

## 충전재 하중이 폴리비닐알코올 및 에그쉘분말 바이오복합체의 특성에 미치는 영향

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## Influence of Filler Loading on Properties of Polyvinyl Alcohol and Eggshell Powder Biocomposite

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**Abstract:** Biocomposite films made up of polyvinyl alcohol (PVA) and eggshell powder (ESP) were prepared by solution casting method. The physical properties, mechanical properties and biodegradability of biocomposites were studied based on various ESP loading (0 to 40 wt%). From raw material characterization, ESP was found to have similar composition to the calcium carbonate, which is widely used as filler in polymer composites. It was found that the tensile properties decreased with increasing ESP loading, attributed from poor interfacial adhesion and ESP agglomeration as proven by field emission scanning electron microscope (FE-SEM) micrographs. Water absorption and water vapour transmission were enhanced with addition of ESP. The biocomposite shows higher biodegradability in both soil burial and natural weathering with increasing ESP loading.

**Keywords:** polyvinyl alcohol, eggshell powder, biocomposite, biodegradability, solution casting.

### Introduction

Over the year, polymer usage is growing wider in almost every sector due to the comparable properties, variability, and lightweight of polymer. However, commodity polymers such as polyethylene and polycarbonate persist for a long time after disposal, causing accumulation of solid waste of these materials. The inertness and long life time span of synthetic, petroleum based polymers are gaining environmental concern. Therefore, studies on biodegradable polymeric materials have been one of the interesting topics among researches and industries. Biodegradable polymers are classified into two major groups, according to the origin, which is from natural resources and from petroleum based. Even though the polymers are derived from crude oil, the chemical structure of the polymer affects biodegradability. For example, ester bonds in polycaprolactone and hydroxyl groups in polyvinyl alcohol is sensitive to hydrolysis, making them biodegradable.<sup>1,2</sup>

Polyvinyl alcohol (PVA) is one of the petrochemical thermoplastic, that is biodegradable due to the hydrophilic characteristic.<sup>3,4</sup> PVA is commercially produced via hydrolysis of polyvinyl acetate (PVAc) and mostly used in textile, coatings, packaging, and printing industries.<sup>5</sup> PVA offers several advantages such as good flexibility, excellent mechanical properties, transparency, nontoxicity and biocompatibility.<sup>6-8</sup> Researches have been conducted to produce biocomposite utilizing biodegradable polymer as the matrix. This is due to the cost of biodegradable polymers are slightly higher compare to commodity plastics and usually the properties need to be tailored to meet the customers' need. Several types of filler can be used in biocomposite such as natural fiber from plants, animals, and mineral filler.

Growing demands in global poultry have significant impact on the environment as the pollution and production of by-products are also increasing.<sup>9</sup> One of the products in poultry is eggshell, which has been reported to be produced almost 72 million tons currently.<sup>10</sup> The potential use of waste eggshell as bio-filler in polymer composite is widely studied by researchers.<sup>11-14</sup> The shell contributes to 11% of the total weight, thus

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eggshell waste is nearly 7.92 million tons.<sup>15</sup> Eggshell is composed of almost 95 wt% mineral phase of calcium carbonate and 5 wt% organic materials.<sup>16,17</sup> Therefore, eggshell has high potential to be used as filler on polymer composite as another alternative to commercial calcium carbonate.

Hassan and co-workers studied the value-added biopolymer nanocomposites from waste eggshell-based calcium carbonate nanocomposite as filler, and it was found that addition of 2 wt% filler enhanced the flexural strength and thermal stability.<sup>18</sup> Besides that, Sutapurn *et al.* utilized calcined eggshell powder (ESP) as filler in high density polyethylene. The mechanical properties such as ultimate stress and young modulus increased, but yield strength and thermal resistance were not improved. In order to further improve the properties, maleic anhydride was grafted on HDPE.<sup>19</sup> Murugan *et al.* investigated the effect of filler loading on structure and properties of PVAc/chicken ESP composites. The decomposition temperature increased with addition of filler. However, tensile strength and elongation at break decreased.<sup>20</sup>

This work aims to produce a new biocomposite made up from ESP and PVA. The ESP will act as a natural filler in the polymer composite, which will affect its properties and also contribute to cost reduction. The effect of ESP loading is studied based on the mechanical properties, physical properties, and biodegradability of the biocomposite.

## Experimental

**Materials.** Polyvinyl alcohol (PVA) with average molecular weight of 7200 g/mol was purchased from Sigma- Aldrich (M) Sdn. Bhd (Kuala Lumpur, Malaysia). Eggshell was collected at Kafe Staf, Universiti Sains Malaysia (Penang, Malaysia), followed by cleaning and drying process. Merck (M) Sdn. Bhd (Selangor, Malaysia) supplied glycerol and Tween80, which act as plasticizer and non-ionic surfactant. Hexamethylenete-

tramine (HMTA) is a hardening reagent with average molecular weight of 140.19 g/mol was applied by Sigma-Aldrich (M) Sdn. Bhd. De-ionized water is used as solvent. All of the chemicals were analytical grade reagents.

**Preparation of Biocomposite.** Prior to biocomposite preparation, eggshell powder (ESP) was obtained via grinding using mini crusher from Chyun Tseh Industrial Co. Ltd (Taiwan), followed by sieving. After that, ESP was dried for 24 h at 70 °C and was kept in dessicator until further use. PVA/ESP biocomposite was prepared by solution casting method accordingly to formulation in Table 1. 200 mL deionized water was used to dissolved PVA and stirred for 10 min at 95 °C. ESP was added, followed by another 10 min of stirring. The additives were added and stirring continued for another 10 min to ensure homogenous mixture. The solution was casted over glass plates and were dried for 24 h at room temperature. The biocomposite was further dried at 70 °C for 2 h in oven. Biocomposite film with thickness of 0.15 mm was peeled off and kept for futher testing.

**Characterization of Biocomposite. Morphological Study:** Field emission scanning electron microscopy (FE-SEM) was used to study the morphology of ESP and surface morphology of biocomposite. Prior to observation, the samples was mounted on aluminium stub with carbon tape, followed by thin gold sputtering to prevent charging and poor resolution.

**Fourier-transform Infrared Spectroscopy (FTIR) Analysis:** The functional groups present in ESP and PVA/ESP biocomposites were analyzed using Fourier transform infrared spectroscopy (FTIR). The scanning was carried out 16 times of range from 400 to 4000 cm<sup>-1</sup>. The chemical structure was determined by the means of peaks in FTIR spectrum.

**Density and Void Measurement:** The density measurement of each biocomposite composition was carried out using Precisa Gravimetric Type 220A, Series 320 XB (Dietikon, Switzerland). The theoretical density was calculated using eq.

**Table 1. Formulation for PVA/ESP Biocomposites**

Biocomposite composition	PVA			ESP		Glycerol	Tween 80	HMTA
	weight%	Actual weight (g)	weight%	Actual weight (g)				
100/0	100	10	0	0	1.5	0.1	0.6	
90/10	90	9	10	1	1.5	0.1	0.6	
80/20	80	8	20	2	1.5	0.1	0.6	
70/30	70	7	30	3	1.5	0.1	0.6	
60/40	60	6	40	4	1.5	0.1	0.6	

(1). By comparing the actual density and theoretical density, the void content was calculated using eq. (2) according to ASTM D2734.

$$\rho_T = \frac{100}{\frac{\text{wt\% of matrix}}{\rho \text{ of matrix}} - \frac{\text{wt\% of filler}}{\rho \text{ of filler}}} \quad (1)$$

$$\text{Void} = \frac{\rho_T - \rho_E}{\rho_E} \quad (2)$$

where wt% is the weight percentage,  $\rho_T$  is the theoretical density,  $\rho_E$  is the experimental density.

**Tensile Properties:** The biocomposite film was cut into dumbbell-shaped (ASTM D638) and the average thickness of film was measured. Tensile properties were evaluated by Instron 3366 testing machine at crosshead speed of 50 mm/min and 10 kN load cell at room temperature. The gauge length was set at 50 mm. The test was repeated for five samples for each composition. The average value of tensile strength, elongation at break and tensile modulus were calculated respectively.

**Water Absorption:** Water absorption test was performed accordingly to ASTM D570. After recording the initial weight, the biocomposite films were immersed in distilled water at room temperature for 24 h. The water on the film surface was wiped and the weight was measured. Water absorption percentage of biocomposite film was calculated as:

$$W(\%) = \left[ \frac{W_f - W_i}{W_i} \right] \times 100 \quad (3)$$

where  $W_f$  is the final weight and  $W_i$  is the initial weight.

**Water Vapour Transmissibility (WVT) Test:** WVT was measured according to ASTM E96-80 (ASTM 1998), modified by Gontard *et al.*<sup>21</sup> 30 mL distilled water was filled in a container, followed by sealing the container with biocomposite film. The changes in weight of the set up was measured and recorded daily until constant weight was achieved. Five containers were prepared for each biocomposite composition. The WVT was calculated by:

$$WVT = \left( \frac{G}{t} \right) / A \quad (4)$$

where  $G$  is the changes in weight,  $t$  of time and  $A$  is the area of the container sealed by biocomposite film.

**Biodegradability Test via Soil Burial and Natural Weathering:** Biodegradability of PVA/ESP biocomposite was determined via weight loss percentage after 14 days of soil burial and weathering (ASTM D1425) respectively. The samples were cut into dumbbell shape Type IV according to ASTM D882 and the initial weight was recorded. The tests were carried out at School of Material and Mineral Resources Engineering, Universiti Sains Malaysia, Nibong Tebal, Penang.

## Results and Discussion

**Characterization of Eggshell Powder.** Figure 1 shows the SEM micrograph of eggshell powder (ESP) at a magnification of 300X. From the micrograph, the shape of ESP was seen to be irregular and the particle size varies from 7.5 to 29.8  $\mu\text{m}$ . Apparently, the agglomeration of ESP was found.

FTIR spectroscopy was used to seek evidence of the functional group presence in ESP. Figure 2 shows the spectrum of ESP. FTIR spectrum for ESP showed the three characteristic absorption bands in the fingerprint region. The strong broad absorption band at 1399.11  $\text{cm}^{-1}$  is assigned to the OH bending vibrations, which is typically in the range from 1440-1395  $\text{cm}^{-1}$ . On the other hand, strong and sharp peaks at 873.54 and 712.70  $\text{cm}^{-1}$  indicate the existence of C-O absorption band, which can be assigned to  $\text{CO}_3$  vibrations in ESP. The IR characteristics of  $\text{CO}_3$  observed is due to the occurrence of calcium carbonate composition. A similar observation was obtained from previous work by Intharapat and co-workers.<sup>22</sup>

**Density and Void Content Measurement.** Density is one of the crucial properties for polymeric composite materials based on the properties-cost relation. Table 2 shows the the-

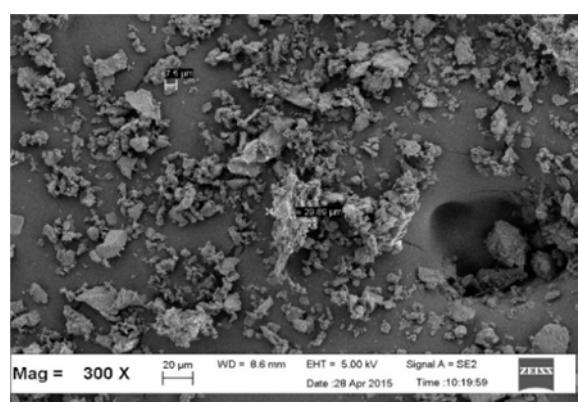


Figure 1. SEM micrograph of ESP.

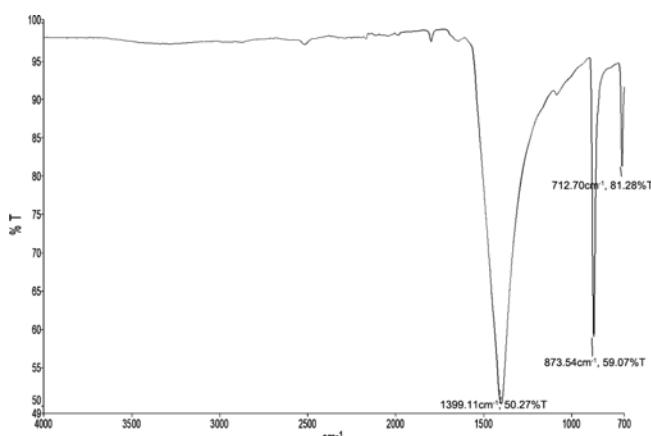


Figure 2. FTIR spectrum for ESP.

Table 2. Density and Void Content of Biocomposite

Composition (PVA/ESP)	Theoretical density, $\rho_T$ (g/cm³)	Experimental density, $\rho_E$ (g/cm³)	Void content
100/0	1.1900	1.189	0.0008
90/10	1.1628	1.119	0.0377
80/20	1.1356	1.073	0.0551
70/30	1.1084	1.032	0.0689
60/40	1.0812	1.001	0.0741

oretical density, experimental density, and the void content of biocomposite at different compositions. Three factors affecting the density of composite are the interfacial bonding, relative densities, and weight fraction of filler and matrix respectively. Theoretical density is solely based on the rule of mixture concept neglecting the flaws within composite. Theoretical density of PVA/ESP biocomposite decreased as the filler loading increased because density of ESP is lower than PVA. Decrement in experimental density an observed as the ESP loading increased. Thus, resulted to increment of void content. Generally, the void in the composite is due to poor interfacial adhesion between filler and matrix and also the agglomeration in the filler, resulted in a bigger gap between the agglomerates and matrix.

**Tensile Properties.** Tensile properties of polymer can be characterized using quantities such as modulus of elasticity, stiffness, elongation, ultimate tensile strength, toughness, and creep. Figure 3 shows the variation of tensile strength with filler content. It was observed that the tensile strength of film exhibited significant decrement with increasing filler content. The decreasing tensile strength may be due to poor interfacial adhesion and distribution of filler within the matrix, thus pro-

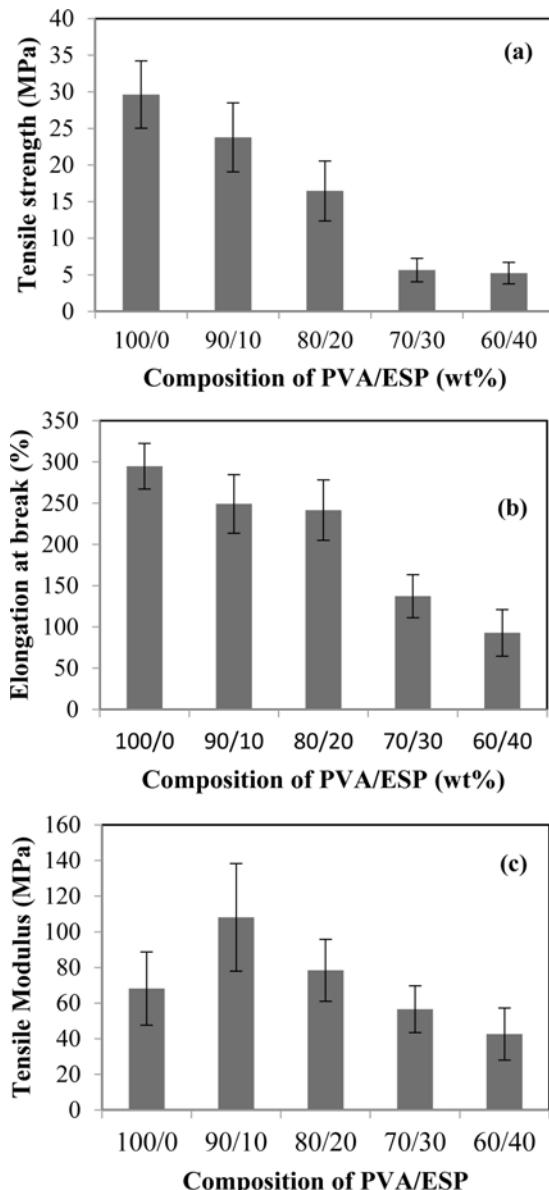


Figure 3. (a) Tensile strength of PVA/ESP biocomposites; (b) elongation at break of PVA/ESP biocomposite; (c) tensile modulus of PVA/ESP biocomposite at different compositions.

viding poor reinforcement. The strength of particulate filled polymer composites depends to a great extent on the interfacial adhesion between the matrix and the filler which facilitate the transfer of a small section of stress to filler particle during deformation.<sup>23</sup>

According to Morreale *et al.*, better stress transfer from matrix to filler can be achieved by strong adhesion between matrix and filler interface, in which leads to a higher tensile strength.<sup>24</sup> Besides that, the distribution of filler at higher filler

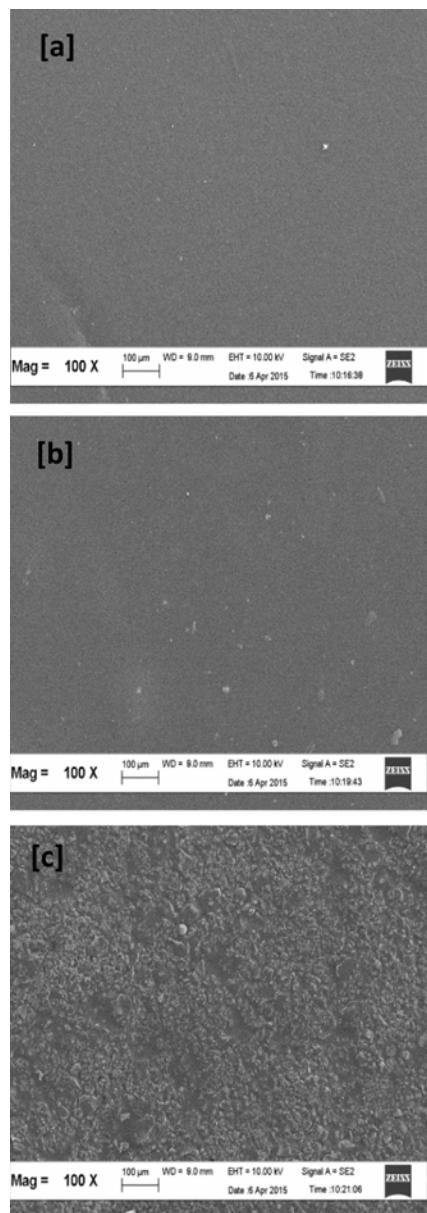
content may become poor, and this caused the stress in the continuous phase to increase and promote poor tensile strength. At lower ESP loading, the distribution is expected to be good and homogenous. The homogeneity could be declining with increasing filler loading. The decrement in tensile strength at higher ESP loading can be explained by the imperfect distribution of filler through the polymer matrix and poor adhesion between matrix and filler. This observation was due to the formation of agglomeration in biocomposite film with heterogeneous surface.<sup>25</sup>

Elongation at the break as seen in Figure 3(b) showed gradual decrement as filler content increased. This is the indication that the filler is incapable of supporting the stress transfer from filler to matrix. The incorporation of filler within PVA matrix decreased the elasticity of the biocomposite. Higher filler loading in PVA matrix resulted in the stiffening and hardening of the film. This reduced its resilience and toughness, and led to lower elongation at the break of the composites.<sup>26</sup>

Figure 3(c) shows the tensile modulus of biocomposite at different ESP loading. Initially, as ESP was incorporated into the PVA, the tensile modulus increased. The increased modulus corresponds to more filler where its intrinsic properties exhibit high stiffness compared to polymeric material.<sup>27</sup> Modulus increased because of the stiffening effect of the filler.<sup>28</sup> The tensile modulus decreased at higher ESP loading was due to poor resistance of material to deformation. This was because at high filler content the film was unable to withstand greater loads. In other words, the applied stress failed to transfer throughout the samples effectively due to poor dispersion and interfacial adhesion.

**Morphological Study.** Morphological analysis using SEM clearly shows difference in the surface morphology of the neat PVA film and PVA/ESP biocomposite film. As shown in Figure 4, neat PVA film contained voids as the result of the entrapment of bubbles in the film during casting. At ESP loading of 20 wt%, ESP distributed more uniformly within PVA matrix as compared to higher filler loading. However, some ESP can be seen on the film surface, which might be due to its larger size. Poor interaction between ESP and PVA will cause poor stress transfer from matrix to filler. Therefore, the tensile properties of PVA with addition of ESP eventually decreased and lower compared to neat PVA.

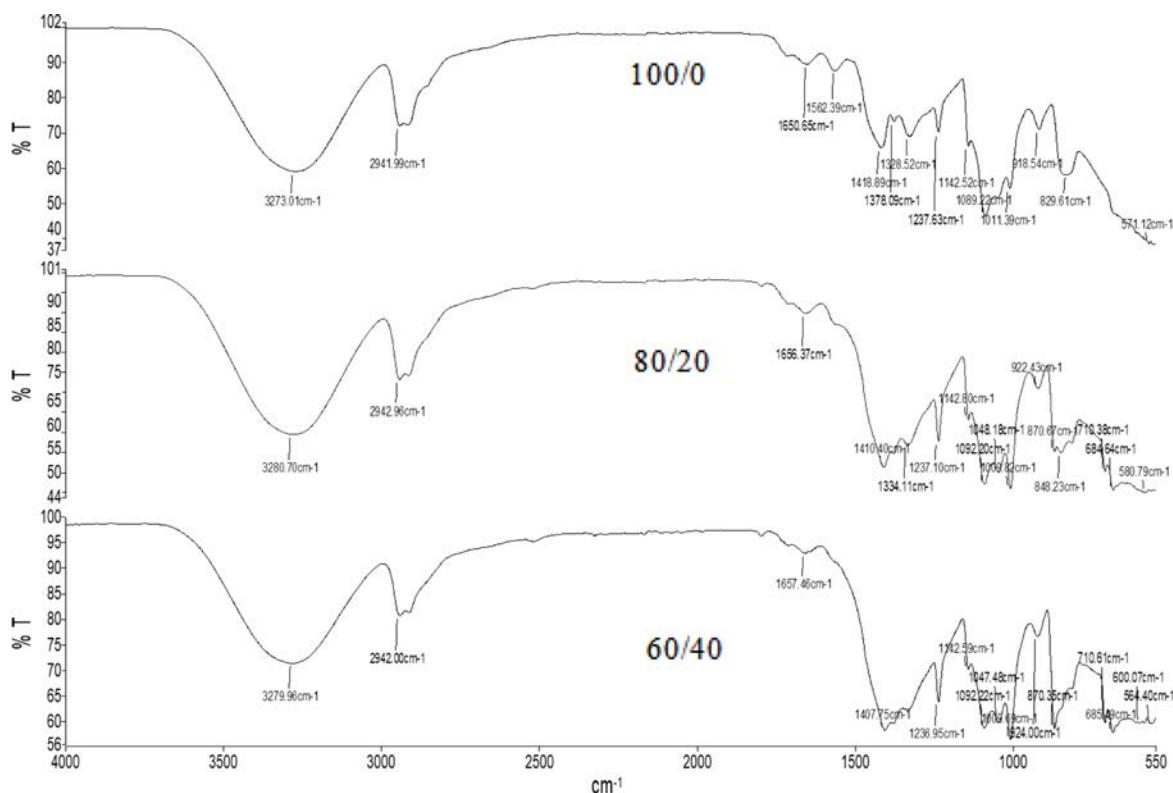
Adding up to 40% ESP caused the surface to become rougher and more brittle. The agglomeration of ESP was clearly observed at the loading of 40 wt%. As the filler loading increases, the formation of the agglomeration was found due to



**Figure 4.** Surface morphology of (a) neat PVA; (b) 80/20 PVA/ESP biocomposite; (c) 60/40 PVA/ESP biocomposite.

the difficulties of achieving a homogenous dispersion of filler at high filler loading. This may explain the decrement in mechanical properties with the incorporation of ESP.

**FTIR Analysis.** Figure 5 shows the FTIR spectrum of neat PVA, 80/20 PVA/ESP and 60/40 PVA/ESP films. It is showed that various absorption bands are observed. For neat PVA film, the significant peak of intensity around  $3273.01\text{ cm}^{-1}$ , is assigned to hydrogen bond from alcohols or phenols. The peak is very broad due to the strong hydrogen bonding and thus obscures other bands in this region. The absorption band at



**Figure 5.** FTIR spectrum of PVA/ESP blend for 100/0 wt%, 80/20 wt %, and 60/40 wt% composition.

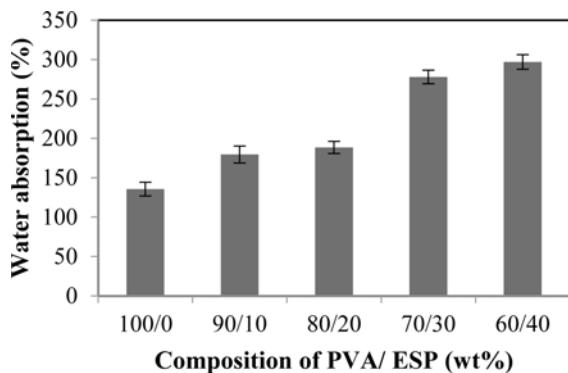
2941.99 cm<sup>-1</sup> was associated with the alkane group. The peak was produced as the C-H bonds stretch.

Bending vibration of C-H also can be found at peak of 1650.65 cm<sup>-1</sup>. At the fingerprint region, the bending vibration for O-H was found at 1418.89 cm<sup>-1</sup>. The C-O absorption bands can also be found at 1142.52 and 1089.22 cm<sup>-1</sup>. These bands generally used as the conformation of alcohol group in the sample. Besides that, there were several peaks that account for the presence of CH<sub>3</sub> scissor vibration in the range of 1260–1050 cm<sup>-1</sup>. The peaks from 600 to 900 cm<sup>-1</sup> were mainly due to the rocking vibration of C-H bond.

Throughout the series, it was observed that the peak of O-H bending vibration was less intense for PVA/ESP blend than the neat PVA. This was due to the fact that weight percentage of PVA decreased, causing the amount of alcohol group to reduce. In comparison to the neat PVA, PVA/ESP films show few additional peaks in the fingerprint region. The additional peaks were at 870.67 cm<sup>-1</sup> for 80/20 blend and 870.35 cm<sup>-1</sup> for 60/40 blend. These peaks were attributed to the CO<sub>3</sub> vibrations in ESP. The IR characteristics of CO<sub>3</sub> observed were due to the occurrence of calcium carbonate composition in ESP.

**Water Absorption.** Figure 6 shows the variation of per-

centage of water absorption with different filler contents. It was observed that the film with higher ESP content has better water absorbing capacity. As the filler content increased, the formation of agglomeration increased due to the difficulties of achieving a homogenous dispersion of filler at higher filler loading content within the matrix. The agglomeration of filler in film increased the water absorption of PVA film. The PVA/ESP biocomposite films demonstrated higher water uptake than pure PVA film. This was due to poor interaction between ESP and the matrix that increased the water absorption by film. The film was not well covered by the PVA matrix, and this will increase the freely available hydroxyl groups and exposed more water-binding site. This is in agreement with work earlier on mechanical and water absorption properties of PVA/sago starch pith waste composite.<sup>29</sup> Besides that, the presence of OH groups in ESP also attributed to higher water uptake due to the formation of hydrogen bonding. As higher ESP loading was incorporated into the films, the more hydroxyl group will present, therefore increased the water absorptivity. On the other hand, the increment of water absorption also can be related to the void content of the biocomposite. At high ESP loading, the void content increased, therefore allowing more water mol-

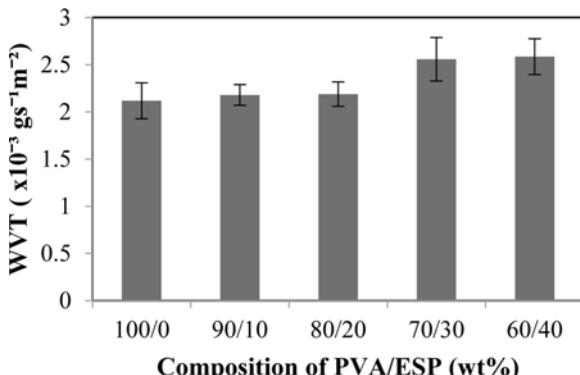


**Figure 6.** Water absorption percentage of PVA/ESP biocomposite at different compositions.

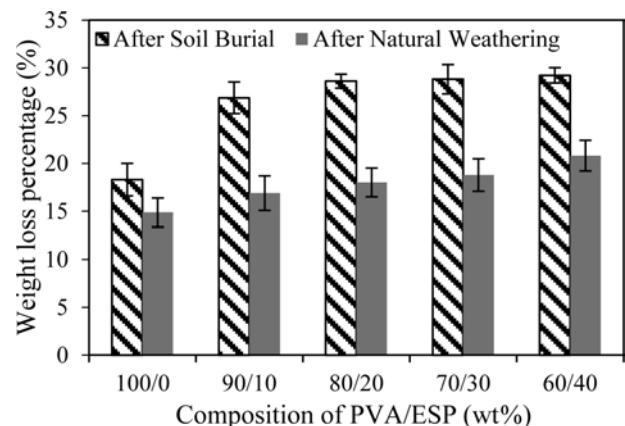
molecules to diffuse into the biocomposite films.

**Water Vapour Transmission (WVT).** Figure 7 signifies the effect of ESP loading on the water vapour transmissibility of PVA/ESP films. It is clearly shown that the WVT increased with increasing ESP loading. The ability to transport moisture over a film can be favourable property in some applications such as in food waste collection system and garden waste sacks. High WVT will avoid fermentation and bad smell, mould and leachate. The increment of WVT at higher filler loading may be due to the fact that the water sensitivity of the films increased due to more hydroxyl groups present. WVT is highly affected by the diffusivity and solubility of water molecules in the film matrix.<sup>30</sup> The hydrophilic nature of PVA and ESP enhanced the absorption of water molecules and at the same time increased the WVT. Besides that, higher void content for composite with high ESP loading also contributed to more space for water vapour to penetrate the film.

**Biodegradability Test via Natural Weathering and Soil Burial.** Figure 8 shows the dependence of weight loss after



**Figure 7.** Water vapour transmission of PVA/ESP biocomposite at different composition.



**Figure 8.** Weight loss of PVA/ESP biocomposite at different composition after soil burial and natural weathering test.

biodegradation on the composition of PVA/ESP film. The increasing ESP loading leads to the increment of weight loss after exposure to natural weathering tests. For PVA, the degradation mechanism is unusual as it occurs randomly along the PVA polymer chain. Typically, many other polymers degrade from chain ends. Several mechanisms may participate in the degradation of PVA such as oxidation of hydroxyl groups to ketone groups and formation of acetic acid. The alcohols and ketones may further metabolize to water and carbon dioxide.<sup>31</sup> The degradation was much more pronounced when ESP loading was high. It has been proven that the incorporation of ESP with PVA increased the degradability of PVA biocomposite films.

In comparison to the neat PVA film, the film incorporated with ESP shows higher weight loss after being buried for fourteen days. As the ESP loading increased, the weight loss for the film also increased. The same result is observed for the films after subjected to natural weathering. This shows that the incorporation of ESP in PVA film improves the film biodegradability. The result obtained can be associated with the organic compounds in the ESP and make it vulnerable to attack by microorganism.

A moist environment is required for microorganisms to survive and able to produce hydrolytic enzymes that break down the biopolymers. When the sample is buried, the water and moisture diffuse into the sample, leading to swelling and improved the biodegradability. Based on the water absorption test, it was shown that the water uptake increased as the ESP loading increased. Therefore, the sample with the highest water absorption capability tends to enhance the biodegradability of the biocomposite the most.

## Conclusions

In this study, preparing PVA/ESP biocomposite is successfully achieved by solution casting method. The tensile properties decreased with increasing ESP loading. This is due to the poor interfacial adhesion between the PVA matrix and filler. Agglomeration of ESP was obvious at higher loading as proven via SEM. Besides that, water absorption and water vapour transmission of biocomposite film increased with increasing ESP loading. The biocomposites are shown to have higher biodegradability with addition of ESP. Based on the natural weathering test and soil burial test, the weight loss increased with increasing ESP loading, which indicate that the biocomposites are able to degrade faster as ESP is incorporated, therefore enhancing the biodegradability.

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