Properties of Polyvinyl Alcohol/Palm Kernel Shell Powder Biocomposites and Their Hybrid Composites with Halloysite Nanotubes

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Biocomposites composed from polyvinyl alcohol (PVOH)/palm kernel shell powder (PKSP) were prepared *via* a solution casting method. Halloysite nanotubes (HNTs) were used to gradually replace PKSP to study the effect of hybrid fillers and also to compare the properties of PVOH/PKSP biocomposites with a commercial filler, HNTs. The effect of HNTs' addition on the biocomposites was investigated based on mechanical properties, physical properties, and its biodegradability. The incorporation of HNTs in the biocomposites enhanced the tensile properties. Scanning electron microscopy (SEM) studies revealed that better filler and matrix interaction was achieved after the incorporation of HNTs. Moreover, the water absorption and water vapour transmissibility (WVT) of biocomposites decreased. The biodegradability of biocomposites filled with HNT was lower compared to the biocomposites filled with PKSP.

Keywords: Biocomposites; Hybrid fillers; Palm kernel shell; Polyvinyl alcohol; Halloysite nanotubes

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INTRODUCTION

Composite materials are made to tailor the desirable properties by combining a few components together. Generally, there are two basic components, known as the matrix and the filler. The filler can be embedded into the matrix in various ways to reinforce and enhance the strength. Over the years, public concern over waste management has increased due to the decreasing availability of landfills, environmental concern, and public perception. As environmental awareness is growing within society, the developments of green composites are very important. By definition, the term biocomposite means that the composite consists of at least one naturally occurring component, which is mostly the filler.

Generally, natural fillers are found in abundance either from industrial waste, agricultural waste, or purposely grown. The commonly studied natural fillers are kenaf (Tan *et al.* 2014), sago starch (Nawang *et al.* 2001; Toh *et al.* 2011; Ismail and Zaaba 2012), rice husk (Tong *et al.* 2014), and palm kernel shell (Jain *et al.* 2013; Shehu *et al.* 2014). Natural fillers offer several advantages over the man-made filler, such as low density, high availability, renewability, low energy consumption, eco-friendly nature, and acceptable specific properties compared to glass fiber (Romisuhani *et al.* 2010; Ismail and Zaaba 2012; Mohaiyiddin *et al.* 2013; Husseinsyah *et al.* 2014). However, the addition of natural filler also has a major adverse effect on the properties of the composite due to the poor compatibility, which leads to formation of weak interfacial adhesion between the filler and matrix. Therefore, various methods have been studied by researchers to enhance the properties of natural filler-filled composites, including the addition of a coupling agent, blending the matrices, and usage of more than one type of filler in the composite. In the past several years, extensive research has been conducted to the development of ternary composites to optimize the properties of the composite (Ismail *et al.* 2009; Deepak and Agrawal 2012; Mohaiyiddin *et al.* 2013; Taghizadeh and Sabouri 2013; Samotu *et al.* 2015). Utilization of hybrid fillers gives the advantages in tailoring and improving the functional and properties of composites. As one filler may not able to satisfy the requirements of having desired properties, hybridization enable to fill the “missing” properties. Although addition of natural filler enhances the biodegradability, it reduces the overall mechanical properties. Therefore, incorporation of reinforcing filler could balance the mechanical properties. The commonly used fillers to be hybrid with natural filler are talc, silica, calcium carbonate, and clay.

Recently, halloysite nanotubes are emerging as one of the promising reinforcing materials for polymer nanotechnology. According to Kamble *et al*. (2012), halloysite nanotubes are unique and versatile nanomaterials composed of double layer aluminosilicate minerals with a predominantly hollow tubular structure in the submicron range. The chemical composition of halloysite nanotubes is $Al_2(OH)_4Si_2O_5(2H_2O)$. They are naturally formed in the earth as the result of a strain caused by a lattice mismatch between adjacent silicon dioxide and aluminum oxide layers. Basically, the halloysite’s layer silicate and the crystal structure are formed by two building blocks, which are sheets of corner-sharing SiO_4 tetrahedral and sheets of edge-sharing AlO_6 octahedral (Rawtani and Agrawal 2012). The reinforcing effects of nano-fillers are generally higher than micron-sized filler due to higher aspect ratio, providing more area for filler and matrix interaction. Halloysite nanotubes have a lot of commercial applications, such as additives in polymer and plastic, electronic components, drug delivery vehicles, cosmetics, and in home and personal care products.

Based on a previous study (Zhong *et al*. 2011), the PVOH/tropical fruit waste flour biocomposite suffered a decrement of tensile strength and elongation at break even though the biodegradability was enhanced. The incorporation of HNT into polymer matrices is shown to enhance the overall mechanical properties (Prashantha *et al.* 2011; Liu *et al.* 2014; Gaaz *et al.* 2015); however no work has been found in literature for the ternary composite of PVOH/PKSP/HNT. Therefore, the purpose of this study was to investigate the effect of partial replacement of PKSP with HNT on the properties of the composite, such as tensile properties, morphology, water absorption, water vapour transmission, and biodegradability.

EXPERIMENTAL

Materials

Polyvinyl alcohol (PVOH) with a density of 1.3 g/cm^3 was purchased from Sigma-Aldrich (M) Sdn. Bhd (Kuala Lumpur, Malaysia), and the average molecular weight is in the range of 89000 g/mol to 98000 g/mol. Palm kernel shell powder with an average particle size of 75 µm was prepared by drying, grinding using a mini crusher, and sieving. The palm kernel shells were obtained from Malpom Industries (M) Bhd, Nibong Tebal, Penang. Glycerol and polyoxyethylene (20) sorbitan monooleate (Tween® 80) were supplied by Merck (Petaling Jaya, Malaysia), while hexamethylenetetramine was purchased from Sigma-Aldrich (M) Sdn. Bhd (Kuala Lumpur, Malaysia). Halloysite nanotubes were obtained from Imerys Tableware Asia Limited (Auckland, New Zealand). The HNTs had dimensions in the range of 150 nm to 2 µm long, 20 nm to 100 nm outer diameter, and 3 nm to 5 nm inner diameter All of the chemicals were analytical grade reagents.

Methods

Biocomposites preparation

The biocomposites were prepared by the solution casting method according to the formulation. The PVOH was initially dissolved in 200 mL of deionized water, followed by stirring for 10 min at 95 °C. Then, the fillers were added into the mixture with continued stirring for another 10 min. The additives were combined followed by stirring for 10 min in order to obtain a homogenous mixture. The solution mixture was casted over glass plates and allowed to dry at room temperature for 24 h. Another drying step was performed for 2 h at 70 °C in the oven. The biocomposite prepared was in film form and was kept in a desiccator until further testing. The PVOH/PKSP/HNT biocomposite was prepared at five different ratios, varying the ratio of PKSP and HNT in each composition.

Tensile properties

The tensile properties of the biocomposite films were measured using an Instron 3366 testing machine (Instron, Petaling Jaya, Malaysia). The samples were cut into dumbbell-shaped (Type IV) samples according to ASTM D638 (2008). The crosshead speed used was 50 mm/min, while the load cell was 10 kN. The gap between the upper and lower clamp was set at 50 mm. The average value of five repeated samples was taken for each composite composition.

Chemical composition by Fourier transform infrared (FTIR)

The functional group of samples was identified using FTIR. The characterization was performed in the ranges from 400 cm^{-1} to 4000 cm^{-1} by spectrometer (Perkin Elmer, Boston, MA, USA). Scanning was repeated 16 times to prevent overlapping of the spectrum and to reduce noise. The means of the peaks in the FTIR spectrum were used to identify the chemical structure in the samples.

Morphological study

Morphological properties of the biocomposites were examined using a field emission scanning electron microscope, FESEM Supra 35VP (ZEISS, Oberkochen, Germany). The failure modes and filler distribution were studied from the tensile–fracture surfaces of the composite. Further, the morphology of the composites was also analyzed after being subjected to natural weathering and soil burial testing. To avoid charging and poor resolution during examination, the samples were sputter coated with a thin gold layer using a Polaran SC 515 sputter coater (Bio-rad, Hercules, CA, USA).

Water absorption

The water absorption (W_a) test of biocomposites was conducted by immersing the samples in distilled water at room temperature. The moisture on the surface of the films was removed and the weights of the films were measured after 24 h. The percentage of water absorption was calculated using Eq. 1,

$$W_a (\%) = [(W_e - W_o) / W_o] \times 100 \quad (1)$$

where W_e is the final weight of samples (g) and W_o is the initial weight of the samples (g).

Water vapour transmissibility

Water vapour transmissibility (WVT) was measured according to ASTM E96 (1998), as modified by Gontard *et al.* (1993). First, 30 mL of distilled water was filled into a container and the top of the container was sealed with the composite film. The initial weight of the container sealed with the film sample was weighed. Then, the containers were placed in the desiccator at room temperature and the containers were weighed daily until the containers reached a constant weight. The WVT was calculated according to Eq. 2,

$$\mathrm{WVT} = (G / t) / A \quad (2)$$

where G is the weight gain (g), t is the time (s), and A is the area of the test area (m^2).

Natural weathering

The dumbbell-shaped (Type IV) (ASTM D638 (2008)) samples were subjected to a weathering test for 14 days at the Universiti Sains Malaysia, Nibong Tebal, Penang. The test was conducted according to ASTM D1435 (1999). The weathering resistance and degradation of the samples were evaluated by observation on the changes in the physical appearance and the weight loss.

Soil burial

Prior to soil burial, the samples were cut into a dumbbell shape (Type IV) according to ASTM D638 (2008) and their initial weight was recorded. The samples were buried in natural soil at the School of Material and Mineral Resources Engineering, Nibong Tebal, Penang for a period of 14 days. The buried specimens were collected from the soil and the dirt was removed. The weights of the buried samples were recorded to calculate the weight loss and the composite surface was observed using SEM.

RESULTS AND DISCUSSION

Tensile Properties

The mechanical properties of the composite materials are strongly influenced by the microstructure, which can provide vital information on the internal structure of the materials (Abdulkhani *et al.* 2013). Tensile strength is defined as the resistance capacity to rupture as the material is submitted to pressure force (Yamashita *et al.* 2006). Figure 1 shows the effects of the HNTs loading on the tensile strength of PVOH/PKSP/HNT biocomposites. The biocomposites filled with only HNT showed the highest tensile strength and apparently, an incorporation of HNT into the biocomposites increased the tensile strength.

The HNT is usually added into a polymer to enhance the mechanical properties (Zhou *et al.* 2009). When two fillers are used in the PVOH film, it is vital to ensure that both fillers are compatible to each other, so that high filler-filler interaction can be achieved. In comparison to neat PLA matrix which has tensile strength of 33.1 MPa, the tensile strength values of these biocomposites were generally lower. The decrement in tensile strength may be due to the imperfect distribution of the filler through the polymer matrix and poor adhesion between the matrix and filler (Buzarovska *et al.* 2008).

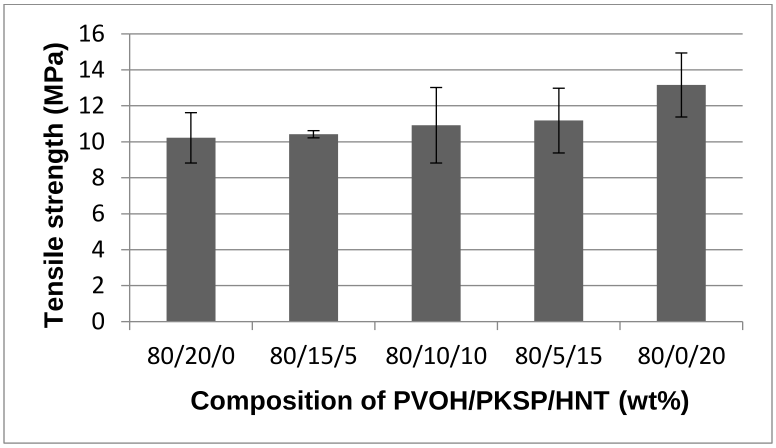

Fig. 1. Tensile strength of PVOH/PKSP/HNT biocomposites at different compositions

In contrast, the elongation at break is related to the elasticity of the sample as it is measured through the extension under traction. Figure 2 displays the elongation at break of PVOH/PKSP/HNT biocomposites. The same trend was observed for the tensile strength (Fig. 1). As the HNTs loading increased, the elongation at break of the biocomposites increased. This was due to better interfacial adhesion between the nano-sized HNT with a PVOH matrix, which allowed for better stress transfer.

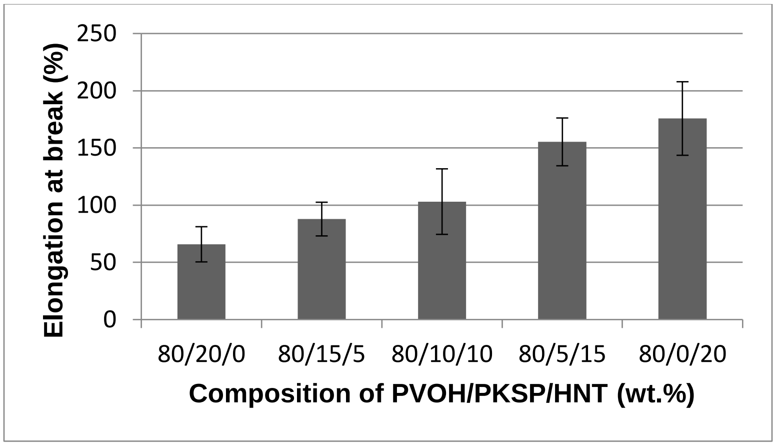

Fig. 2. Elongation at break of PVOH/PKSP/HNT biocomposites at different compositions

Tensile modulus is defined as the measure of force required to deform the sample at a specific amount and is actually a measure of the stiffness of the sample (Ismail *et al.* 2009). Figure 3 shows the tensile modulus of PVOH/PKSP/HNT biocomposites at different compositions. The tensile modulus for neat PLA is 90.84 MPa, and it was observed that the tensile modulus increased as the HNT content increased. The tensile modulus exhibited a similar trend in the tensile strength (Fig. 1). The highest tensile modulus was exhibited by the biocomposites filled with HNTs, while the lowest tensile modulus was obtained from the biocomposites with PKSP. This was due to the better interfacial adhesion between the PVOH matrix and HNTs, as shown later in the morphology study.

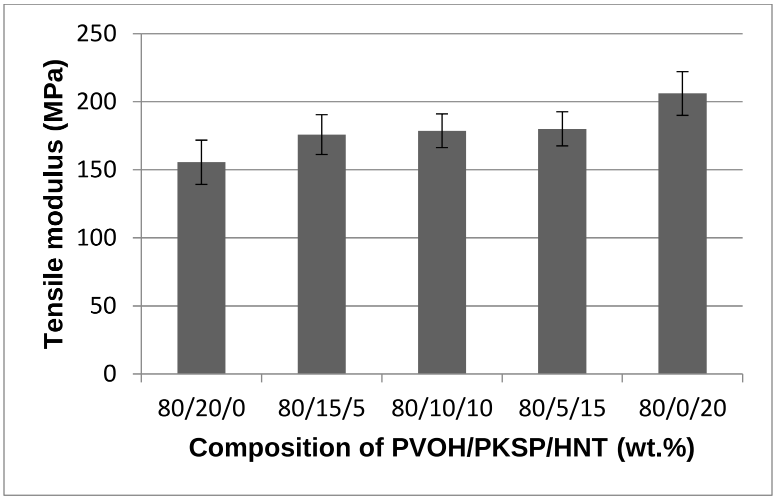

Fig. 3. Tensile modulus of PVOH/PKSP/HNT biocomposite at different compositions

Fracture Surface Morphology

The fractured surface of PVOH/PKSP/HNT at 80/20/0 is shown in Fig. 4. Some holes on the surface were visible, which indicated the occurance of filler pull out. Filler pull out was initiated by the debonding process due to interfacial failure. This was due to poor filler-matrix interaction. Generally, there are two types of fracture that may occur, which are brittle and ductile fracture. Obvious plastic deformation occurred on the fracture surface, which implied that the composite failed in ductile mode.

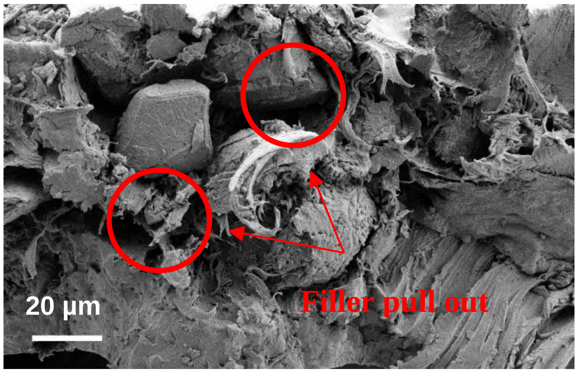

Fig. 4. Fracture surface morphology of PVOH/PKSP/HNT biocomposite at 80/20/0 composition at 700× magnification

Figure 5 shows the fractured surface of the tensile samples of PVOH/PKSP/HNT biocomposites at 80/10/10 composition. It was clearly shown that more plastic deformation occurred as the matrix became further elongated to bear the load. The incorporation of HNTs into the composite increased the tensile properties. This can be attributed to the larger surface area, and it induced better filler-matrix interaction. HNTs are comprised of siloxane and hydroxyl group, providing higher potential to form hydrogen bond with PVOH matrix. As the interaction was stronger, more energy was required to rupture the film. Moreover, less PKSP pull out was observed on the fracture surface, which indicated an improvement in the interaction between filler and matrix.

The PKSP and HNTs have different size and shape. The PSKP is a micro-sized filler with an irregular shape, resulting in a non-uniform dispersion. However, the small size HNTs are able to fill in between any gap or void in the composite, reducing the stress concentration area. Similar observations were made by Mohaiyiddin *et al.* (2013) in the system of palm kernel shell/polypropylene biocomposites. When two or more fillers are utilized in a single matrix, the most important parameter is the compatibility between the fillers. Based on the micrograph of fracture surface at higher magnification, it was shown that PKSP and HNTs were well dispersed and seemed to be compatible within the matrix. Therefore, better properties were obtained for the composite.

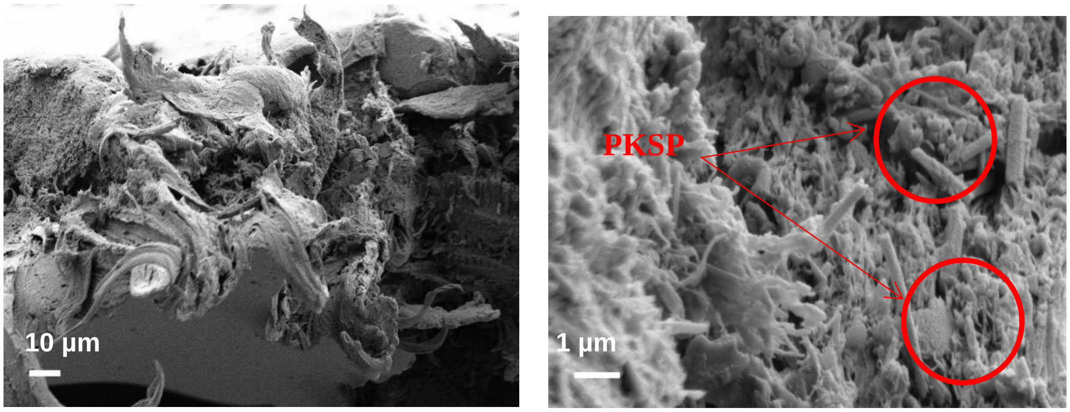

Fig. 5. Fracture surface morphology of PVOH/PKSP/HNT biocomposites at 80/10/10 composition at 700× magnification and 10.0k magnification

Figure 6 shows the fractured surface morphology of biocomposites with an incorporation of 20 wt.% HNT. The keys to fabrication of composites with enhanced mechanical properties are to achieve a good dispersion of the filler in the polymer matrix and strong filler-matrix interfacial bonding (Gaaz *et al.* 2015). The plastic deformation of the matrix in Fig. 6 is obviously shown to be more, which was reflected in the increment of the elongation at break and tensile strength.

Fig. 6. Fracture surface morphology of PVOH/PKSP/HNTs biocomposites at 80/0/20 composition

Chemical Composition by FTIR

Figure 7 illustrates the FTIR spectra for PVOH/PKSP/HNT biocomposites at 80/20/0, 80/10/10, and 80/0/20 compositions. Numerous characteristic peaks were identified, which corresponded to the functional groups in both the polymer matrix and fillers. In the FTIR spectra, the presence of an intense –OH stretching absorption between 3100 cm^{-1} and 3600 cm^{-1} indicated the existence of strong intermolecular and intramolecular hydrogen bonding, which corresponds to the PVOH component (El-Shinawy *et al.* 1998). Due to the stretching vibrations of $–CH_2$ and –CH groups, the characteristic absorption appeared around 2942 cm^{-1}. In the fingerprint region, the bending vibration for O-H was around 1420 cm^{-1}. The C-O absorption bands were also found at 1142.52 cm^{-1} and 1089.22 cm^{-1} as the conformation of an alcohol group in the sample. Peaks in the range of 1050 cm^{-1} to 1260 cm^{-1} indicated the presence of C-H scissor vibration, which occurred in both symmetric and asymmetric vibration. These bands were attributed to methyl and methylene groups. The peaks from 600 cm^{-1} to 900 cm^{-1} were mainly due to the rocking vibration of C-H bond.

Additional peaks were observed as HNT was incorporated into the biocomposite. According to Prashantha *et al.* (2011), HNT is mainly composed of aluminosilicate with a chemical composition of $Al_2(OH)_4Si_2O_5(2H_2O)$. The presence of HNTs was confirmed by some peaks in the FTIR spectra. The peaks in the range of 500 cm^{-1} to 700 cm^{-1} corresponded to the bending vibration of the Si-O and Al-O bond. Another peak that can be attributed to HNTs is the Al-OH band, which appeared around 911.9 cm^{-1}. Meanwhile, the bands in region of 1000 cm^{-1} to 1130 cm^{-1} are from Si-O-Si bond. The peaks were observed at 1008.32 cm^{-1} and 1006.37 cm^{-1} for 80/10/10 and 80/0/20 films, respectively.

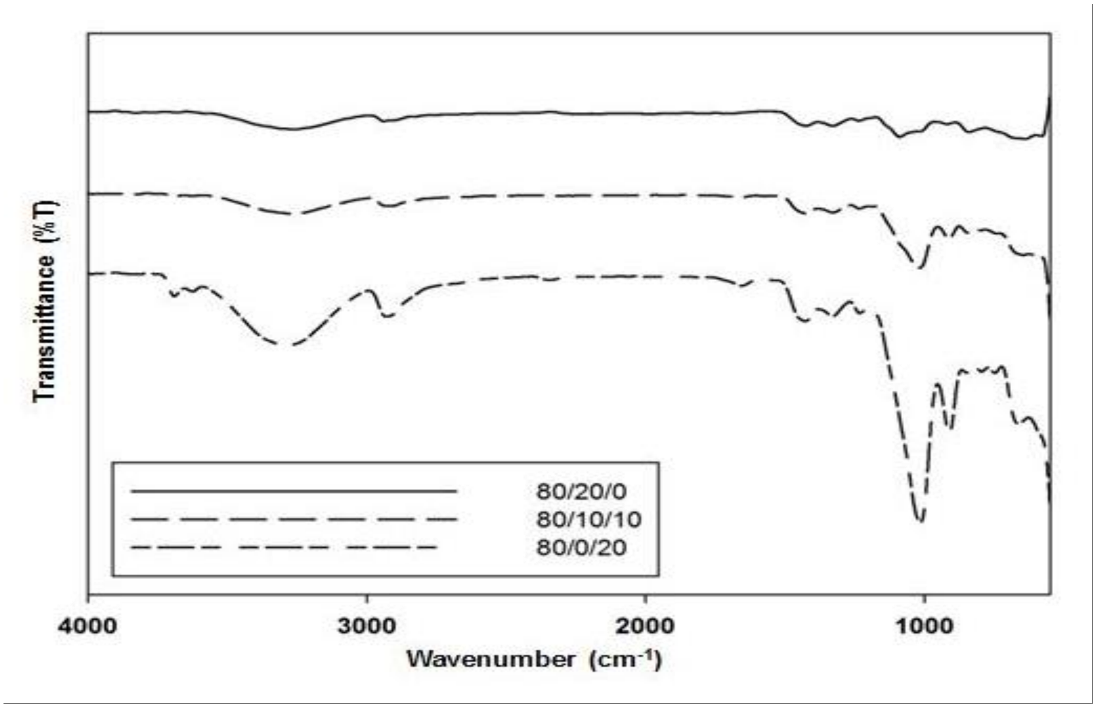

Fig. 7. FTIR spectrum for PVOH/PKSP/HNTs biocomposites at 80/20/0, 80/10/10, and 80/0/20 compositions

Water Absorption

The water absorption results are essential to determine the performance of PVOH composites, because the moisture absorption intimately relates to the composite properties (Messiry *et al.* 2015). Figure 8 shows the percentage of water absorption for different compositions of PVOH/PKSP/HNT biocomposites. The biocomposites incorporated with higher HNTs loading showed lower water absorption. This was due to the better and stronger interaction between HNTs as the filler and PVOH matrix compared to PKSP as the filler. The interaction reduced the number of free hydroxyl groups in the biocomposites, which provided less availability of a hydroxyl group to bind with water molecules. According to Ismail *et al.* (2009), HNTs also acted as a barrier and blocked the water from penetrating into the film, therefore the moisture absorption was reduced.

The water absorption capability is highly dependent on the hydrophilicity of the composite. Palm kernel shell is a natural filler that is comprised of high polarity lignocellulosic materials. High amounts of hydroxyl groups in the lignin, cellulose, and hemicellulose increased the ability for water to form hydrogen bonds and bind to the biocomposites. Therefore, the biocomposites with PKSP exhibited higher water absorption capability compared to PVOH filled with HNT. Another factor that may have affected the water absorption of biocomposites was the compatibility of the filler and matrix interaction. Poor compatibility of PKSP and PVOH resulted in more inter-chain spacing, which enabled more water molecules to penetrate into the biocomposites. Similar observations were observed by Zhong *et al.* (2011) and Ismail *et al.* (2009).

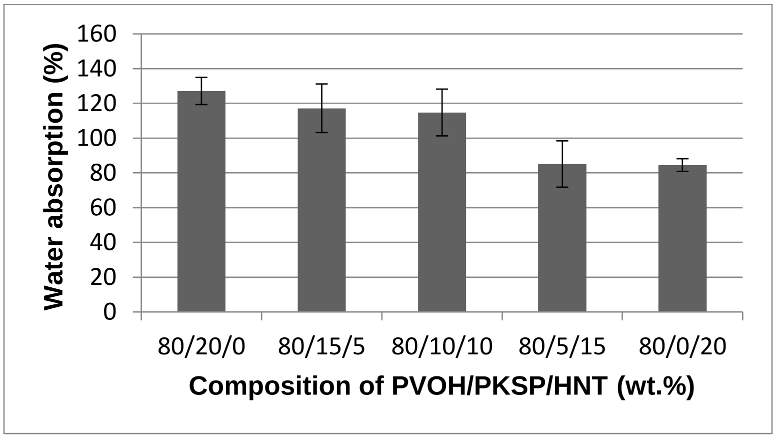

Fig. 8. Water absorption percentage of PVOH/PKSP/HNTs biocomposites at different compositions

Water Vapour Transmission

Water vapour transmission is vital to measure the capability of moisture to penetrate through any material. Both diffusivity and solubility affect the water vapour transmissibility of hydrophilic biocomposites. The sensitivity of biocomposites towards water can affect the WVT rate (Gontard and Guilbert 1994). Water vapour transmission of PVOH/PKSP/HNTs biocomposites at different compositions is shown in Fig. 9. As illustrated, the WVT decreased as the HNTs content into the biocomposites increased. The PKSP had higher sensitivity in absorbing moisture than HNT due to its structure and size. Smaller size HNT enabled better filler-matrix interaction, therefore less inter-chain spacing was left. Smaller inter-chain spacing resulted in less water molecules that were able to penetrate into the biocomposite, which decreased the WVT.

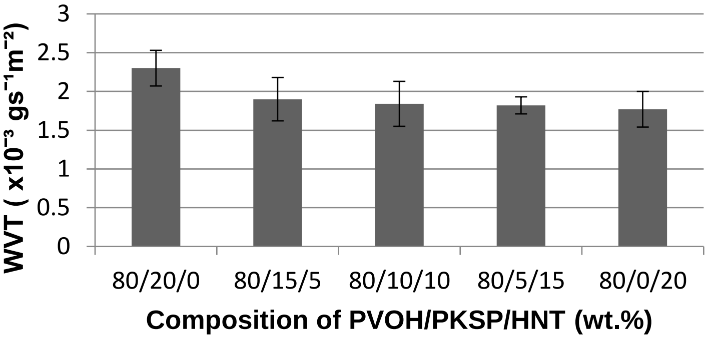

Fig. 9. Water vapour transmissibility of PVOH/PKSP/HNT biocomposites at different compositions

Natural Weathering

As polymeric materials are exposed to the environment, deterioration is caused by a combination of weather factors, including solar radiation, moisture, and atmospheric contaminant. Degradation by ultraviolet light may have occurred as the biocomposites were exposed to natural weathering and could be indicated as the weight loss. Figure 10 depicts the weight loss after weathering of PVOH/PKSP/HNT biocomposites at different compositions. The weight loss decreased as the loading of HNTs increased. The highest weight loss was exhibited by the biocomposites filled with PKSP, while the lowest weight loss was shown by the biocomposites filled with HNTs. Therefore, it implied that the addition of PKSP caused the biocomposites to degrade easier due to weathering compared to HNTs.

The weight loss could have been related to molecular weight changes. The weight loss indicated that PVOH underwent chain scission after natural weathering. The ultraviolet rays absorbed by the polymeric material have sufficient energy to break chemical bonds, which initiated the photo degradation process. The same observation was reported by Sam *et al.* (2011) in their study on the effect of cobalt stearate on the natural weathering of LLDPE/soya powder blends.

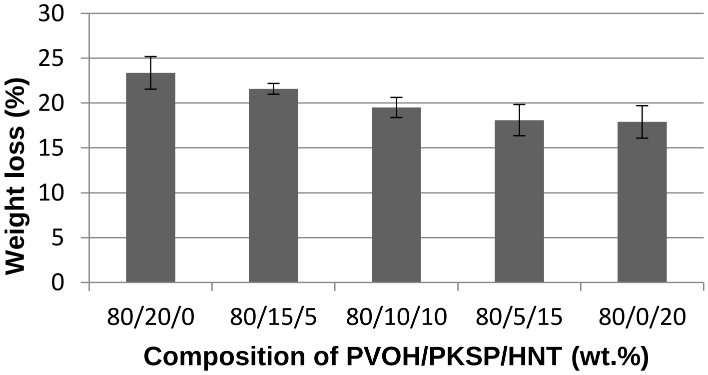

Fig. 10. Weight loss percentage after natural weathering of PVOH/PKSP/HNT biocomposites at different compositions

Figure 11 shows the SEM micrographs of the surface of PVOH/PKSP/HNT biocomposites after natural weathering at three different compositions, which were 80/20/0, 80/10/10, and 80/0/20. The PVOH filled with 20 wt.% PKSP biocomposites appeared to have the roughest surface, which indicated that the filler popped out to the surface. It was shown that the PKSP was agglomerated, which contributed roughness to the biocomposites. In comparison, the biocomposites filled with HNTs had a smoother surface that indicated the biocomposites degraded slower than PVOH/PKSP biocomposites. This was in agreement with the reduction in the weight loss of biocomposites.

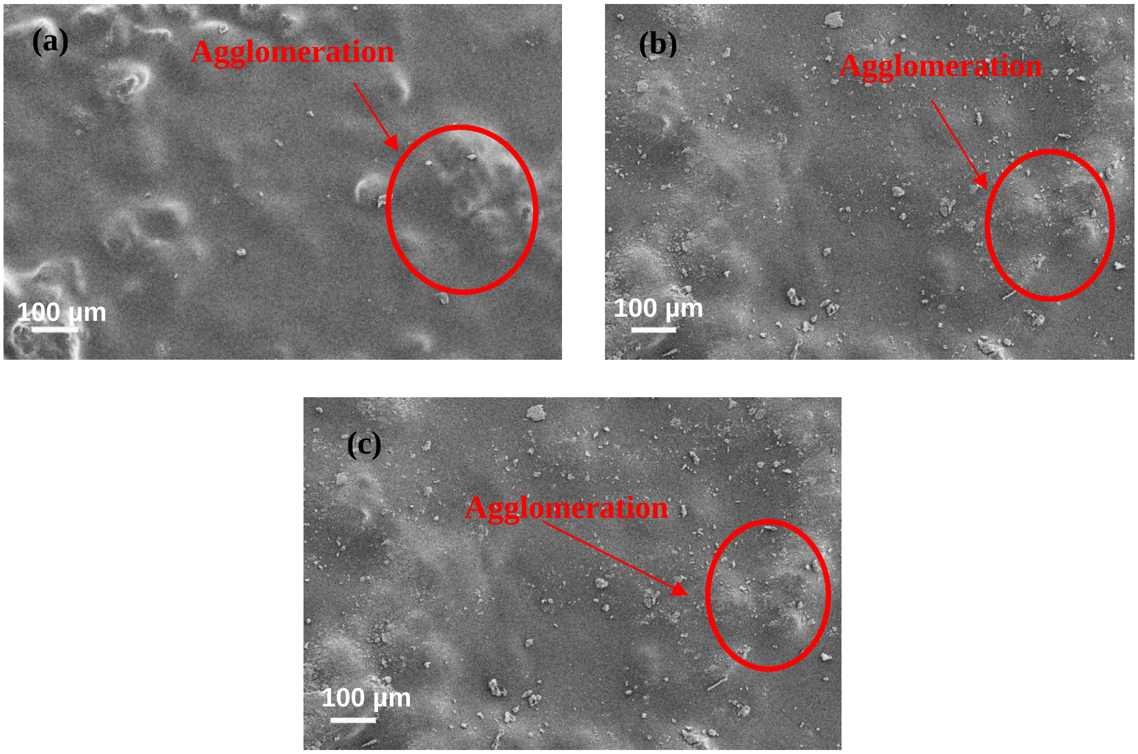

Fig. 11. Surface morphology of PVOH/PKSP/HNTs biocomposites with different compositions after natural weathering: (a) 80/20/0, (b) 80/10/10, and (c) 80/0/20 (wt.%)

Soil Burial

Figure 12 shows the dependence of weight loss after the soil burial test on the HNTs loading on PVOH biocomposites. The weight loss of the biocomposites showed a decreasing trend as higher HNT content was incorporated. Microbial degradation generally results from the action of naturally occurring microorganisms such as bacteria, fungi, algae, and others. The lowest weight loss was depicted by biocomposites with 20 wt.% HNTs. This may have been due to the fact that HNTs had a higher resistance towards microbial, which took longer to degrade. Microbial activities enhanced the degradation of plastic films and decompose them into smaller fragments. Basically, the entire microbial action is vital for degradation, not only of the filler but also the PVOH matrix (Rahmah *et al.* 2015).

The highest weight loss was exhibited by the biocomposites with 20 wt.% PKSP. This implied that PKSP may have had better hydrolysis capability to convert hydroxyl for esterification. These results suggested that the addition of PKSP to the biocomposites increased their degradation more than the addition of HNTs. The PKSP had better attraction for microbes to penetrate and initiate enzymatic attack and continue the degradation process. It was shown that the PVOH filled with PKS increased the degradability of the biocomposites compared to PVOH filled with HNTs.

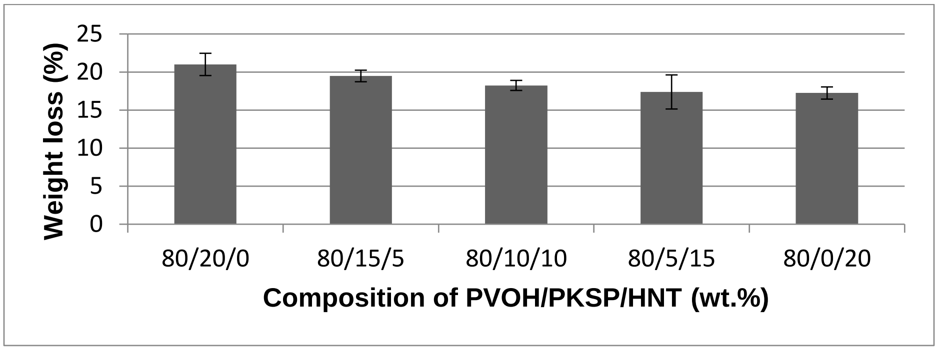

Fig. 12. Weight loss percentage after soil burial of PVOH/PKSP/HNTs biocomposites

The surface morphology of the biocomposites was examined by SEM after soil burial to study the surface degradation, as shown in Fig. 13. Incorporation of PKSP into PVOH enhanced the degradation compared to HNTS. From Fig. 12, a few hollows and cracks were observed on the surface of biocomposites with PKSP. As HNTs was added, no obvious crack or holes were seen on the surface. The PKSP was a natural filler from organic sources, where many microorganisms grew on the biocomposites filled with PKSP. To grow, these microorganisms attacked the biocomposites, which caused degradation to occur. These observations correlated with the weight loss of the biocomposites.

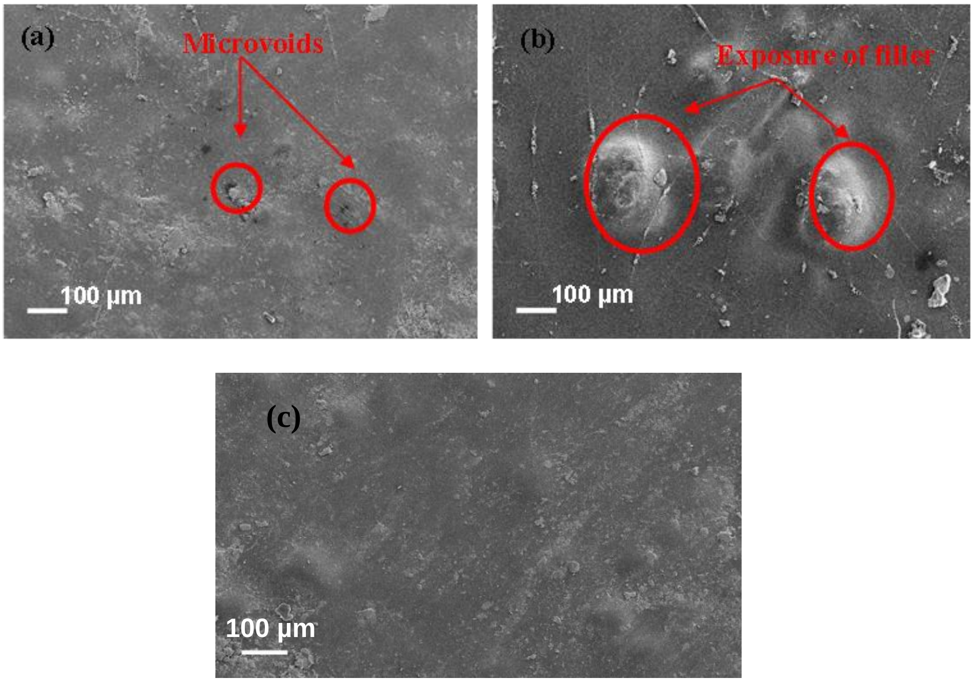

Fig. 13. Surface morphology of PVOH/PKSP/HNTs biocomposites with different compositions after soil burial: (a) 80/20/0, (b) 80/10/10, and (c) 80/0/20 (wt.%)

CONCLUSIONS

1. In summary, the polyvinyl alcohol/ palm kernel shell powder/ halloysite nanotubes (PVOH/PKSP/HNTs) biocomposite showed a higher tensile strength, tensile modulus, and elongation at break as the HNT content increased.
2. The scanning electron microscopy (SEM) study revealed that good dispersion of HNTs existed on the fractured surface of the biocomposites. This was due to the high specific surface area of HNTs, which provided more area for filler-matrix interaction.
3. Water absorption and water vapour transmission of biocomposites decreased with increased HNTs content. This was mainly due to less hydroxyl groups in HNTs compared to the natural filler, such as PKSP.
4. Moreover, the biodegradability properties tested in soil burial and natural weathering decreased with higher HNT content.

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