

Physical, Tensile, and Biodegradability Properties of Cross-linked Polyvinyl Alcohol/Palm Kernel Shell Powder Biocomposites

Nur Fazreen Alias,^a Hanafi Ismail,^{a,*} Mohamad Kahar Ab. Wahab,^b Santiagoo Ragunathan,^c Hosta Ardhyanta,^d and Sam Sung Ting^e

Polyvinyl alcohol/palm kernel shell powder biocomposites were prepared by using a solution casting method. To enhance the properties, the crosslinking agent glutaraldehyde (GA) was added to the composition. The effect of the crosslinking agent on the biocomposite was studied based on the change in the tensile properties, physical properties, and biodegradability. The optimum GA content was found to be 2 phr because the tensile properties tended to decrease with higher GA contents. The water absorption percentages and water vapour transmissibility decreased until the GA content reached 2 phr and then increased. It was found that the biodegradability of the film decreased when GA was added.

Keywords: Biocomposites; Crosslinking agent; Glutaraldehyde; Palm kernel shell; Polyvinyl alcohol

Contact information: a: School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia, b: School of Materials Engineering, Universiti Malaysia Perlis, 02600 Jejawi, Arau, Perlis, Malaysia, c: School of Environmental Engineering, Universiti Malaysia Perlis, 02600 Jejawi, Arau, Perlis, Malaysia, d: Materials and Metallurgical Engineering Department, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember, Surabaya 60111, Indonesia; e: School of Bioprocess Engineering, Universiti Malaysia Perlis, 02600 Jejawi, Arau, Perlis, Malaysia; *Corresponding author: ihanafi@usm.my

INTRODUCTION

Plastic materials usually create problems and pollution because of the long life cycle of these materials. As plastic materials accumulate in ecosystems, they cause many environmental hazards, such as the shortage of landfill space, air pollution caused by the open burning of plastic materials, and water pollution. Because of waste management problems, degradable polymeric materials have become one of the major focuses for researchers. A known green polymer is polyvinyl alcohol (PVOH), which is prepared by partial or complete hydrolysis of polyvinyl acetate with methanol or water. However, there are a few disadvantages associated with PVOH, such as the cost, process, and properties. Polyvinyl alcohol is relatively expensive compared with other polymers and has poor moisture barrier properties. To overcome the limitations and disadvantages of PVOH, different modifications can be carried out, such as blending with other polymers and incorporation a filler into the PVOH.

Composite materials are made up of at least two different components, which are commonly known as the matrix and filler. Additionally, the constituent phases must be chemically dissimilar and separated by a distinct interface. Many reinforcements are now available, and some are designed for a particular matrix system. Carbon, nanotubes, graphene, and aramid fibres are now used extensively in polymer matrix composites (Sapuan 2017). As man-made fillers are generally high cost and can be environmentally

hazardous, research has been done to develop biocomposites. Bio-based polymer composites are developed from renewable resources so they are environmentally friendly, do not contribute to the depletion of energy resources, and offer great energy and greenhouse gas emission savings (Avella *et al.* 2009).

Palm kernel shell (PKS) is one of the by-products from the palm oil industry and up to 4 million tons of PKS is produced annually (Husseinsyah *et al.* 2016). Currently, PKS is used as a biomass because it has a high calorific value. For example, in palm oil production, the mesocarp fibres and shells are used as energy sources in palm oil mills. In previous studies, PVOH/PKS powder (PKSP) biocomposites have been successfully prepared. However, the overall mechanical properties were not enhanced (Alias 2016). The major drawback of incorporating natural fibres into thermoplastic is the low compatibility. Most research has found that there is a reduction in the mechanical properties when natural fibres are incorporated into polymer matrices; therefore, this study was performed to improve the properties of PVOH/PKSP biocomposites.

The properties of a biocomposite can be enhanced by various methods, such as the addition of additives, use of a filler treatment, and optimising processing conditions. Commonly used additives act as plasticising and crosslinking agents. Essentially, the chemical crosslinking of linear polymers may provide feasible routes for the improvement of the mechanical and thermal stability. Crosslinking may also affect the barrier properties of a polymer, which is very important especially for packaging applications. Crosslinking is an efficient tool for decreasing moisture sensitivity of bio-based composites. Glutaraldehyde (GA) is one of the most commonly used crosslinking agents in polymeric materials. Several studies have been conducted on the usage of GA as a crosslinking agent (Parra *et al.* 2004; Abdeen 2011; Distantina *et al.* 2013; Yeng *et al.* 2013; Yan *et al.* 2015).

Based on the knowledge of the authors, no research has focused on the use of GA as a crosslinking agent in PVOH/PKSP biocomposites. Therefore, the objective of this work was to study the effect of the addition of GA on the properties of PVOH/PKSP biocomposites and to determine the optimum GA content that should be added to optimise the properties. The investigated properties were the tensile properties, water absorption, water vapour transmission (WVT), morphology, and biodegradability.

EXPERIMENTAL

Materials

The PVOH was supplied by Sigma-Aldrich (Kuala Lumpur, Malaysia) with an average molecular weight of 89000 g/mol to 98000 g/mol and density of 1.3 g/cm³. The PKS was supplied by Malpom Industries (Nibong Tebal, Malaysia). To prepare the PKSP, the shells were dried, ground using a mini crusher (Model C03-43B0, Chyun Tseh Industrial Co. Ltd, Taichung, Taiwan), and sieved to obtain a powder with an average particle size of 75 µm. Glutaraldehyde, glycerol, and tween 80 were supplied by Merck (Petaling Jaya, Malaysia), while hexamethylenetetramine was obtained from Sigma-Aldrich. All of the chemicals were of analytical grade.

Methods

Biocomposites preparation

The biocomposites were prepared using a solution casting method. A 200-mL portion of deionized water was measured and mixed with PVOH. Then, the mixture was

stirred for 10 min at 95 °C. The PKSP was added, which was followed by another 10 min of stirring. The additives were then added and the mixture was stirred for a further 10 min. The solution mixture was casted over glass plates and dried at room temperature overnight. The composite films were further dried in an oven at 70 °C for 2 h. The films were peeled off and kept in a sealed bag until further characterisation. The PVOH/PKSP biocomposites were prepared with five different amounts of GA (0 phr, 1 phr, 2 phr, 3 phr, and 4 phr) and the constant weight percent of PVOH/PKSP was 80 wt.%/20 wt.%.

Tensile properties

An Instron 3366 testing machine (Petaling Jaya, Malaysia) was used to evaluate the tensile properties of the composites. Five dumb-bell shaped samples (Type IV) prepared according to ASTM D638 (2008) were cut, which was followed by measuring the thickness along the test length using a dial thickness gauge (Model 7301, Mitutoyo, Kawasaki, Japan). The crosshead speed used was 50 mm/min and the load cell was 10 kN. The gauge length was set at 50 mm. The test was done at room temperature and the average value of five tests was calculated.

Chemical composition according to FTIR spectroscopy

Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer, Boston, USA) was used to analyse the functional groups in the composites. The characterising range was from 400 cm⁻¹ to 4000 cm⁻¹ with 16 scans to reduce noise and prevent overlapping of the spectra. The means of the peaks in the FTIR spectra were used for characterisation.

Morphological study

Field emission scanning electron microscopy (SEM) (Supra 35VP, ZEISS, Oberkochen, Germany) was used to study the morphological properties of the biocomposites. The morphological properties studied were the tensile fractured surface and the composite surface after the biodegradability tests, which were natural weathering and soil burial, respectively. Prior to examination, the films were mounted on aluminium stubs with carbon tape and sputter coated with a thin gold layer to avoid charging and poor resolution during examination using a Polaron SC 515 sputter coater (Bio-rad, Hercules, CA, USA).

Water absorption

Water absorption tests were performed by immersing the dried plastic films in distilled water at room temperature (25 °C). After 24 h, the moisture on the surface of the films was removed, and the weight of the films was recorded. The percentage of water absorption (W_a , %) of the plastic films was calculated with Eq. 1,

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

where W_e is the weight of the sample at equilibrium (g) and W_o is the initial dry weight of the sample (g).

Water vapour transmissibility

Gontard *et al.* (1993) modified ASTM E96-80 (1998), and this method was used to measure the WVT. A composite film sample was used to cover a container with 30 mL of distilled water and the initial weight was recorded. The containers were placed in a

desiccator at room temperature. The containers were weighed daily with an analytical balance until they achieved a constant weight. The WVT was then calculated using Eq. 2,

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

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

Natural weathering

Samples in the shape of a dumb-bell (Type IV) were subjected to a weathering test for 14 d (ASTM D638 2008). The test was conducted according to ASTM D1435 (1999). After 14 d, the samples were collected and cleaned. The changes to the dimensions, physical appearances, and weight were evaluated to determine the weathering resistance and degradation of the samples.

Soil burial

Dumb-bell shaped samples (Type IV) were buried in natural soil according to ASTM D638 (2008) at the School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia in Nibong Tebal, Malaysia for 14 d. After removing the dirt, the weights of the buried samples were measured and the weight changes were calculated.

RESULTS AND DISCUSSION

Tensile Properties

The tensile properties can provide an indication of the strength and elasticity of a film, which can be reflected by the tensile strength, elongation at break, and tensile modulus. Figure 1 shows the tensile strength for the PVOH/PKSP biocomposite films with different GA contents. It was found that the highest tensile strength was obtained when 2 phr of GA was incorporated into the film. The tensile strength decreased as higher amounts of GA were added.

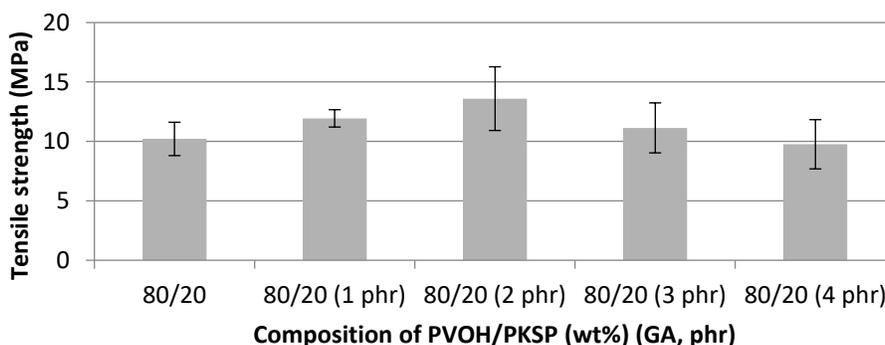


Fig. 1. Tensile strength of the PVOH/PKSP biocomposite films with different GA contents

When a low content of GA was added, there may not have been as high of a crosslinking degree because some of the aldehyde groups in the GA did not react. At the optimum content of GA, which was 2 phr, the GA promoted the formation of crosslinkages at both aldehyde sides. However, when more than 2 phr of GA was added, there was the tendency for over-crosslinking, which may have resulted in the deterioration of the

mechanical properties. Similar observations were made by Parra *et al.* (2004) and Ismail and Zaaba (2012), who found that the addition of a crosslinking agent over the optimum content reduced the tensile properties. Higher degrees of crosslinking in a biocomposite film reduces the chain mobility and ductility; therefore, the film was not able to restrain the stress applied during the tensile test and the strength was reduced (Yeng *et al.* 2015).

The elongation at break was determined as the point when a film broke under a tensile stress and it was expressed as the percentage of the final length before failure over the original length of sample. The elongation at break is an indication of the flexibility and stretchability. The effect of the addition of GA on the elongation at break of the PVOH/PKSP biocomposite films is shown in Fig. 2. The elongation at break decreased as the GA content in the films increased above 2 phr. The elongation at break of the film with 1 phr of GA was lower than that of the film with 2 phr of GA. This may have been because of insufficient crosslinking agent in the composite, which caused the interaction of the GA and polymer chain to be slightly lower. However, when 2 phr of GA was added, the GA was able to adequately crosslink the film and thus, improved the strength. Higher amounts of crosslinking agent may have led to over-crosslinking.

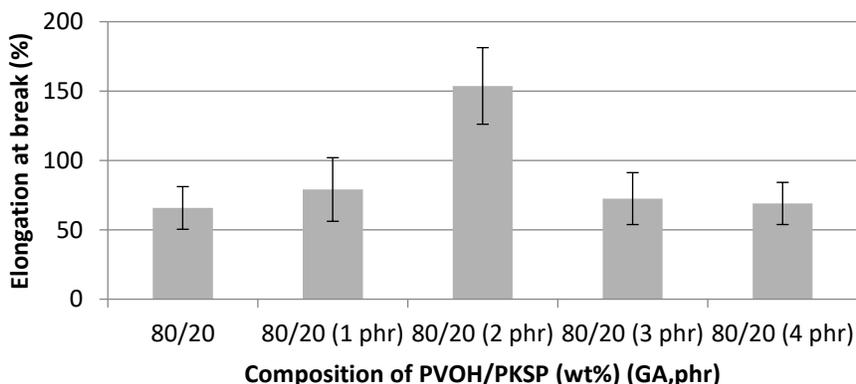


Fig. 2. Elongation at break of the PVOH/PKSP biocomposite films with different GA contents

Figure 3 shows the effect of the incorporation of GA into the PVOH/PKSP biocomposite films on the tensile modulus. The increase in the GA content caused an increase in the tensile modulus of the PVOH/PKSP films with up to 2 phr of GA. The tensile modulus measures the resistance of a material to deformation. The high tensile modulus obtained with 2 phr of GA was because of crosslinking in between the polymer chains. The crosslinks present in the structure prevented the molecules from sliding past each other under deformation, which made the film stiffer. The tensile modulus of the films decreased drastically with more than 2 phr of GA.

For the control sample (0 phr GA), the tensile modulus was lower than that of the film with the optimum GA content. This was because the absence of a crosslinking structure results in weaker intermolecular forces. Beyond 2 phr GA content, tensile modulus of biocomposites decreased. According to Krumova *et al.* (2000), the reduction in the properties can be explained as the result of competitive action of three factors during crosslinking, which are the diminution of the existing physical network caused by hydrogen bonding, formation of a chemical network, and introduction of flexible moieties caused by specific chemical structures.

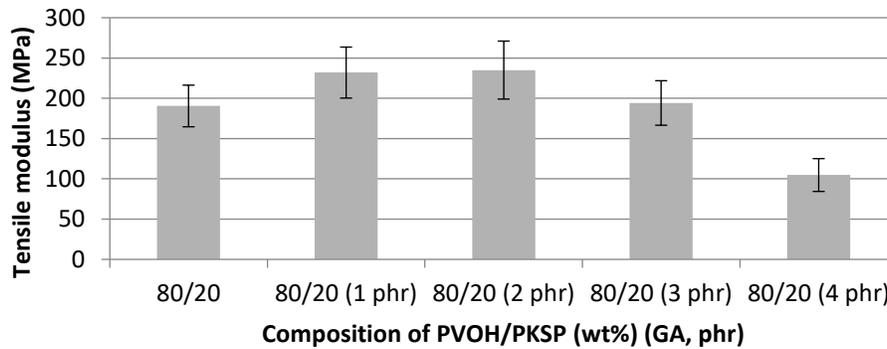


Fig. 3. Tensile modulus of the PVOH/PKSP biocomposite films with different GA contents

Fracture Surface Morphology

Scanning electron microscopy can provide diversified qualitative and quantitative information on many physical properties, including the size, morphology, surface texture, roughness, and chemical composition (Liu *et al.* 2010). Figure 4 shows the fractured surface of the PVOH/PKSP biocomposite films without GA and with 2 phr GA. When a crosslinking agent is added, less detachment is observed because the interfacial adhesion is stronger.

Crosslinking in a composite also reduces the polymer chain mobility. Therefore, the elongation at break decreased with the addition of GA. Plastic deformation was observed in the SEM images, which indicated more energy was required to fracture the film with GA compared with the film without GA. The SEM micrographs show the correlation to the obtained tensile properties.

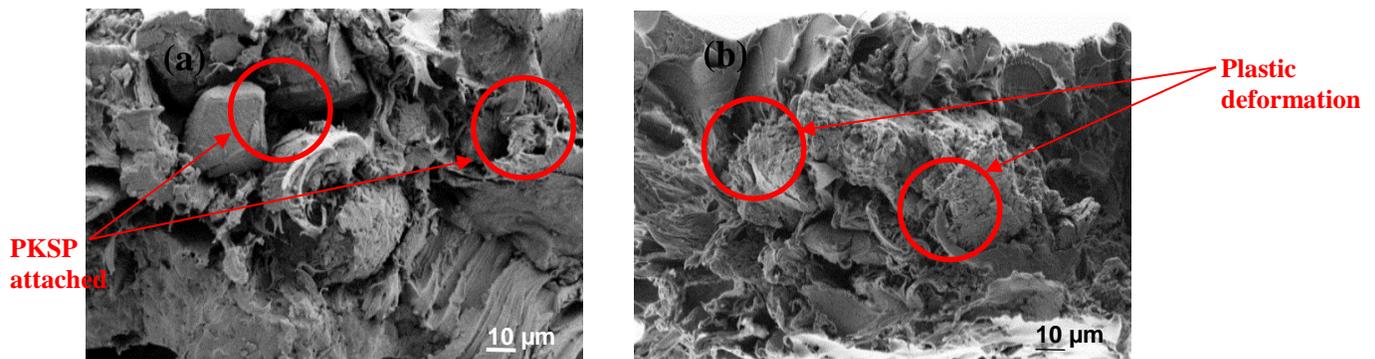


Fig. 4. Fracture surface morphology of the PVOH/PKSP biocomposite films with (a) 0 phr GA and (b) 2 phr GA

However, the excessive addition of the crosslinking agent tended to reduce the tensile properties of the PVOHPKSP films. Over-crosslinking may have stiffened the composite, which reduced the flexibility. By analysing the tensile properties, 2 phr GA was determined to be the optimum crosslinking agent amount.

At higher amounts of GA, the properties were reduced drastically. The fracture surface morphology of the film with 4 phr GA is shown in Fig. 5. The presence of voids was caused by pull out and detached PKSP. The filler pull-out indicated insufficient adhesion between the filler and matrix.

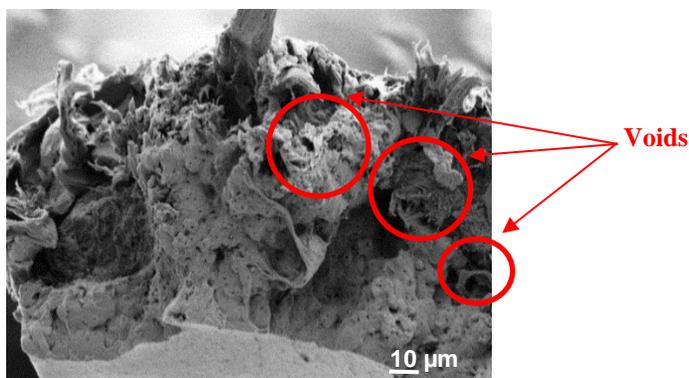


Fig. 5. Fracture surface morphology of the PVOH/PKSP biocomposite with 4 phr GA

Chemical Composition According to FTIR Spectroscopy

Fourier transform infrared spectroscopy uses the capacity of different absorption bands to characterise the interaction of polymers in a composite structure. Figure 6 shows the FTIR spectra of the PVOH/PKSP biocomposite films with GA. The broad band from 3600 cm^{-1} to 3100 cm^{-1} , which was due to the O-H stretching vibration in the PVOH, provided information concerning hydrogen bonds. Additionally, the FTIR absorption band around 1400 cm^{-1} was assigned to symmetric CH_2 bending vibrations.

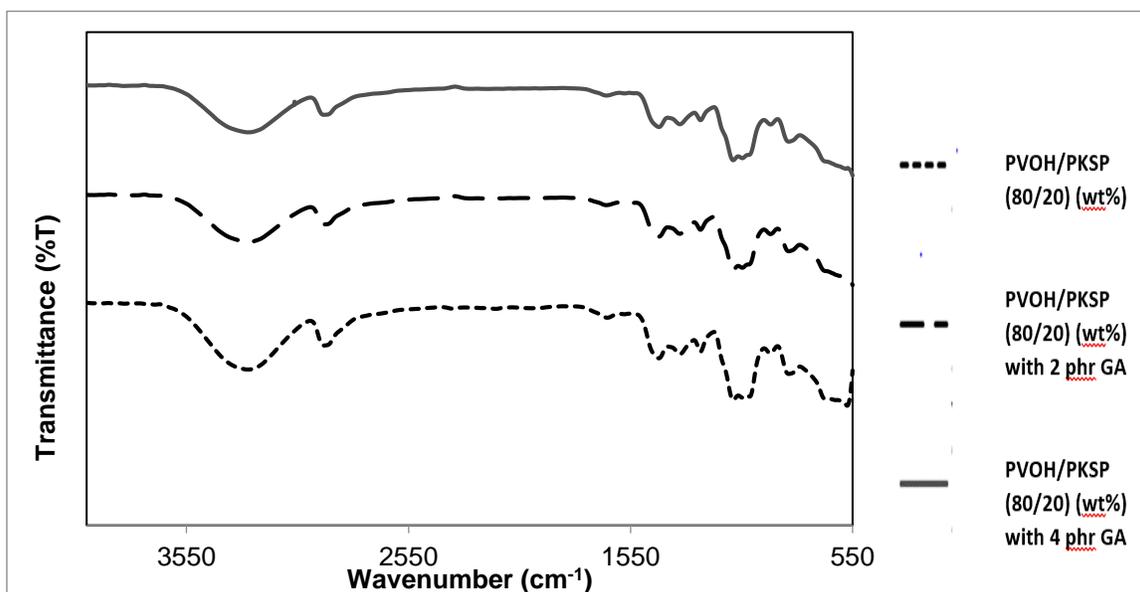


Fig. 6. FTIR spectra for the PVOH/PKSP biocomposite films with different GA contents

The absorption band from 2938.25 cm^{-1} to 2938.82 cm^{-1} was associated with the alkane group. This peak was produced by the stretching of C-H bonds in alkanes. This band is known as the crystallinity band, and an increase in the intensity reflects a change in the degree of crystallinity of the samples (Abdulkhani *et al.* 2013). Based on the changes seen in the tensile properties, 2 phr GA favourably affected the crosslinking in the polymer chain, which was associated with a higher film crystallinity. However, the intensities of the C-H band in both the biocomposites with GA and the neat biocomposite were only slightly different.

The peaks in the 1000 cm^{-1} to 1150 cm^{-1} region were attributed to C-O-H stretching vibrations, which occur in both antisymmetric and symmetric stretching vibrations. There was no occurrence of new peaks with the addition of GA that may have arisen because of changes to the functional groups. Glutaraldehyde is a bi-functional crosslinker, meaning that both aldehyde groups may react with the hydroxyl groups in PVOH; therefore, no additional functional groups were found.

By looking at all three FTIR spectra, it was observed that there were differences in the intensities of the peaks, such as the O-H bending peak. As GA was incorporated into the biocomposites, the hydroxyl groups were reduced. This was because of the utilisation of hydroxyl groups to form crosslinking in the biocomposites. The shifting of the wavenumber of the strong, broad O-H band indicated that there was an increase in intermolecular hydrogen bonding. A similar observation was made by Kim *et al.* (1994) when studying the kinetics of the crosslinking reaction of the PVOH membrane with GA.

Water Absorption

The most important properties for biodegradable materials are the water absorption capacity and degradability. Figure 7 shows the variation in the percentage of the water absorption of the PVOH/PKSP biocomposite films. The water absorption tended to decrease with an increase in the GA. The water absorption was the highest for the control sample because no crosslinking agent was used to counter the water-soluble characteristic of the PVOH, which was similar to what has been reported in earlier works on the water absorption properties of kenaf fibre-PVOH composites (Tan *et al.* 2014). The hydroxyl group is hydrophilic and caused a high amount of water absorption into the films. It was observed that only a slight decrease in the water absorption occurred with the addition of 1 phr GA.

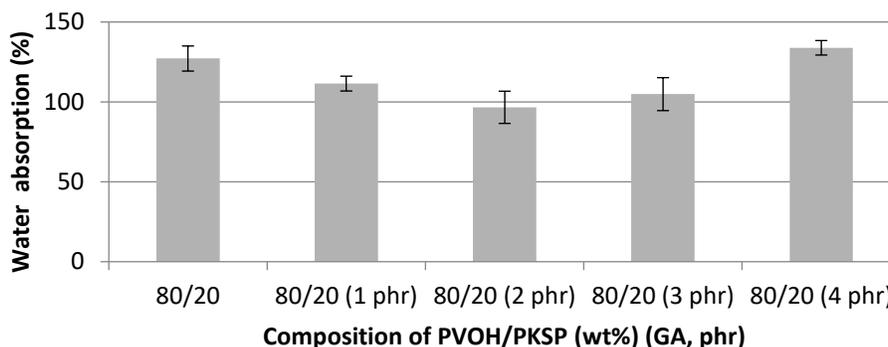


Fig. 7. Water absorption of the PVOH/PKSP biocomposite films with different GA contents

The decrease in the water absorption was more noticeable when 2 phr GA was added. The observed decrease was caused by the crosslinking effect of the GA and polymer, which caused lower water to penetration the film. This was because of the formation of a network structure by the crosslinking agent, which improved the water resistance and prevented water molecules from dissolving into the films. With the incorporation of GA, the immobilised phases increased and inclusion of water into the polymer was difficult. According to Ismail and Zaaba (2014), heterogeneous crosslinking with GA produced a more hydrophobic structure, where the network structure prevented water molecules from dissolving into the film and at the same time improved the water

resistance of the films. The water absorption of the films increased with more than 2 phr GA because of the network formed and the effectiveness of GA at higher contents was no longer optimal.

Water Vapour Transmission

The WVT is generally used to measure the capability of water vapour to penetrate through a material. Figure 8 shows the WVT of PVOH/PKSP biocomposite films with different GA contents. The addition of GA varied the WVT of the PVOH/PKSP biocomposite films. Initially as GA was added, the WVT decreased; however, when more than 2 phr GA was added, the WVT increased remarkably. Crosslinking in between the polymer chain tended to reduce the intermolecular space between the chain, and therefore resulted in the reduction of the WVT.

Incorporation of GA improved the interaction between the molecules, improved the cohesiveness of the biopolymer matrix, and decreased the water sensitivity (Taghizadeh and Sabouri 2013). For the PVOH/PKSP film with 2 phr GA, the reduction in the water permeability originated from the increased path tortuosity of the penetrant molecules, which are water molecules, and also enhanced the modulus of the polymer matrix in the composite films (Strawhecker and Manias 2006).

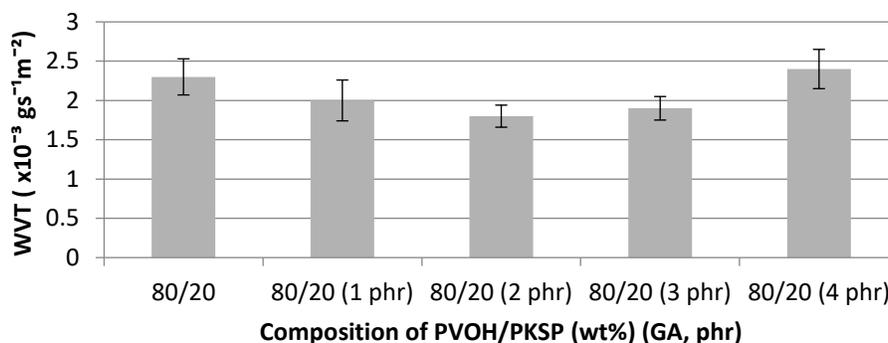


Fig. 8. WVT of the PVOH/PKSP biocomposite films with different GA contents

Natural Weathering

One of the most important characteristics related to ultraviolet degradation is the weight loss of the biocomposite, which generally indicates the breakage of polymeric bonds in the system (Rahmah *et al.* 2015). Figure 9 depicts the weight loss after weathering of the PVOH/PKSP biocomposite films with different amounts of GA. The weight loss varied with the GA content. The highest weight loss for the film occurred for the biocomposite film without GA. From previous research, PVOH/PKSP biocomposites without crosslinking agent showed higher biodegradability in both natural weathering and soil burial (Alias 2016). This was because there was no crosslinking in the structure, which caused degradation to occur more easily than in the films with a crosslinked structure. The lowest weight loss was exhibited by the film with 2 phr GA, which was considered the optimum amount of crosslinking agent. This implied that this amount of GA had a higher crosslinking formation, which made the film more resistant to degradation.

The weight loss increased slightly with more than 2 phr GA. This may have been because of an ineffectively crosslinked structure, as these films were generally saturated or over-crosslinked.

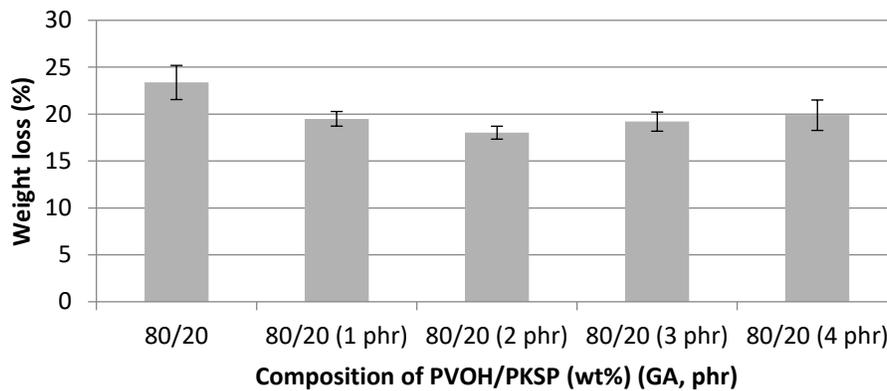


Fig. 9. Weight loss after weathering of the PVOH/PKSP biocomposite films with different GA contents

Figure 10 shows morphological images of the films after they were subjected to a natural weathering test for 14 d. The deterioration of the surface was the highest in the film without GA. Although agglomeration and exposure of the filler was evident in all of the film surfaces, the severity varied. At the optimum amount of GA (2 phr), the weight loss of the film was the lowest and this was proven in the SEM image, as the surface appeared to be smoother and fewer filler agglomerations were observed.

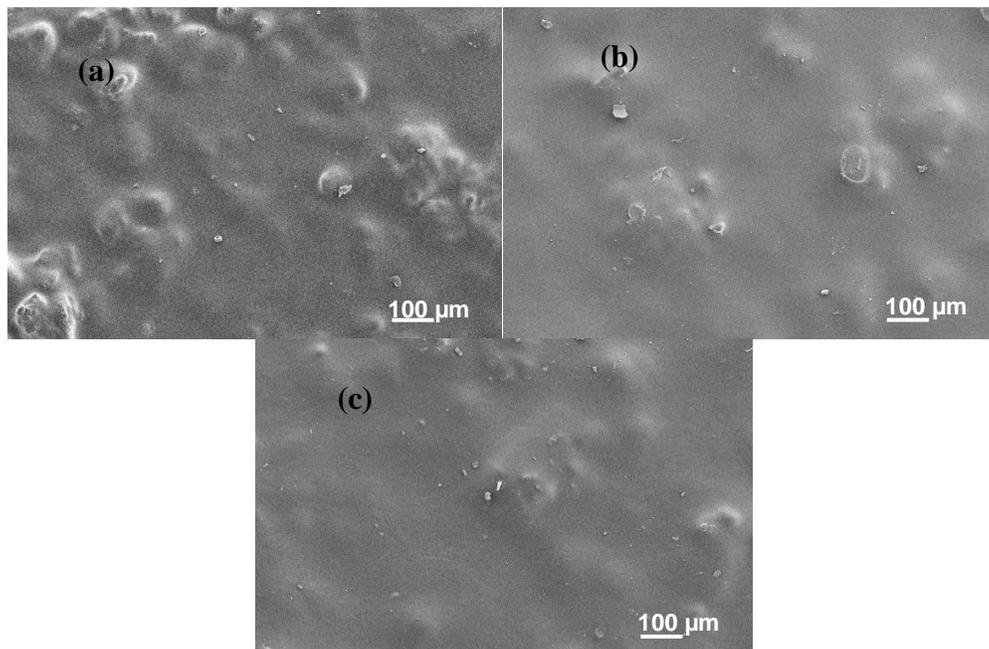


Fig. 10. Surface morphology of the PVOH/PKSP biocomposite films with different GA contents after natural weathering: (a) 0 phr GA, (b) 2 phr GA, and (c) 4 phr GA

Soil Burial

Soil burial is a method to evaluate the biodegradability of polymeric materials, in which the weight loss and properties are measured (Siddiqui *et al.* 2018). Kale *et al.* (2007) reported that PVOH is a biodegradable material because of its hydrolysability, where the molecular weight is reduced by hydrolysis depolymerisation. An important factor that influences the degradability of a polymer is the hydrophilicity because an increase in hydrophilicity facilitates biodegradation. While buried in soil, water diffuses into the film, which causes swelling and enhances biodegradation. Figure 11 shows the weight loss after soil burial for the PVOH/PKSP films with different contents of GA. The same trend as for the weight loss from natural weathering (Fig. 9) was observed.

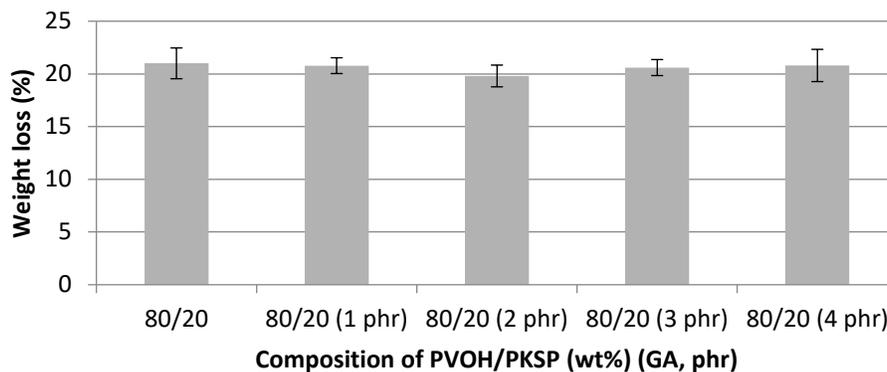


Fig. 11. Weight loss after soil burial for the PVOH/PKSP biocomposite films with different GA contents

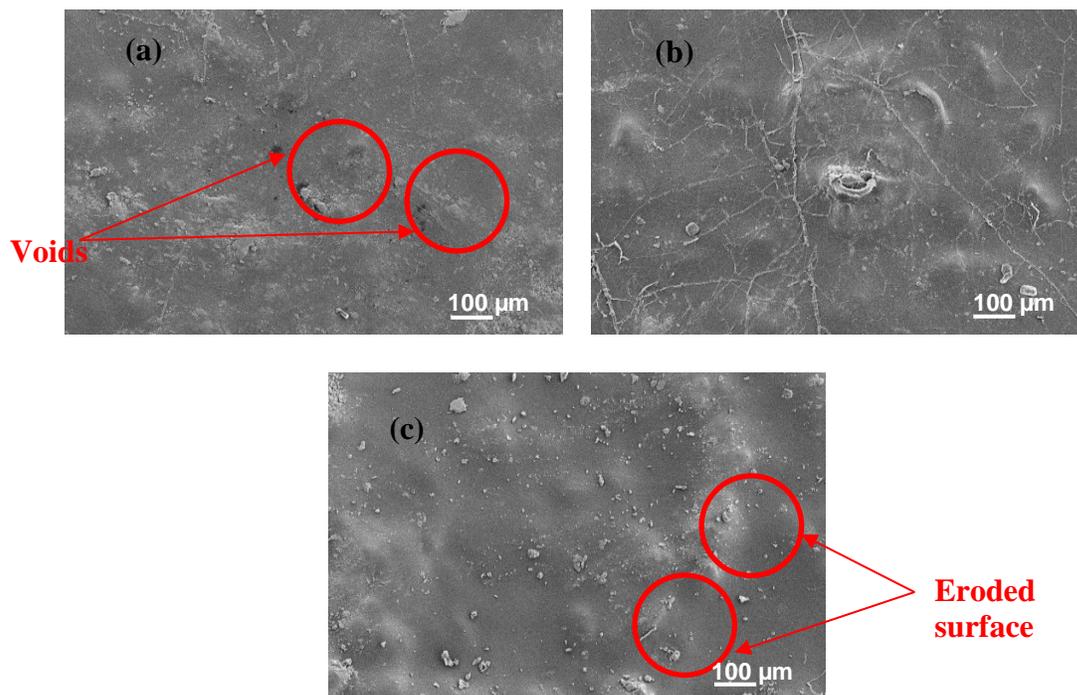


Fig. 12. Surface morphology of the PVOH/PKSP biocomposite films with different GA contents after soil burial: (a) 0 phr, (b) 2 phr, and (c) 4 phr

The main factor that was considered was the effect of the crosslinked network formed by the GA on the degradation. From the graph, the lowest weight loss was observed for the film with 2 phr GA, which proved the optimum crosslinking formation in that PVOH film. Additionally, the crosslink structure reduced the penetration of water into the film, which may have slowed down the degradation process.

In a soil burial test, the degradation rate of the polymeric materials is affected by various factors, such as the microbial activity, moisture level, temperature, and pH. The surface degradation after soil burial was examined with SEM and is illustrated in Fig. 12. For the film without the crosslinking agent, some hollows and tiny cracks were observed, which is shown in Fig. 12a. While buried in soil, the films underwent swelling and shrinkage depending on the humidity. This eventually caused cracking on the surface. When comparing the biocomposite films with the crosslinking agent, the surface morphology of the film with 4 phr GA showed a more eroded surface as the PKSP popped out of the surface. In contrast, the biocomposite film with 2 phr GA showed less surface erosion.

CONCLUSIONS

1. Glutaraldehyde enhanced the tensile properties of the polyvinyl alcohol/palm kernel shell (PVOH/PKSP) biocomposite films.
2. The tensile properties of the films increased with increasing content, up to 2 phr GA, and the tensile properties decreased when higher amounts of GA were added.
3. The physical properties were found to be greatly affected by the addition of the crosslinking agent. The PVOH/PKSP biocomposite film with 2 phr of GA showed the lowest water absorption and WVT.
4. It was found that the addition of a crosslinking agent tended to reduce the biodegradability. Crosslinking enhanced the network structure, which made it more difficult to degrade with weathering and soil burial.

ACKNOWLEDGEMENTS

The author N. F. Alias would like to thank the Ministry of Higher Education for providing financial support.

REFERENCES CITED

- Abdeen, Z. (2011). "Swelling and reswelling characteristics of cross-linked poly(vinyl alcohol)/chitosan hydrogel film," *J. Disper. Sci. Technol.* 32(9), 1337-1344.
DOI: 10.1080/01932691.2010.505869
- Abdulkhani, A., Marvast, E. H., Ashori, A., Hamzeh, Y., and Karimi, A. N. (2013). "Preparation of cellulose/polyvinyl alcohol biocomposite films using 1-n-butyl-3-methylimidazolium chloride," *Int. J. Biol. Macromol.* 62, 379-386.
DOI: 10.1016/j.ijbiomac.2013.08.050

- Alias, N. F. (2016). *Preparation and Properties of Polyvinyl Alcohol/Palm Kernel Shell Powder Biocomposite*, Master's Thesis, Universiti Sains Malaysia, Penang, Malaysia.
- ASTM D638 (2008). "Standard test method for tensile properties of plastics," American Society for Testing and Material, West Conshohocken, Pennsylvania, USA.
- ASTM D1435 (1999). "Standard practice for outdoor weathering of plastics," American Society for Testing and Material, West Conshohocken, Pennsylvania, USA.
- ASTM E96 (1998). "Standard test method for water vapor transmission of material," American Society for Testing and Material, West Conshohocken, Pennsylvania, USA.
- Avella, M., Buzarovska, A., Errico, M. E., Gentile, G., and Grozdanov, A. (2009). "Eco-challenges of bio-based polymer composites," *Materials* 2(3), 911-925.
DOI: 10.3390/ma2030911
- Distantina, S., Rochmadi, R., Fahrurrozi, M., and Wiratni, W. (2013). "Preparation and characterization of glutaraldehyde-crosslinked kappa carrageenan hydrogel," *Eng. J.-Canada* 17(3), 57-66. DOI: 10.4186/ej.2013.17.3.57
- Gontard, N., Guilbert, S., and Cuq, J.-L. (1993). "Water and glycerol as plasticizers affect mechanical and water vapor barrier properties of an edible wheat gluten film," *J. Food Sci.* 58(1), 206-211. DOI: 10.1111/j.1365-2621.1993.tb03246.x
- Husseinsyah, S., Chun, K. S., Hadi, A., and Ahmad, R. (2016). "Effect of filler loading and coconut oil coupling agent on properties of low-density polyethylene and palm kernel shell eco-composites," *J. Vinyl Addit. Techn.* 22(3), 200-205.
DOI: 10.1002/vnl.21423
- Ismail, H., and Zaaba, N. F. (2012). "Tensile properties, degradation behavior, and water absorption of sago starch plastic films," *J. Vinyl Addit. Techn.* 18(4), 235-240.
DOI: 10.1002/vnl.20300
- Ismail, H., and Zaaba, N. F. (2014). "The mechanical properties, water resistance and degradation behaviour of silica-filled sago starch/PVA plastic films," *J. Elastom. Plast.* 46(1), 96-109. DOI: 10.1177/0095244312462163
- Kale, G., Kijchavengkul, T., Auras, R., Rubino, M., Selke, S. E., and Singh, S. P. (2007). "Compostability of bioplastic packaging materials: An overview," *Macromol. Biosci.* 7(3), 255-277. DOI: 10.1002/mabi.200600168
- Kim, K.-J., Lee, S.-B., and Han, N.-W. (1994). "Kinetics of crosslinking reaction of PVA membrane with glutaraldehyde," *Korean J. Chem. Eng.* 11(1), 41-47.
DOI: 10.1007/BF02697513
- Krumova, M., López, D., Benavente, R., Mijangos, C., and Pereña, J. M. (2000). "Effect of crosslinking on the mechanical and thermal properties of poly(vinyl alcohol)," *Polymer* 41(26), 9265-9272. DOI: 10.1016/S0032-3861(00)00287-1
- Liu, F., Wu, J., Chen, K., and Xue, D. (2010). "Morphology study by using scanning electron microscopy," *Microscopy: Science, Technology, Applications and Education* 3, 1781-1792.
- Parra, D. F., Tadini, C. C., Ponce, P., and Lugão, A. B. (2004). "Mechanical properties and water vapor transmission in some blends of cassava starch edible films," *Carbohydr. Polym.* 58(4), 475-481. DOI: 10.1016/j.carbpol.2004.08.021
- Rahmah, M., Aziz, N. Z. A., Fahimi, M. M., and Farhan, M. (2015). "Weight loss degradation of hybrid blends LLDPE/starch/PVA upon exposure to UV light and soil burial," *Int. J. Biol. Biomol. Agri. Food Biotechnol. Eng.* 9(4), 413-416.
- Sapuan, S. M. (2017). *Composite Materials: Concurrent Engineering Approach*. Butterworth-Heinemann, Technology & Engineering, Oxford, UK.

- Siddiqui, M. W., Rahman, M. S., and Wani, A. A. (eds.). (2018). *Innovative Packaging of Fruits and Vegetables: Strategies for Safety and Quality Maintenance*. Apple Academic Press, New York, USA.
- Strawhecker, K., and Manias, E. (2006). "Nanocomposites based on water soluble polymers and unmodified smectite clays," in: *Polymer Nanocomposites*, Z.-Z. Yu (ed.), Woodhead Publishing, Sawston, UK, pp. 206-233.
- Taghizadeh, M. T., and Sabouri, N. (2013). "Biodegradation behaviors and water adsorption of poly(vinyl alcohol)/starch/carboxymethyl cellulose/clay nanocomposites," *Int. Nano Lett.* 3, 51-58. DOI: 10.1186/2228-5326-3-51
- Tan, B. K., Ching, Y. C., Gan, S. N., Ramesh, S., and Rahman, M. R. (2014). "Water absorption properties of kenaf fibre–poly(vinyl alcohol) composites," *Mater. Res. Innov.* 18(S6), 144-146. DOI: 10.1179/1432891714Z.000000000946
- Yan, E.-K., Cao, H.-L., Zhang, C.-Y., Lu, Q.-Q., Ye, Y.-J., He, J., Huang, L.-J., and Yin, D.-C. (2015). "Cross-linked protein crystals by glutaraldehyde and their applications," *RSC Adv.* 5(33), 26163-26174. DOI: 10.1039/C5RA01722J
- Yeng, C. M., Husseinsyah, S., and Ting, S. S. (2013). "Chitosan/corn cob biocomposite films by cross-linking with glutaraldehyde," *BioResources* 8(2), 2910-2923. DOI: 10.15376/biores.8.2.2910-2923
- Yeng, C. M., Husseinsyah, S., and Ting, S. S. (2015). "Effect of cross-linking agent on tensile properties of chitosan/corn cob biocomposite films," *Polym.-Plast. Technol.* 54(3), 270-275. DOI: 10.1080/03602559.2014.977090

Article submitted: April 16, 2018; Peer review completed: May 24, 2018; Revised version received and accepted: June 1, 2018; Published: June 8, 2018.
DOI: 10.15376/biores.13.3.5711-5724