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PROPERTIES OF LOW DENSITY POLYETHYLENE (LDPE) / EGGSHELL POWDER (ESP) COMPOSITES: THE EFFECT OF ETHYLENE DIAMINE-ISOPTHALIC ACID

A.G. SUPRI & SITI SHUHADAH

Division of Polymer Engineering, School Of Material Engineering, Universiti Malaysia Perlis (Unimap), 02600 Jejawi, Perlis, Malaysia

ABSTRACT

`The effect of ethylene diamine-isophthalic acid on tensile properties, morphology properties, water absorption, and thermal properties of the low density polyethylene/eggshell powder composites were studied. The both composites, low density polyethylene/eggshell powder (LDPE/ESP) and low density polyethylene / modified eggshell powder ($LDPE/ESP_M$) composites were prepared with Z-Blade Mixer at 180^0C and rotor speed of 50 rpm. The results indicate that the addition of ethylene diamine-isophthalic acid increased the tensile strength, Young's modulus, glass transition temperature (T_g), melting temperature (T_m), and water absorption resistance but lower percentage of crystallinity and the elongation at break of the LDPE/ESP composites. The micrographs of SEM showed that the eggshell powder was more widely dispersed in the LDPE matrix with the addition of ethylene diamine-isophthalic acid as a coupling agent.

KEYWORDS: Low Density Polyethylene, Ethylene Diamine-Isophthalic Acid, Eggshell Powder

INTRODUCTION

In recent decades, growing environmental awareness has resulted in renewed interest in the use of natural materials for different applications. Increasingly more stringent environmental policies have forced industries such as the automotive, packaging and construction industries to search for new materials that can substitute traditional composite materials consisting of a plastic matrix and inorganic reinforcement [1-2].The incorporation of mineral fillers into thermoplastics has been widely practiced in industry to extend them and to enhance certain properties. Fillers often increase the performance of polymeric products.

The degree of improvement on the judicious choice of filler origin, particle size and shape, the fraction of filler, and the surface treatment promoting interaction between the polymer matrix and filler [3]. The addition of fillers to polymers is a fast and cheap method to modify the properties of the base materials. For this reason, particulate filled polymers have been, and are, a subject of increasing interest in both industry and research. In this way, strength, stiffness, electrical and thermal conductivity, hardness and dimensional stability, among other properties can be tailored to the required values. The modification of the interfacial and interphase properties of polymer composites is mainly carried out in order to achieve a certain degree of compatibilization in the system.

As described before, there are two ways to improve mechanical properties through the use of filler: by changing its particle size and by treating it with coupling agents [4]. Scanning electron microscopy (SEM) is routinely used for morphology investigation of polymer blends and composites. Sample surface is observable by the SEM method and the elements of the structure can be identified. A study of the surface after fracture is a frequently used mode of sample preparation in SEM study of polymer morphology [5]. This article reports that an investigation on the mechanical

properties, thermal properties, water absorption, and morphology of unmodified (ESP) and modified eggshells powder (ESP_M) into low density polyethylene / eggshell powder composites.

MATERIALS AND EXPERIMENTAL

Materials

Low density polyethylene (LDPE) grade L705 (MFI 7g/10 min and density 0.918 g/cm^3) was obtained from Polyolefins Company, Singapore. The eggshell was obtained from local market. Ethanol (C_2H_5OH), sodium hydroxyl (NaOH), ethylene diamine, and isophthalic acid with Mr 166.14 were supplied from Sigma-Aldrich Chemie GmbH, Penang, Malaysia.

Preparation of Eggshell Powder

Eggshells were washed, dried and grinded. Eggshell was grinded to powder using the blender. Sieve was used to obtain an average filer sizes of 63 µm. Eggshell Powder was dried in vacuum oven at 80^{0}C till the constant weight is occurred to make it free from moisture. After that the Eggshells Powder were examined using the X-ray fluorescene spectrometer as shown in Table 1.

Treated the Eggshell Powder

Eggshell powder has been average sizes of 63 µm was treated by using the sodium hydroxide (NaOH). The eggshell powder was mixed with the solution of 10% NaOH. The eggshell powder was mixed with the solution and stirred for 6 minutes at room temperature until two layers is formed. The upper layer is decanted and the deprotenized layer that is precipitate is washed with distilled water**.** The wash precipitated sample is dried in the oven at 105^{0}C till the constant weight obtained

Modified the Eggshell Powder

Chemical modification of modified eggshell powder was carried out by adding ethylene diamine-isophthalic acid and ethanol. The eggshell powder was dipped in an ethanol solution containing ethylene diamine-isophthalic acid (6% by weight of ESP) at 48 hours at 50^{0}C. The eggshell powder then decanted and dried in an air oven at temperature of 70^{0}C for 2 hours.

Composite Preparation

The formulation of low density polyethylene/eggshell powder (LDPE/ESP) composites and low density polyethylene /modified eggshell powder (LDPE/ESP_M) is given in Table 1. The Z-Blade mixer was set at temperature of 180ºC and a rotor speed of 50 rpm. Low density polyethylene was then charged into Z-blade mixer to start the melt mixing. LDPE was preheated for 20 minutes in the mixing chamber. Next, eggshell powder (ESP) or modified eggshell powder (ESP_M) are added to the soften LDPE. The mixing process was allowed for another 5 minutes in order to obtain homogeneous composites. The composites was discharged from the mixing chamber and pressed into thick round pieces. The discharged composites were then allowed to cool.

Compression Molding

Samples of LDPE/ESP and LDPE/ESP_M 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 180ºC for both top and bottom platen. Then, the composites were put into the mould, preheated for 8 minutes followed by compression for 4 minutes at the same temperature and subsequently cooled under pressure for 4 minutes**.**

Mechanical Properties Test

Tensile properties were determined according to ASTM D638 by using the Instron 5569. Dumb-bell shaped specimens were conditioned at ambient temperature (25 ± 3) ^{0}C and relative humidity (30 ± 2) % before testing. A cross head speed of 50mm/min was used. The average of five samples was used during the test.

Scanning Electron Microscopy

Studies on morphology of the tensile fracture surface of LDPE/ESP composites and LDPE/ESP$_M$ composites were carried out using a scanning electron microscopy (SEM) using SEM, model JEOL JSM 6460LA. Surfaces of the samples were coated with a thin palladium layer of about 12 µm thickness using Auto Fine Coater, model JEOL JFC 1600.

Water Absorption Test

Water absorption test was carried out according to ASTM standard D750-95.It involved total immersion of three samples in distilled water at room temperature. All the specimens were previously dried in an oven at 50^{0}C for 24 h and stored in desiccators. The water absorption was determined by weighing the samples at regular interval. A Mettler balance type AJ150 was used with a precision of ± 1 mg. The percentage of water absorption (Mt) was calculated by:

$$Mt = \frac{W_N - W_d}{W_d} x100\% \quad (1)$$

Where W_d and W_N are original dry and weight after exposure respectively. The average reading of three samples was taken.

Differential Scanning Calorimetry Analysis

Thermal analysis measurements of selected system were performed using a Perkin Elmer DSC-7 analyzer. Samples of about 4 mg were heated from 25 to 250^{0}C using a nitrogen air flow of 50 ml/min and heating rate of 10^{0}C/min.The melting and crystallization behavior of selected composites also performed using a Perkin Elmer DSC-7 analyzer. The % crystallinity of composites was determined using the following relationship;

$$\% \text{ Crystallinity} = \frac{\Delta H_f}{\Delta H^\circ_f} \text{ x } 100\% \quad (2)$$

Where ΔH_f and ΔH^o_f are enthalpy of fusion of the composite and enthalpy of fusion of LDPE, respectively. The value for ΔH^o_f (LDPE) is 293.6J/g

RESULTS AND DISCUSSION

Mechanical Properties

Figure 1 shows the tensile strength of LDPE/ESP and LDPE/ESP$_M$ composites with different filler loading. It can be seen that the tensile strength of the both composites decreases with increasing the filler loading. The decreases of tensile strength were due to the poor adhesion of filler-matrix and agglomeration of filler particles. At similar filler loading, the tensile strength of LDPE/ESP$_M$ composites is higher than LDPE/ESP composites.

This is probably because of a better interfacial adhesion between the filler and the matrix after chemical modification was done. Strong adhesion between filler and matrix interface cause batter stress transfer from matrix into the filler leads to a higher tensile strength [6]. Ethylene diamine-isopthalic acid reacts with the surface of the inorganic and

forming bonds. The usage of coupling agent was proven effective in entering the dispersion; adhesion and compatibility of system consist of a hydrophilic filler and hydrophobic matrix.

Figure 2 shows the elongation at break of LDPE/ESP and LDPE/ESP_M composites with different filler loading. It can be seen that the elongation at break of the composites decreases with increasing filler loading. Increased the filler loading in the LDPE matrix resulted in composite becoming stiffer and harder. This will reduce the composite resilience and toughness and lead to lower elongation at break [7]. Figure 2 also shows the elongation at break of LDPE/ESP_M composites is lower than LDPE/ESP composites. This observation was due to the stiffness of the composites increased gradually with associated decrease in elongation at break.

Figure 3 shows the Young's modulus of LDPE/ESP and LDPE/ESP_M composites with different filler loading. Generally an increase in Young's Modulus indicates that the stiffness of all samples increased. As expected, the Young's Modulus, which indicates the material stiffness increases steadily with filler content. This is because at high filler loading the composite will be able to withstand more loads.

The original purpose of the incorporation of fillers, especially the particulate filler, into the polymer matrix is to improve the modulus of the resulting composites. Young's modulus of the composites is affected by the filler modulus, filler loading, and filler aspect ratio [8]. LDPE/ESP_M composites had a higher Young's modulus than LDPE/ESP composites. This was due to the better interfacial interaction between filler and the polymer matrixes in LDPE/ESP composites

Morphology Properties

Figure 4 shows the micrographs of tensile fracture of the LDPE/ESP and LDPE /ESPM composites with different filler loading. The agglomeration and cavities tend to form as more filler were added to the LDPE matrix. Figure 4 (a,c) indicated an extensive filler full out from the matrixes than 5 (b,d). From SEM micrographs, the eggshell modified with ethylene diamine-isophthalic acid in Figure 5 (b,d) look well contacted in LDPE matrix with good adhesion characteristics, which coincides with the result of the tensile strength as shown in Fig. 1.

As the amount of eggshell powder loading increases in the composites, the tendency for filler-filler interaction increases rather than filler-matrix interaction to form agglomeration. This was due to the difficulties to achieve homogenous dispersion of filler at higher filler loading [9-10]. This resulted in poor dispersion of filler in higher filler loading as shown in Figure 4 (e,f). These morphological results were also well matched with the tensile strength results in Figure 1.

Water Absorption Analysis

Figures 5 and 6 Show the percentage of water absorption versus time for LDPE/ESP composites and LDPE/ESP_M with different filler loading while Figure 7 shows the equilibrium water absorption for LDPE/ESP and LDPE/ESP_M composites. The water absorption increased with time. LDPE/ESP composites with higher eggshells powder loading shows more water absorption. This is due to the higher contents of filler in the composites that can absorb more water. As the filler loading increase, the formation of agglomeration is found due to the difficulties to achieve homogenous dispersion of filler at high filler loading. The agglomeration of the filler in composites increases the water absorption of the composites. The Figures also show the percentage of water absorption for LDPE/ESP_M was lower than LDPE/ESP composites due to the better interfacial adhesion between LDPE and ESP with the presence of ethylene diamine-isophthalic acid as a coupling agent.

Thermal Properties

Figure 8 shows the DSC curve of LDPE/ESP_M composites with different filler loading whereas Table 3 shows the glass transition temperature (T_g), melting temperature (T_m), and % crystallinity of LDPE/ESP and LDPE/ESP_M composites. From Table 3, it can be seen that the T_g and T_m of the composites increase with increasing of filler loading. Glass transition temperature and melting temperature for LDPE/ESPM composites are higher than LDPE/ESP composites due to the better interaction adhesion between LDPE and ESP with the presence of ethylene diamine-isophthalic acid. The result also shows that the percentage of crystallinity of the composites increased with increasing the filler loading. This is due to increasing composition of eggshell powder in the composites. However, the percent crystallinity of the LDPE/ESP composites slightly decrease with the addition of ethylene diamine-isophthalic acid .

CONCLUSIONS

The addition of ethylene diamine-isophthalic acid a coupling agent into LDPE/ESP composites enhanced interfacial adhesion between LDPE and ESP which improved the tensile strength, Young's modulus and reduce the percentage of water absorption of the composites as evidenced by the morphological study by SEM. The presence of ethylene diamine-isophthalic acid has also increased the Tg and Tm of LDPE/ESP composites. The percentage of crystallinity of LDPE/ESP composites increased with increasing filler loading but decreases with the presence of ethylene diamine-isophthalic acid.

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APPENDICES

Table 1: Inorganics Compound of Eggshell Powder Investigated by Using X-Ray Fluorescene Spectrometer

Elements	Concentration (%wt)
Al_2O_3	0.001
SiO_2	0.001
S	0.001
Cl	0.009
CaO	99.83
Cr_2O_3	0.003
MnO	0.001
CuO	0.001
LOI	0.153

Table 2: Formulation of LDPE/ESP and LDPE/ESP_M Composites at Different Eggshell Powder Loading

Composites Code	LDPE (Wt %)	Eggshell Powder (Wt %)
LDPE	100	-
LDPE/ESP5	95	5
LDPE/ESP10	90	10
LDPE/ESP15	85	15
LDPE/ESP20	80	20
LDPE/ESP25	75	25
LDPE/$ESP5_M$	95	5*
LDPE/$ESP10_M$	90	10*
LDPE/$ESP15_M$	85	15*
LDPE/$ESP20_M$	80	20*
LDPE/$ESP25_M$	75	25*

*Ethylene diamine-isophthalic acid was added at 6 wt % of eggshell powder

Table 3: The Data of Thermal Parameter from DSC Of LDPE/ESP and LDPE/ESP_M Composites

Composites Code	T_g (˚C)	T_m (˚C)	% Crystallinity (%)
LDPE	46.11	107.69	28.40
LDPE/ESP5	46.63	107.57	34.90
LDPE/ESP15	46.64	107.97	35.04
LDPE/ESP25	46.89	108.33	35.50
LDPE/$ESP5_M$	47.86	110.02	34.12
LDPE/$ESP15_M$	48.21	110.59	34.92
LDPE/$ESP25_M$	48.91	110.76	35.15

FIGURES

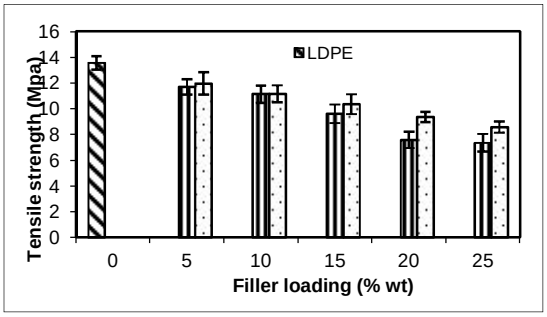


Figure 1: Effect of Filler Loading on the Tensile Strength of LDPE/ESP and LDPE/ESP$_M$ Composites

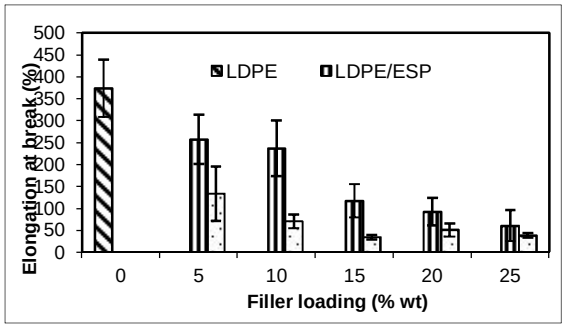


Figure 2: Effect of Filler Loading on Elongation at Break of LDPE/ESP and LDPE/ESP$_M$ Composites

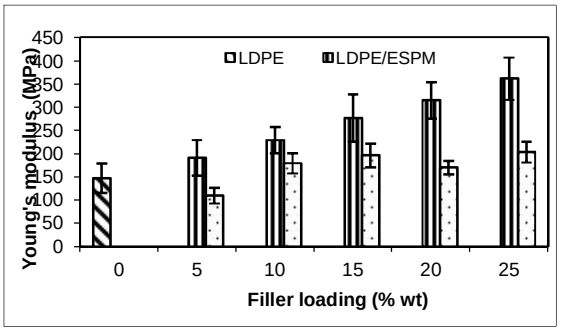
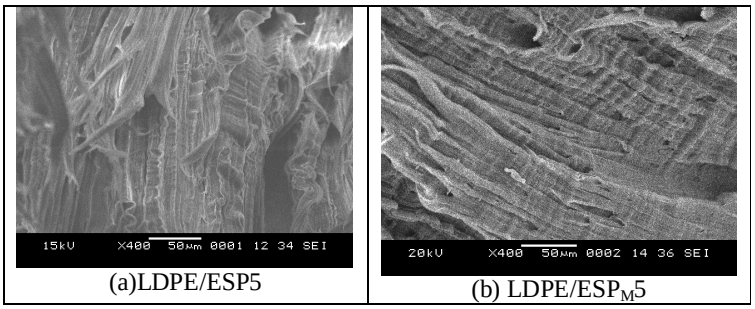
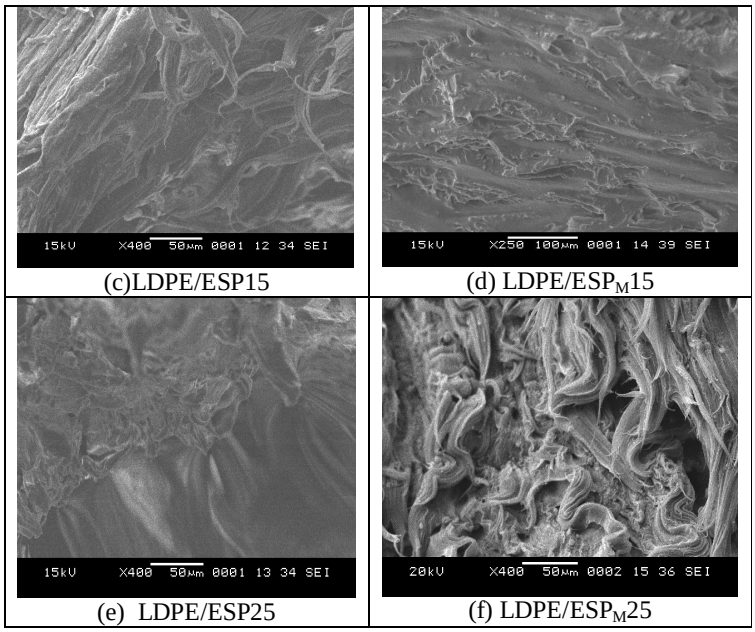


Figure 3: Effect of Filler Loading on the Young's Modulus of LDPE/ESP and LDPE/ESP$_M$ Composites



(a)LDPE/ESP5 (b) LDPE/ESP$_M$5



(c)LDPE/ESP15 (d) LDPE/ESP$_M$15

(e) LDPE/ESP25 (f) LDPE/ESP$_M$25

Figure 4: SEM Micrographs of Tensile Fracture Surfaces of LDPE/ESP Composites: (A)LDPE/ESP5, (B)LDPE/ESP$_M$5, (C)LDPE/ESP15, (D)LDPE/ESP$_M$15 (E) LDPE/ESP25 and (F) LDPE/ESP$_M$25.

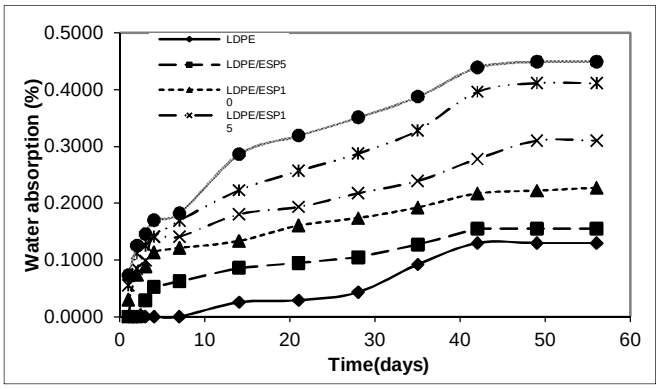


Figure 5: Water Absorption Versus Time of LDPE/ESP Composites with Different Filler Loading

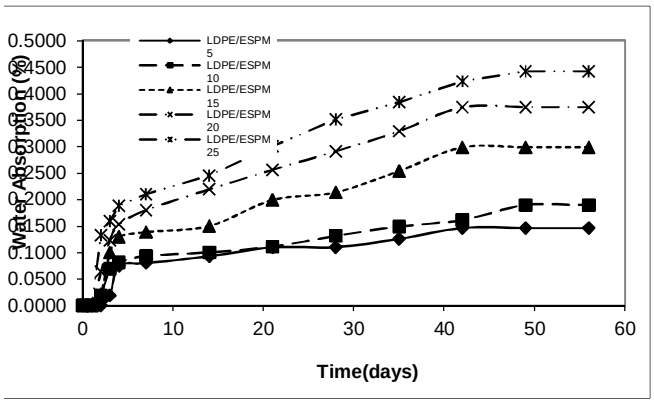


Figure 6: Water Absorption Versus Time of LDPE/ESP$_M$ Composites with Different Filler Loading

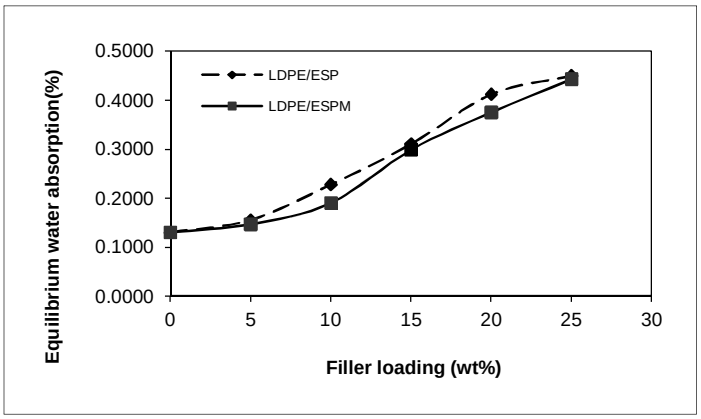


Figure 7: Percentage of Equilibrium water Absorption Versus Filler Loading of LDPE/ESP and LDPE/ESP$_M$ Composites

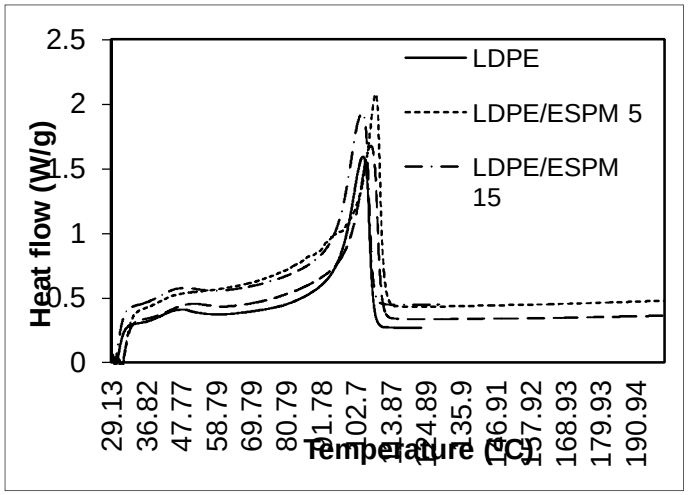


Figure 8: Differential Scanning Calorimetry Thermogram of LDPE/ESP$_M$ with Different Filler Loading