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Tensile and Water Absorption Properties of Eggshell Powder Filled Recycled High-Density Polyethylene/Ethylene Vinyl Acetate Composites: Effect of 3-Aminopropyltriethoxysilane

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Abstract – *The effect of 3-aminopropyltriethoxysilane (APTES) coupling agent on tensile and water absorption properties of eggshell powder (ESP) filled recycled high-density polyethylene/ethylene vinyl acetate (rHDPE/EVA) composites were investigated. The composites were prepared using a Brabender internal mixer at 190 °C and rotor speed of 50 rpm, where ESP loadings (0, 5, 10, 15, 20, 25 phr) and constant rHDPE/EVA (50/50) were used. The results indicate that the tensile modulus and water absorption increased, but tensile strength and elongation at break decreased, with increased ESP loading. The addition of the APTES to the composites exhibited a higher tensile strength and tensile modulus, but lower elongation at break and equilibrium water absorption percentage than composites without APTES. The presence of APTES has enhanced the interfacial adhesion between rHDPE/EVA matrices and ESP which result in higher tensile strength and modulus.* ***Copyright © 2015 Penerbit Akademia Baru - All rights reserved.***

Keywords: Composites; Eggshell; Recycled high-density polyethylene; Ethylene vinyl acetate; 3-aminopropyltriethoxysilane

1.0 INTRODUCTION

According to the Food Agriculture Organization of the United Nations (2013), the Asia region is the highest contributor of the eggshell from 1992 to 2011. Specifically in Malaysia, the production of the eggshell has been rapidly increased from about 330,000 tons to 530,000 tons in 2011. Usually, the eggshell wastes are used as fertilizer to correct the pH of acid soils in the agricultural industries. However, this waste product is still undervalued due to its abundance and they still have not gained sufficient attention with regard to converting them from waste to new materials [1]. The main constituent of eggshell is calcium carbonate in the form of calcite which constitutes about 94 % by weight [2–4]. Therefore, the use of these eggshells as an alternative source of calcium carbonate ($CaCO_3$) may reduce the number of the eggshell wastes. Previous study by Hassan et. al found that the presence of high levels of inorganic calcium carbonate in the eggshells and no impurities were observed [5].

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There has been increasing demands for developing new polymeric materials with enhanced properties since the last few decades. Therefore, blending of different polymers has continuously on the rise among the industry and researcher to meet the demands and exploring the potential of the new developed polymers [6–10]. Polymer-inorganic composites have attracted a lot of attention because of their unique properties and numerous potential applications from the combination of organic and inorganic hybrid materials. This include enhancement of conductivity, toughness, optical activity, chemical selectivity, etc. Therefore, the composites have been widely used in the various fields such as military equipment, safety, protective garments, automotive, aerospace, electronics and optical devices [11].

The inorganic particles added into the polymer are expected to homogenously disperse in the polymer matrices to improve its mechanical properties such as tensile strength, modulus or stiffness. However, poor compatibility between the polymer matrices and the inorganic particles in composites prepared by simple physical mixing will affect the mechanical properties of the composites [12]. Without proper chemical treatment, it is very common for particles to agglomerates and not able to disperse individually and uniformly in the polymer matrices [1,13]. This incompatibility between the hydrophilic filler particles and hydrophobic polymer matrices can be reduced by introducing coupling agent to the composites [14–17]. In this research work, the effects of coupling agent 3-aminopropyltriethoxysilane (APTES) on tensile and water absorption properties of rHDPE/EVA/ESP composites were studied.

2.0 METHODOLOGY

2.1 Materials

Recycled HDPE pellets with a melt flow index of 0.7 g/10 min (190 °C) and a density of 939.9 kg/m^3 and EVA contains 6.5 wt. % VA, with melt index of 2.5 g/10 min (80 °C; 2.16 kg) and density of 0.93 g/cm^3 was supplied from A.R. Alatan Sdn. Bhd., Kedah Darul Aman, Malaysia. The chicken eggshells were obtained from local food industry in Negeri Sembilan, Malaysia and the 3-aminopropyltriethoxysilane (APTES) was purchased from Sigma Aldrich Chemie GmbH, Penang, Malaysia.

2.2 Preparation of Eggshell Powder

The eggshells were washed and crushed into small pieces. Then they were dried in an oven at 80 °C until the moisture in the eggshell is evaporated where the weight is become constant. Then, by using a kitchen blender, the dried eggshells were grinded to powder which is designated as ESP. A sieve was used to obtain an average filler size of 63 µm. The ESP was dried in a vacuum oven at 80 °C till the weight is constant as reported in Shuhadah et. al [18].

2.3 Filler treatment

The 3-aminopropyltriethoxysilane (APTES) was diluted in the ethanol by using a stirrer. The amount of the APTES used in 6 wt% of the filler weight. The solution was slowly stirred to ensure uniform distribution of the APTES. This step is continuous for an hour before the filler is being filtered out and dried in the convection oven at 80 °C for 24 hours to allow a complete evaporation of the ethanol.

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2.3 Composites Preparation

Table 1 presents the formulation and designation of the samples in this study. All formulations used in this study involve matrices of 50 wt% rHDPE and 50 wt% of EVA. For the composites preparation, the compounding of the blends was carried out by melt blending in an internal mixer (Plasticoder, Brabender). The rHDPE was first charged into the internal mixer at 190 °C, 50 rpm for 4 minutes, and then the pre-weighed EVA and ESP or treated ESP were added to the soften rHDPE. The mixing process continued for another 10 minutes in order to obtain homogenous composites. The composites was discharged from the mixing chamber and pressed into thick round pieces. The discharged composites were then allowed to cool.

Table 1: Formulation of rHDPE/EVA/ESP composites

Composite code	rHDPE (phr)	EVA (phr)	ESP (phr)	ESP_{APTES} (phr)
rHDPE/EVA/ESP0	50	50	-	-
rHDPE/EVA/ESP5	50	50	5	-
rHDPE/EVA/ESP10	50	50	10	-
rHDPE/EVA/ESP15	50	50	15	-
rHDPE/EVA/ESP20	50	50	20	-
rHDPE/EVA/ESP25	50	50	25	-
rHDPE/EVA/$ESP5_{APTES}$	50	50	-	5*
rHDPE/EVA/$ESP10_{APTES}$	50	50	-	10*
rHDPE/EVA/$ESP15_{APTES}$	50	50	-	15*
rHDPE/EVA/$ESP20_{APTES}$	50	50	-	20*
rHDPE/EVA/$ESP25_{APTES}$	50	50	-	25*

*3-aminopropyltriethoxysilane (APTES) was added at 6wt% of eggshell powder

2.4 Compression Molding

Samples of rHDPE/EVA/ESP composites were compressed via an electrical heated hydraulic press to produce the composites in plate form. The hot press machine was set at the temperature of 190 °C for both top and bottom platen. Then the composites were put into the mould, preheated for 4 minutes followed by compression for 2 minutes at the same temperature and subsequently cooled under pressure for 4 minutes.

2.5 Tensile test

Tensile properties were determined according to ASTM D638 by using the Instron 5569 with a crosshead speed of 50 mm/min. Five dumb-bell shaped samples of each formulation were conditioned at ambient temperature (25±3) °C and relative humidity (30±2) % before testing.

Tensile strength, elongation at break, and Young's modulus of each composite were obtained from the test.

2.6 Water Absorption Test

Water absorption test was carried out according to ASTM D750-95 standard. It involved total immersion of five samples in distilled water at room temperature. All samples were previously dried in an oven at 50 °C for 24 hours and stored in desiccators. The water absorption was determined by weighing the samples at regular interval. A Mettler balance type AJ150 was used with precision of ±1 mg. The percentage of water absorption (Mt) was calculated using Eqn. 1, where W_d and W_N are original dry and weight after exposure, respectively.

$$M_t = \frac{W_N - W_d}{W_d} \times 100\% \quad (1)$$

3.0 RESULTS AND DISCUSSION

3.1 Tensile Properties

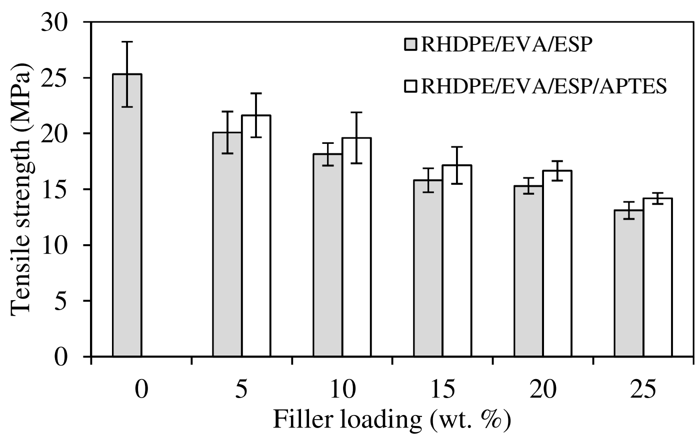

Figure 1: Tensile strength of rHDPE/EVA/ESP composites with and without 3-aminopropyltriethoxysilane.

Figures 1-3 show the tensile properties of rHDPE/EVA/ESP composites with and without the APTES coupling agent at different filler loadings. It can be clearly seen that the tensile strength of both composites decreased steadily as the concentration of ESP increased in the composites. This may be due to the incompatibility between the hydrophobic rHDPE/EVA matrices and the hydrophilic ESP that resulted in weak interfacial adhesion. This is not surprising since other studies have also indicated that the incorporation of filler into thermoplastic matrix may not necessarily increase the tensile strength of a composite [19].

Similar to other work [20], the results show a decreasing in composites strength as the filler loading increases from 5 to 25 phr. The reduction of strength on the addition of eggshell powder filler was expected due to filler-matrix incompatibility. For filler additions of 5 phr, silane treatment generally resulted in improvement in tensile strength compared to untreated eggshell powder filler composites, although not above that of the matrix only value of 25.3

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MPa. One explanation for the general reduction in the strength for the treated eggshell powder filler as the filler loading increases could be related to filler agglomeration, which would be more likely at higher filler contents. At similar filler loading, the addition of the coupling agent has obtained higher tensile strength compared to the untreated composites. APTES promotes better interfacial adhesion between hydrophobic rHDPE/EVA and hydrophilic ESP. As a result, better stress transfer through ESP was achieved, and the tensile strength of rHDPE/EVA/ESP composites was improved. The utilization of coupling agent was proven effective in enhancing the compatibility of the system consists of hydrophilic filler and hydrophobic polymer matrix.

Figure 2 shows the elongation at break of rHDPE/EVA/ESP composites with and without APTES coupling agent at different filler loadings. The results show that the incorporation of ESP into rHDPE/EVA matrices has resulted in a reduction in the elongation at break. The ductility of rHDPE/EVA matrices, as indicated by its high elongation at break, which is about 740.9%, has been reduced by the presence of ESP fillers. Similar observations have been reported in several studies for other thermoplastic composites [21].

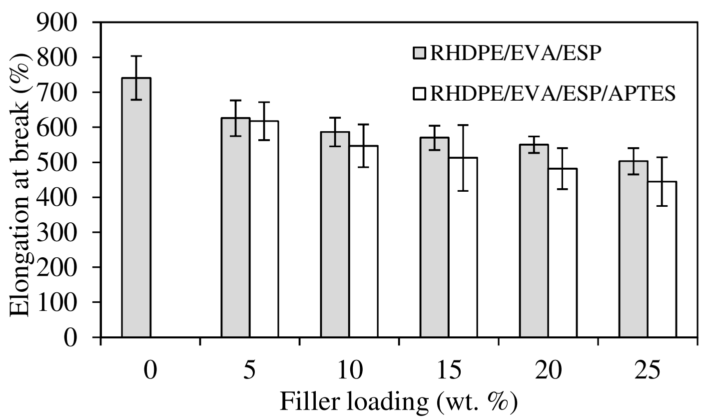

Figure 2: Elongation at break of rHDPE/EVA/ESP composites with and without 3-aminopropyltriethoxysilane.

Increased filler loading in the rHDPE/EVA matrices resulted in composite becoming stiffer and harder. The chain mobility of rHDPE/EVA matrices has been restricted due to the rigid interface between the filler and the matrices and therefore leading to a higher breaking tendency (lower deformation) of the composites. At similar ESP loadings, the addition of APTES has reduced the ductility of the rHDPE/EVA/ESP composites, therefore lowered the elongation at break for composites. This clearly indicates that the improvement in the filler-matrix adhesion is giving a positive contribution for the enhancement of stiffness of the rHDPE/EVA/ESP composites. A similar effect has been reported by Li et. al in their study on wood flour filler filled HDPE composites [22].

Figure 3 shows the Young’s modulus of rHDPE/EVA/ESP composites with and without APTES coupling agent at different filler loading. The results show that the Young’s modulus was increased in an increase of ESP loading. The addition of the particulate filler of ESP has added stiffness and rigidity to the composites. At higher filler loading, the composites will be able to withstand more loads. The addition of ESP filler has improved the modulus of the resulting composite. This is due to the ability of the ESP filler to increase the stiffness of rHDPE/EVA composites. This is in agreement with the trend observed in other [23]. It can be seen that for composites with APTES, the modulus increased significantly with the addition of 6% coupling agent. This may be attributed by the presence of coupling agent have led to a significant improvement in the filler-matrix interfacial bonding, and therefore it will obviously results in an increase in the efficiency of stress transfer from the matrix to the filler, which consequently gives rise to higher modulus.

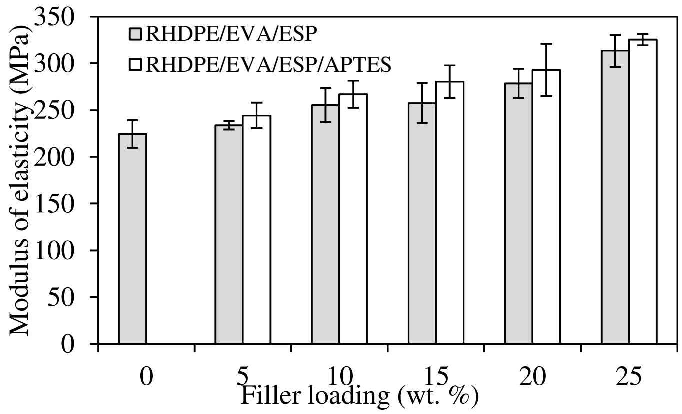

Figure 3: Modulus of elasticity of rHDPE/EVA/ESP composites with and without 3-aminopropyltriethoxysilane.

3.2 Water Absorption Analysis

Figure 4 shows the equilibrium water absorption of rHDPE/EVA/ESP composites with and without the APTES coupling agent for different ESP loadings. It can be seen that the water absorption by all composites increased with increasing ESP filler loadings. rHDPE/EVA/ESP composites with higher eggshell powder loading shows more water absorption. This is due to the higher content of filler in the composites that can absorb more water. The presence of high level of $CaCO_3$ in the eggshell powder is able to absorb more water, so it increase the water absorption as the filler is increasing [24].

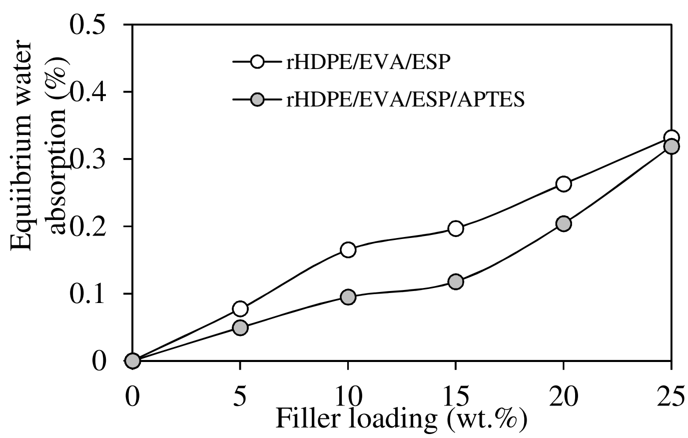

Figure 4: Equilibrium water absorption of rHDPE/EVA/ESP composites with and without 3-aminopropyltriethoxysilane.

As the filler loading increase, the formation of agglomeration of the filler in composites increases the water absorption of the composites due to the difficulties to achieve homogenous dispersion of filler [2,19,25]. Similar findings have been reported by other researchers [19,26]. In addition to that, greater water absorption by samples with higher ESP loading was due to the increasing amount of voids between ESP fillers and rHDPE/EVA matrices. Figure 4 also shows that the percentages of water absorption for rHDPE/EVA/ESP with APTES was lower than rHDPE/EVA/ESP without APTES at similar filler loading. Pang et. al (2013) reported similar findings [27]. This result clearly indicates that the presence of the APTES coupling agent enhances the interfacial adhesion between the rHDPE/EVA matrices and ESP.

4.0 CONCLUSION

The addition of 3-aminopropyltriethoxysilane (APTES) coupling agent into rHDPE/EVA/ESP composites enhanced interfacial adhesion between rHDPE/EVA matrices and ESP which improved the tensile strength, Young's modulus and reduce the percentage of water absorption of the composites.

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