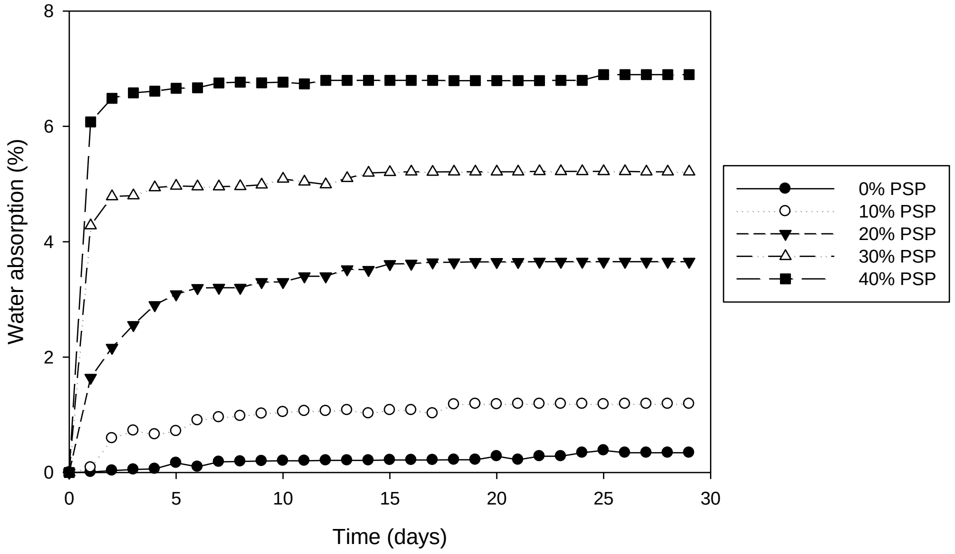


Fig. 7. Water absorption over 30 days of RPP/PSP-H_2O_2 at different filler loadings

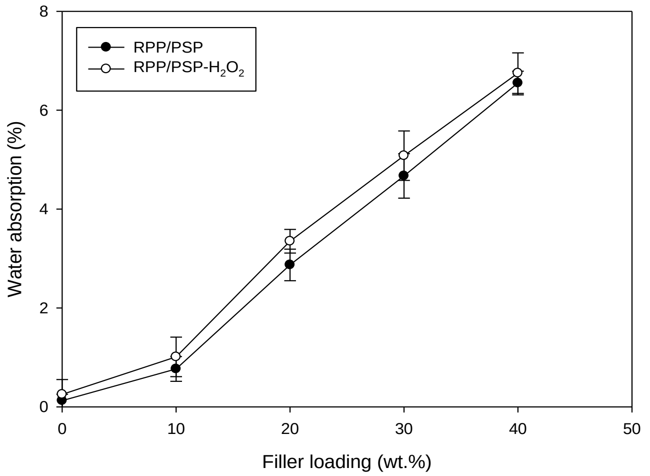


Fig. 8. Equilibrium water absorption of RPP/PSP and RPP/PSP-H_2O_2 composites at 30 days

PSP pre-treatment with alkaline peroxide also affected water absorption in RPP/PSP composites. IR spectra showed that alkaline peroxide pre-treatment increased the number of hydrophilic carboxyl groups (Fig. 4), which facilitate PSP dissolution in water. Therefore, water absorption in treated composites was higher than in untreated composites (Fig. 8).

CONCLUSIONS

1. RPP/PSP-H_2O_2 composites showed an improvement in the stabilization torque, tensile strength, elongation at break, and tensile modulus.
2. Water absorption in RPP/PSP-H_2O_2 composites also increased due to the increase in carboxyl groups resulting from the alkaline peroxide pre-treatment. These groups facilitated PSP dissolution in water.
3. IR spectra and SEM showed that the elimination of lignin strongly influenced the fracture surface and the chemical characteristics of RPP/PSP-H_2O_2 composites.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support provided by a Research University Grant from UniversitiSains Malaysia (USM) and MyBrain15 from the Ministry of Education of Malaysia.

REFERENCES CITED

Abdul Khalil, H. P. S., Chow, W. C., Rozman, H. D., Ismail, H., Ahmad, M. N., and Kumar, R. N. (2001). The effect of anhydride modification of sago starch on the tensile and water absorption properties of sago filled linear low density polyethylene (LLDPE)," *Polymer Plastic Technology and Engineering* 40, 249-263. DOI: 10.1081/PPT-100000246

ASTM D570-98. (2010). “Standard test method for water absorption of plastics,” ASTM International, West Conshohocken, PA.

ASTM D638 - 14 (1994). “Standard test method for tensile properties of plastics,” ASTM International, West Conshohocken, PA.

Averous, L., and Le Digabel, F. (2006). "Properties of biocomposites based on lignocellulosic fillers," *Carbohydrate Polymers* 66, 480-493. DOI: 10.1016/j.carbpol.2006.04.004

Cao, X. V., Ismail, H., Rashid, A. A., Takeichi, T., and Huu, T. V. (2011). "Mechanical properties and water absorption of kenaf powder filled recycled high density polyethylene/natural rubber biocomposites using mape as a compatibilizer," *BioResources* 6, 3260-3271. DOI: 10.15376/biores.6.3.3260-3271

Chen, F., and Dixon, R. A. (2007). "Lignin modification improves fermentable sugar yields for biofuel production," *Nature Biotechnology* 25, 759-761. DOI: 10.1038/nbt1316

Gauthier, R., Joly, C., Coupas, H., Gauthier, H., and Escoubes, M. (1998). "Interfaces in polyolefin/cellulosic fiber composites: Chemical coupling, morphology, correlation with adhesion and aging in moisture," *Polymer Composites* 19, 287-300. DOI: 10.1002/pc.10102

Habibi, Y., El-Zawawy, W. K., Ibrahim, M. M., and Dufresne, A. (2008). "Processing and characterization of reinforced polyethylene composites made with lignocellulosic fibers from Egyption agro-industrial residues," *Composites Science and Technology* 68, 1877-1885. DOI: 10.1016/j.compscitech.2008.01.008

Ismail, H., Abdullah, A. H., and Bakar, A. A. (2011). "Influence of acetylation on the tensile properties, water absorption, and thermal stability of (High density polyethylene)/(soya powder)/ (kenaf core) composites," *Journal of Vinyl and Additive Technology* 17, 132-137. DOI: 10.1002/vnl.20262

Ismail, H., Edyham, M. R., and Wirjosentono, B. (2002). "Bamboo fiber filled natural rubber composites: The effect of filler loading and bonding agents," *Polymer Testing* 21, 139-144.

Ismail, H., Nizam, J. M., and Abdul Khalil, H. P. S. (2001). "The effect of a compatibilizer on the mechanical properties and mass swell of white rice hulk ash filled natural rubber/linear low density polyethylene blends," *Polymer Testing* 20, 125-133.

Ismail, H., and Salmah, M. N. (2001). "Dynamic vulcanization of rubberwood-filled polypropylene/natural rubber blends," *Polymer Testing* 20, 819-823. DOI: 10.1016/S0142-9418(01)00010-1

Jacob, M., Varughese, K. T., and Thomas, S. (2005). "Water sorption studies of hybrid biofiber-reinforces natural rubber biocomposites," *Biomacromolecules* 6, 2969-2979. DOI: 10.1021/bm050278p

López Rivilli, P., Alarcón, R., Isasmendi, G. L., and Pérez, J. D. (2012). "Stepwise isothermal fast pyrolysis (Sifp). Part II. Sifp of peanut shells - Antifungal properties of phenolic fractions," *BioResources* 7, 112-117.

Najafi, S. K., Tajvidi, M., and Chacharmahli, M. (2006). "Long term water uptake behaviour of lignocelluloseic-high density polyethylene composites," *Journal of Applied Polymer Science* 102, 3907-3911. DOI:10.1002/app.24172

Nakagame, S., Chandra, R. P., Kadla, J. F., and Saddler, J. N. (2011). "Enhancing the enzymatic hydrolysis of lignocellulosic biomass by increasing the carboxylic acid content of the associated lignin," *Biotechnology Bioengineering* 108, 538-548. DOI:10.1002/bit.22981

Obasi, H. C., Igwe, I. O., and Madufor, I. C. (2013). "Effect of soil burial on tensile properties of polypropylene/plasticized cassava starch blends," *Advances in Materials Science and Engineering* 2013, 1-5. DOI:10.1155/2015/673025

Othman, N., Ismail, H., and Mariatti, M. (2006). "Effects of compatibilisers on mechanical and thermal properties of bentonite filled propylene composites," *Polymer Degradation and Stability* 91, 1761-1774. DOI: 10.1016/j.polymdegradstab.2005.11.022

Pracella, M., Chionna, D., Irene Anguillesi, I., Kulinski, Z., and Piorkowska, E. (2006). "Functionalization, compatibilization and properties of polypropylene composites with hemp fibres," *Composites Science and Technology* 66, 2218-2230. DOI: 10.1016/j.compscitech.2005.12.006

Qin, W., Cui, G., Liang, W., and Yu, H. (1999). "Study on DMD pretreatment and totally chlorine-free bleaching," *Chemistry and Industry of Forest Products* 19, 1-15.

Rahikainen, J., Mikander, S., Marjamaa, K., Tamminen, T., Lappas, A., Viikari, L., and Kruus, K. (2011). "Inhibition of enzymatic hydrolysis by residual lignins from softwood-study of enzyme binding and inactivation on lignin-rich surface," *Biotechnology Bioengineering* 108, 2823-2834. DOI: 10.1002/bit.23356

Ray, D., Sarkar, B. K., Rana, A. K., and Bose, N. R. (2001). "The mechanical properties of vinylester resin matrix composites reinforced with alkali-treated jute fibres," *Composites: Part A* 32**,** 119-127. DOI: 10.1016/S1359-835X(00)00101-9

Rozman, H. D., Saad, M. J., and Mohd Ishak, Z. A. (2003). "Flexural and impact properties of oil palm fruit bunch (EFB) - polypropyene composites - The effect of maleic anhydride chemical modification of EFB," *Polymer Testing* 22, 335-341.

Rozman, H. D., Tay, G. S., Kumar, R. N., Abusamah, A., Ismail, H., and Mohd Ishak, Z. A. (2006). "The effect of oil extraction of the oil palm empty fruit bunch on the mechanical properties of polypropylene-oil palm empty fruit bunch-glass fibre hybrid composites," *Polymer Plastic Technology and Engineering* 40, 103-115. DOI:10.1081/PPT-100000058

Sareena, C., Ramesan, T., and Purushothaman, E. (2011). "Utilization of peanut shell powder as a novel filler in natural rubber," *Journal of Applied Polymer Science* 125, 2322-2334. DOI: 10.1002/app.36468

Siriwardena, S., Ismail, H., Ishiaku, U. S., and Perera, M. C. S. (2002). "Mechanical and morphological properties of white rice husk ash filled polypropylene/ethylene-propylene-diene terpolymer thermoplastic elastomer composites," *Journal of Applied Polymer Science* 85, 438-453. DOI: 10.1002/app.10713

Studer, M. H., Demartini, J. D., Davis, M. F., Sykes, R. W., Davison, B., Keller, M., Tuskan, G. A., and Wyman, C. E. (2011). "Lignin content in natural *Populus* variants affects sugar release," *Proceeding of the National Academy of Sciences USA* 108, 6300-6305.

Sun, R. C., Sun, X. F., Fowler, P., and Tomkinson, J. (2002). "Structural and physico-chemical characterization of lignins solubilized during alkaline peroxide treatment of barley straw," *European Polymer Journal* 38, 1399-1407. DOI: 10.1016/S0014-3057(01)00303-2

Sun, R. C., Tomkinson, J., and Jun, Y. (2003). "Physico-chemical and structural characterization of residual lignins isolated with TAED activated peroxide from ultrasound irradiated and alkali pre-treated wheat straw," *Polymer Degradation and Stability* 79, 241-251. DOI: 10.1016/S0141-3910(02)00287-2

Supri, A. G., Tan, S. J., Ismail, H., and Teh, P. L. (2013). "Enhancing interfacial adhesion performance by using polyvinyl alcohol in low-density polyethylene/natural rubber/water hyacinth fiber composites," *Journal of Vinyl and Additive Technology* 19, 47-54. DOI: 10.1002/vnl.20315

Van Soest, P. J. (1994). *Nutritional Ecology of the Ruminant*, (2nd Ed.), Cornell University Press, Ithaca.

Yang, B., and Wyman, C. E. (2004). "Effect of xylan and lignin removal by batch and flowthrough pretreatment on the enzymatic digestibility of corn stover cellulose," *Biotechnology Bioengineering* 86, 88-98. DOI: 10.1002/bit.20043

Zaaba, N. F., Ismail, H., and Mariatti, M. (2013). "Effect of peanut shell powder content on the properties of recycled polypropylene (RPP)/ peanut shell powder (PSP) composites," *BioResources* 8, 5826-5841. DOI: 10.15376/biores.8.4.5826-5841

Zhao, Q., Sun, D. Z., Wang, Z. H., Pu, J. W., Jin, X. J., and Xing, M. (2012). "Effects of different activation processes on H_2O_2/TEAD bleaching of *Populus nigra* chemi-thermo mechanical pulp," *BioResources* 7, 4889-4901. DOI:10.15376/biores.7.4.4889-4901

Article submitted: October 7, 2015; Peer review completed: December 29, 2015; Revised version received and accepted: February 19, 2016; Published: February 24, 2016.
DOI: 10.15376/biores.11.2.3524-3537