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Effects of Partial Replacement of Eggshell Powder by Halloysite Nanotubes on the Properties of Polyvinyl Alcohol Composites

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Abstract. Polyvinyl alcohol (PVA)/eggshell powder (ESP) were prepared via solution casting method. The effects of gradual replacement of ESP by halloysite nanotubes (HNTs) were investigated based on tensile properties, physical properties and biodegradability. The main objective is to study the effect of hybrid fillers and also to compare the properties of PVA/ESP composite with conventional filler, HNT. The tensile properties decreased with increasing HNT loading. Scanning electron microscopy (SEM) studies showed that agglomeration of filler were present throughout the composites. Due to the presence of hydroxyl group on the outer and inner surface of HNT, the water absorption and water vapor transmissibility were found to increase with increasing HNTs loading. The biodegradability of film filled with HNT is lower compared to the film filled with ESP.

1. Introduction

The tremendous production and use of plastics in every segment of our life have increased the plastic waste in huge scales. Since polymeric materials do not decompose easily, disposal of waste plastics is a serious environmental problem. Plastic waste is now regarded as a worldwide environmental problem [1]. Over the years, public concern over waste management has increased due to the decreasing availability of landfills, environmental concern and public perception. Due to the waste management problems, degradable polymeric materials have become one of the major focuses for research.

Polyvinyl alcohol (PVA) is a useful polymer, which have been synthesised with a backbone consist primarily of –OH bond. The hydroxyl group makes it biodegradable and highly soluble and therefore widely used for packaging application. The advantages of PVA are good film formation, strong conglutination and high thermal stability. Generally, PVA films have been used for packaging application, where the contents need to be dissolved or dispersed in water because it is water soluble.

Recently, most researchers are interested to utilize agricultural wastes such as corn cob, palm kennel shell and eggshell. Eggshell is considered to be used as bio-filler because it is abundant, inexpensive and environmental friendly [2]. Basically, eggshell is an aviculture byproduct that has been listed as one of the worst environmental problems especially when egg product industry is well developed [3]. Eggshell is a natural bio-ceramic composite as it consists of both inorganic and organic components. Calcium carbonate is the main constituent of eggshell about 94% by weight. The unique chemical composition and substantial availability makes eggshell a potential candidate for bio-based calcium carbonate [4].
Halloysite nanotubes (HNTs) are eco-friendly nanotubes with low cost compared to carbon nanotubes. HNTs 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. They are naturally formed in the earth as the result of strain caused by lattice mismatch between adjacent silicon dioxide and aluminium oxide layers. HNTs have been reported to be used in several researches as filler to enhance final properties of composites [5-6].

Development of ternary composite either by blending the matrices or using hybrid fillers is currently gaining interest among researchers [7-9]. HYBRID fillers provide the advantages to modify the overall properties by balancing the properties that lack in one filler by incorporating another filler. From previous study, PVA/palm kernel shell powder composites showed to have low tensile strength after addition of the natural filler. However, when HNTs was incorporated, the tensile properties were enhanced [10]. There is no work has been found in literature on PVA/ESP/HNTs ternary composites. The purpose of this series is to study the effect of partial replacement of ESP with HNTs on mechanical, physical and biodegradability properties of composites.

2. Experimental procedures

2.1. Materials
PVA with average molecular weight of 72000 and density of 1.3 g/cm³ was supplied by Sigma-Aldrich (M) Sdn. Bhd (Kuala Lumpur, Malaysia). Eggshell waste was collected from Kafe Staff in Universiti Sains Malaysia (Penang, Malaysia). Glycerol (1,2,3-propanetriol) used as a plasticizer and was supplied by Merck (M) Sdn. Bhd (Selangor, Malaysia). Hexamethylenetetramine (HTMA) was supplied by Sigma-Aldrich (M) Sdn. Bhd (Kuala Lumpur, Malaysia). It is a reagent with molecular weight of 140.19 g/mol. Tween 80 with density of 1.070 g/cm³ was supplied by Merck (M) Sdn. Bhd. (Selangor, Malaysia). De-ionized water is used as a solvent. Halloysite nanotube was supplied by Imerys Tableware New Zealand Ltd. (Auckland, New Zealand). The HNT has typical dimension in range of 150 nm-2 µm long, 20-100 nm outer diameter and 5-3 nm inner diameter.

2.2. Preparation of eggshell powder (ESP)
The chicken eggshell was thoroughly cleaned with tap water to remove the chicken dung and the residual of albumen (egg white) and yolk adhering to the eggshell. After cleaning, the eggshell was subsequently dried in an open air for 24 hours. The ESP was prepared by grinding the eggshell by using mini crusher from Chyun Tseh Industrial Co. LTD, Taiwan. Sieving process was carried out by using 3 sieving plates with size of 1000, 600, and 75 micron. After that, the ESP was dried for 24 hours at 70˚C. The ESP was kept in dessicator for subsequent composites preparations.

2.3. Preparation of composites
The composites were prepared by solution casting method. Deionized water (200 ml) was used to dissolve PVA. The mixture was stirred for 10 minutes at 95 °C. The filler was added and continued to stir for 10 minutes. The additives were added and let to stir for another 10 minutes to ensure homogenous mixture. The solution was casted over glass plates and dried at room temperature for 24 hours. The film was then further dried in oven for 2 hours at 70˚C. The film was peeled off and reserved for further testing. PVA/ESP/HNTs composite was prepared at five different ratios, varying the ratio of ESP and HNT, while keeping the PVA/filler composition constant at 80/20 wt%.

2.4. Characterization methods
2.4.1. Tensile properties. The tensile properties of the composite films were evaluated by using Instron 3366 universal testing machine (Instron, Petaling Jaya, Malaysia). Five dumbbell shaped samples (Type IV) (ASTM D638) (2008). The crosshead speed used for tensile test was 50 mm/min and the load cell was 10 KN. The gauge length was set at 50mm. The test was carried out at room temperature and an average value five repeated tests were taken for each composition.
2.4.2. Morphological study. The surface morphology of composite was observed by using scanning electron microscope (SEM) Supra 35VP (ZEISS, Oberkochen, Germany). The composite film was mounted on aluminium stubs with carbon tape and then sputter coated with thin gold layer to avoid charging and poor resolution during examination.

2.4.3. Water absorption. The water absorption ($W_a$) of films was performed as described by Yun et al., (2008). Dried plastic films were immersed in distilled water at room temperature (25 ºC). After the 24 hours, moisture on the surface of the films was removed, and the weight of the films was measured. The water absorption was calculated as:

$$W_a(\%) = \left(\frac{W_e - W_o}{W_o}\right) \times 100 \quad (1)$$

$W_e$ is final weight (g), and $W_o$ is the initial weight (g).

2.4.4 Water vapour transmissibility. Water vapour transmissibility, WVT was measured according to ASTM E96 (1998), modified by Gontard et al. A container of about 30ml distilled water was sealed on top by film sample. The initial weight of container sealed with film sample was weighed and recorded. Then, containers were all placed in the desiccator at room temperature. The containers were weighted daily using analytical balance until constant weight. The WVT was then calculated using:

$$WVT = \frac{G}{t} / A = \left(\frac{G}{t}\right) / A \quad (2)$$

Where G is the weight gain, t is the time and A is the area of test area.

2.4.5. Natural weathering. The samples were cut into dumbbell shape (Type IV) (ASTM D638) (2008) from the film of each composition. The samples were subjected to weathering test for fourteen days. The test was carried out according to the ASTM D1435. The weathering resistance and the degradation of the samples were determined by observation on the changes in dimension, physical appearance and the weight changes.

2.4.6. Soil burial. The samples were cut into dumbbell shaped (Type IV) (ASTM D638) (2008) and buried in the natural soil at School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Nibong Tebal, Seberang Perai Selatan, Penang for a period of fourteen days. The degradation of the samples was determined by observation on the changes in dimension, physical appearance and the weight changes.

3. Results and discussion

3.1. Tensile properties

Figure 1 shows the effects of HNT loading on the tensile strength of PVA films. The film filled with only ESP shows the highest tensile strength and apparently, incorporation of HNT into the film reduced the tensile strength. HNT is usually added into polymer to enhance the mechanical properties [11]. However the result obtained shows that addition of HNT reduces the chain mobility, resulting lower tensile strength of film as compares to PVA film with ESP. It is believed to be due to the poor wettability and interfacial interaction between filler and matrix. The continuous of filler addition can cause the phase separation problem arising from particles agglomeration [12].

When two fillers is used in the PVA film, it is vital to ensure that both fillers are compatible to each other, so that, high filler-filler interaction can be achieved. The decrement in tensile strength can be explained by the imperfect distribution of the filler through the polymer matrix and poor adhesion between matrix and filler [13]. Tensile strength of film filled with hybrid filler, which is ESP and HNT is showed to be low due to the incompatibility of the fillers and the matrix.

On the other hand, 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 PVA/ESP/HNT films. As HNT loading increased, the elongation at break of the film decreases. This is due to increasing HNT loading in PVA matrix resulted in the stiffening and hardening of the film. This
reduces the resilience and toughness, and causes the decrement in elongation at break. This decrement is due to the fact that addition of filler promotes brittleness and increases rigidity of the composite.

![Figure 1](image1.png)

**Figure 1.** Tensile strength of PVA/ESP/HNT composite at different compositions.

Another factor that may explain the decrement of tensile properties as HNT is incorporated to the matrix is the high specific area to volume ratio of the filler itself. According to Bhushan et al. [14], due to the high surface area to volume ratio, the nano-sized filler has the tendency to agglomerate as the loading increase, which could prevent homogenous dispersion. As agglomeration occurs in the matrix, it will act as the stress concentration area that may lead to premature failure.

![Figure 2](image2.png)

**Figure 2.** Elongation at break of PVA/ESP/HNT composite at different compositions.

![Figure 3](image3.png)

**Figure 3.** Tensile modulus of PVA/ESP/HNT composite at different compositions.
Tensile modulus is defined as the measure of force required to deform the sample at specific amount and it actually a measure of the stiffness of the sample [15]. Figure 3 shows the tensile modulus of PVA/ESP/HNT film at different compositions. It is observed that the tensile modulus decreased as the loading of HNT increased. Tensile modulus exhibited a similar trend in tensile strength. The highest tensile modulus is exhibited by the film filled with ESP, while the lowest tensile modulus is obtained from film with HNT. This might be due to the weak interfacial adhesion between the PVA matrix and HNT. Besides that, the decrement also may arise due to the agglomeration of the filler as the homogenize filler distribution is not achieved.

3.2. Surface Morphology
Figure 4 shows the surface morphology of composites at different compositions. From the micrograph, agglomeration occurs throughout the surface. Some of the fillers are not properly wetted by PVA matrix, therefore indicates the poor interfacial adhesion between filler and matrix. Agglomeration of HNT was observed throughout the surface. The keys to fabricate composites with enhance mechanical properties are by achieving a good dispersion of the filler in polymer matrix and strong filler-matrix interfacial bonding.

This may explained the decrement of tensile properties as HNT is added. Nanotubes have the tendency to gather and form bundles or micron-sized agglomeration due to their high specific surface area, which adversely affect the mechanical properties of nanocomposites [16]. Agglomeration of HNT will cause accumulation or concentration of stress that eventually promote the rupture of the composite.

![Surface morphology of PVA/ESP/HNT (wt%) composite](image)

3.3. Water absorption
The water absorption test are essential for empathetic the performance of PVA composites, since the moisture pickup intimately relates to the composite properties as mechanical strength, dimensional stability and its appearance [17]. Figure 5 shows the percentage of water absorbance for different composition of PVA/ESP/HNT films. The films with higher HNT loading show more water absorption because higher content of filler that can absorb more water.
Water absorption percentage increased with higher content of HNT due to the properties of HNT itself whereby HNT is naturally hygroscopic. Another factor that may contribute to the increment of water absorption is the agglomeration of filler. As higher HNT loading is used, the formation of agglomerations increases due to the difficulties of achieving homogenous dispersion of filler at high filler loading. The agglomeration of filler basically increases the water absorption of the film because there will be poor interfacial adhesion, allowing water easily penetrate into the film.

3.4. Water Vapour Transmissibility (WVT)

Water vapour transmission of PVA/ESP/HNT film at different composition is shown in Figure 6. As illustrated, the WVT increases as the HNT loading into the film increases. The sensitivity of film matrix towards water can affect the WVT rate. HNT is capable to absorb moisture due to the structure, in which inner and outer surface of HNT is covered by OH groups and oxygen [18]. Another factor that may contribute to the increment of WVT as HNT loading increase is the agglomeration. These agglomerations will cause poor interaction between matrix and filler. Besides that, the poor compatibility also will increase the WVT because the interchain spacing will increases, allowing more water molecules to penetrate or diffuse through the film. This is similar to observation made by Ooi et al. [19].

3.5. Natural Weathering

Degradation by UV may occur as films were exposed to natural weathering and it may be indicated as the weight loss [20]. Figure 7 depicts the weight loss after weathering of PVA/ESP/HNT film at different compositions. The weight loss decreases as the loading of HNT increases. Highest weight loss was exhibited by the film filled with ESP, while the lowest weight loss was shown by film filled
with HNT. Therefore, it implied that the addition of ESP causes the film to degrade easier due to weathering as compared to HNT.

The weight loss can be related to molecular weight changes. The weight loss indicated that PVA underwent chain scission after natural weathering. The same observation was reported by Sam et al. [21] in their study in effect of cobalt stearate on natural weathering of LLDPE/soya powder blends. In general, the weight losses are found to be small as the film may have absorbed water and humidity upon rainfall and weathering.

![Figure 7. Weight loss after weathering of PVA/ESP/HNT film at different compositions.](image)

3.6. Soil Burial

In order to evaluate the degradation of the films, the weight loss of films was evaluated. Figure 8 shows the dependence of weight loss after soil burial test on the HNT loading on PVA films. The weight loss of the film showed a decrement as higher HNT loading is incorporated. In soil burial test, the possibility of microbial degradation is high. The lowest weight loss was depicted by film with 20% HNT. This may be due to the fact that HNT has higher resistance toward microbial, causing it to take longer time to degrade.

Microbial activities enhance the degradation of plastic films and decompose them into smaller fragments. Highest weight loss was exhibited by the film with 20 wt% ESP. This implies that ESP may have better hydrolysis capability to convert hydroxyl for esterification [22, 23]. These results suggest that the addition of ESP to the films increased their degradation more than the addition of HNT. ESP has better attraction for microbe to penetrate and initiate enzymatic attack and continue the degradation process. It is shown that PVA filled with ESP can increase the degradability of film compared to PVA filled with HNT.

![Figure 8. Weight loss after soil burial of PVA/ESP/HNT composite at different compositions.](image)
4. Conclusions
In summary, the PVA/ESP/HNT composite show lower tensile strength, modulus and elongation at break as HNT loading increases. The SEM study reveals that poor dispersion and present of HNT agglomeration on film surface. This is due to the high specific surface area of HNT, which prone to agglomeration. Based from micrograph obtained from SEM, it is proven that agglomeration of HNT is present throughout the surface. Water absorption and water vapour transmission of film increase with increasing HNT loading. The biodegradability properties tested in soil burial and natural weathering is showed to decrease with higher HNT loading. In comparison to the film filled with ESP, the weight loss of HNT filled film is lower, indicating that the microorganism and UV attack is not favourable toward HNT.

5. References
[1] Nawang R, Danjajaji I D, Ishiaku U S, Ismail H and Mohd Ishak A M 2001 Polymer Testing 20 167-172
[2] Kang D J, Pal K, Park S J, Bang D S and Kim J K 2010 Mater. Des. 31 2216–2219
[3] Siti Shuhadah and A G.Supri 2009 Journal of Physical Science 20(1) 87–98
[4] Hassan S B, Aigbodion V S and Patrick S N 2012 Tribology in Industry 34(4) 217–225
[5] Prashantha K, Lacrampe M F and Krawczak P 2013 Advanced Materials Manufacturing & Characterization 3(1) 11–14
[6] Fernández A, Muniesa M and González J 2013 Journal of Mechanical Engineering 59 183–192
[7] Samotu I A, Dauda M, Anafi F O and Obada D O 2015 Tribology in Industry 37(2) 142–153
[8] Majdzadeh-Ardakani K and Nazari B 2010 Composites Science and Technology 70(10) 1557–1563
[9] Taghizadeh M and Sabouri N 2013 International Nano Letters 3 51
[10] Alias N F, Ismail H and Ab Wahab M K 2017 BioRes 12(4) 9103-9117
[11] Zhou X Y, Cu Y F, Jia D M and Xie D 2009 Polymer-Plastic Technology and Engineering 48(5) 489-495
[12] Ismail H and Zaaba N F 2012 Journal of Elastomers and Plastics 46(1) 96-109
[13] Buzarovska A, Bogoeva-Gaceva G, Grozdanov A, Avella M, Gentile G and Errico M 2008 Australian Journal of Crop Science 1(2) 37-42
[14] Bhushan B, Luo D, Schrickers S, Sigmund W and Zauscher S 2014 Handbook of Nanomaterials Properties. Berlin, Heidelberg: Springer.
[15] Toh W Y, Lai J C, Wan A and Wan A R 2011 Journal of Composite Materials 45 1201-07
[16] Bregg R New Frontiers In Polymer Research 2006 Nova Science Publishers: New York
[17] Messiry M El, Deeb R El and Tarfawy S. El 2015 Recent Manufacturing Technologies Conference 234–244.
[18] Liu F, Wu J, Chen K and Xue D 2010 Microscopy: Science, Technology, Applications and Education 1781–1792.
[19] Zhong O X, Ismail H, Abdul Aziz N A and Abu Bakar A 2011 Polymer-Plastics Technology and Engineering 50 705–711
[20] Borsos Z, Paun V P, Botez I C, Stoica C M, Vizurean P and Agop M 2008 Revista de chimie 59 1169-71
[21] Sam S T, Ismail H, Ahmad Z 2011 Polymer-Plastics Technology and Engineering 50 957–968.
[22] Gawdzinska K, Nabialek M, Bryll K, Szymanski P and Sandu A V 2017 Materiale Plastice 54(3) 539-542
[23] Borsos Z, Paun V P, Botez I C, Stoica C M, Vizurean P and Agop M 2008 Revista de chimie 59 1169-71

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