LDPE-Isophthalic Acid-Modified Egg Shell Powder Composites (LDPE/ESP_I)

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Abstract: *The effects of chemical modification on the mechanical properties, morphology and water absorption of low density polyethylene/egg shell powder composites were studied. The mechanical and morphological properties of low density polyethylene/egg shell powder composites with and without modifications (NaOH-isophthalic acid) have been characterised by an Instron machine and by scanning electron microscopy (SEM). The composites were prepared by using a Z-blade mixer at 180°C and at a rotor speed of 50 rpm for 6 min. The interfacial adhesion has enhanced the tensile strength and water absorption resistance of the LDPE/modified egg shell powder composites (LDPE/ESP_I), as compared to LDPE/unmodified egg shell powder composites (LDPE/ESP). Both the introduction of interfacial adhesion to composites and better interaction adhesion between LDPE and egg shell powder are responsible for the improvement of the mechanical properties of the LDPE/ESP_I, as evidenced by SEM on the tensile fracture surface of the composites.*

Keywords: egg shell powder, low density polyethylene, isophthalic acid, chemical modifications, mechanical properties

Abstrak: *Kesan pengubahsuai secara kimia ke atas sifat-sifat mekanikal, morfologi dan keterapan air bahan komposit/serbuk kulit telur dikaji. Sifat-sifat mekanikal dan morfologi LDPE / serbuk kulit telur yang diubahsuai (ESP_I) dengan asid isofetalik dan yang tidak diubah suai (ESP) telah dikaji menggunakan mesin Instron dan mikroskop pengimbas elektron (SEM). Bahan komposit disedia menggunakan pengaduk Z-blade pada suhu 180^0C dan pada kelajuan 50 rpm selama 6 min. Didapati sentuhan dalaman telah meningkatkan kekuatan tensil dan rintangan keterapan air komposit LDPE/ESP_I banding komposit LDPE/serbuk kulit telur yang tidak diubahsuai (LDPE/ESP). Pengenalan rekatan dalaman dan rekatan yang bagus di antara kulit telur dan LDPE telah menyebabkan peningkatan sifat-sifat mekanikal komposit LDPE/ESP_I seperti yang dilihat pada permukaan patah menggunakan SEM.*

Kata kunci: serbuk kulit telur, polietelina ketumpatan rendah, asid isofatalik, terubahsuai secara kimia, sifat-sifat mekanik

1. INTRODUCTION

Composite materials are those that are formed by the combination of two or more materials to achieve properties that are superior to those of their constituents.[1] Polymer composites consist of a polymer resin as the matrix, with fibres as the reinforcement medium.[2] Considerable interest has been generated in the manufacture of thermoplastic composites due to their unique properties, including their good mechanical properties, their thermal stability, and a reduced product cost.[3–4] Due to the combination of more than one material, the properties of composites are influenced by many factors such as filler characteristics, filler content, and interfacial adhesion.[5–6]. This can cause the behaviour of filled polymers to be more complex than their unfilled counterpart.[7] This study was based on the modification of egg shell powder, an inorganic material, in the LDPE/egg shell powder composites. Inorganic materials usually require chemical modifications to increase filler/polymer interactions. Polyethylene is a hydrophobic polymer, while egg shell powder is hydrophilic filler.[8] The chemical modification acts as a "bridge" between the inorganic filler and the organic polymer matrix. The "bridge" must adhere or bond to the filler and in turn must strongly interact with the polymer.[9] This article reports an investigation on the mechanical properties and morphology of ESP_I and ESP in a LDPE/egg shell powder composite.

2. EXPERIMENTAL

2.1 Materials

LDPE grade L705 (MFI 7 g 10 min^{-1} and density 0.918 g cm^{-3}) was obtained from Polyolefins Company, Singapore. The egg shell was obtained from a local market. Isophthalic acid with Mr 166.14 was supplied by Sigma-Aldrich Chemie GmbH, and sodium hydroxide pellets were obtained from Chemer TM.

2.2 Preparation of Egg Shell Powder

The egg shells were washed, dried and ground to a powder using the blender. A sieve was used to obtain an average particle size of 63 µm. The egg shell powder was dried in a vacuum oven at 80^{o}C until a constant weight was observed. The powder was then examined using the X-ray fluorescence spectrometer shown in Table 1.

Table 1: Inorganic compounds in ESP investigated by using X-ray Fluorescence Spectrometer.

Elements	Concentration (%)
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

Note: LOI – Loss of Ignition

2.3 Treatment of the Egg Shell Powder

The egg shell powder with an average particle size of 63 µm was treated with a solution of 10% NaOH. The powder was mixed with the solution and stirred for 6 min, then kept at room temperature until two layers is formed. The upper layer was decanted, and the deproteinised layer of precipitate was washed with distilled water**.** The washed precipitate was dried in the oven at 80°C until a constant weight was observed. The powder was then stirred in a mixture of 6% of isopthalic acid and ethanol for an hour, whereupon the treated powder was dried in the oven at 80°C until the constant weight.

2.4 Compounding of Composites

The composites were prepared in a Z-Blade Mixer. LDPE was first charged to start the melt mixing. After 3 min, the filler was added. The mixing continued for another 3 min, and then continued until a constant torque was obtained for a total mixing time of 6 min. The composites were then discharged from the mixer. LDPE Mixing was done at 180°C and rotor speed of 50 rpm. A sample of the composite was moulded in an electrically heated Hydraulic press. Hot press procedures involved preheating at 180°C for 4 min, followed by compression for 2 min at the same temperature and subsequent cooling under pressure for 2 min. The formulation of ESP_I filled LDPE composites is shown in Table 2.

Table 2: Formulation of ESP_I-filled LDPE composites

Code	LDPE (%)	Egg Shell Powder (%)
LDPE	100	0
LDPE/ESP_I5	95	5
LDPE/ESP_I10	90	10
LDPE/ESP_I15	85	15
LDPE/ESP_I20	80	20
LDPE/ES_I25	75	25

2.5 Mechanical Properties Test

Tensile properties were determined according to ASTM D638 by using the Instron 5569. Dumbbell-shaped specimens were conditioned at ambient temperature (25^{o}C $\pm$ 3 ^{o}C) and relative humidity (30% $\pm$ 2%) before testing. A cross head speed of 50 mm min^{-1} was used. The average of five samples was used during the test.

2.6 SEM Studies

Studies on the morphology of the tensile fracture surface of LDPE/ESP and LDPE/ESP_I composites were carried out using an SEM, model JEOL JSM 6460LA. Sample surfaces were coated with a thin layer of palladium about 12 µm thick using Auto Fine Coater, model JEOL JFC 1600.

2.7 Water Absorption Test

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

$$Mt = \frac{W_N - W_d}{W_d} x\ 100\% \quad (1)$$

where W_d and W_N are the dry and wet weights after exposure, respectively. The average reading of three samples was taken.

3. RESULTS AND DISCUSSION

3.1 Mechanical Properties

Figure 1 shows the effect of filler loading on the tensile strength of ESP and ESP_I-filled LDPE composites. It can be seen that the tensile strength for the composites decreases with increasing filler loading. This result is similar to reports by Sangeeta et al. and Fernanda et al.[10–11] According to Salmah et al.[12] the decreases in tensile strength are due to the poor adhesion of the filler-matrix and the agglomeration of filler particles. The tensile strength for ESP_I is higher than for ESP. This is probably because of a better interfacial adhesion between the filler and the matrix after chemical modification. Strong adhesion between filler and matrix interface can cause better stress transfer from the matrix to the filler leads to a higher tensile strength.[13] Isopthalic acid, which has a hydrophilic side that is compatible with the filler and a hydrophobic side that is compatible with the LDPE, reacts with the surface of the inorganic and to form bonds. Without the chemical modification, there is simply adhesion of the polymer to the filler through weak bonding, i.e., van der Waals or induction interactions.[9]

*Similar compositions were prepared for unmodified egg shell powder.

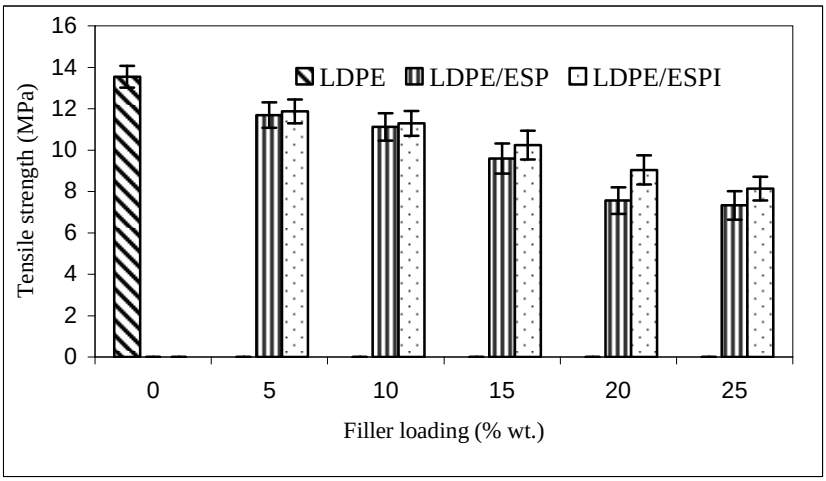

Figure 1: Effect of filler loading on the tensile strength of ESP-filled LDPE composites

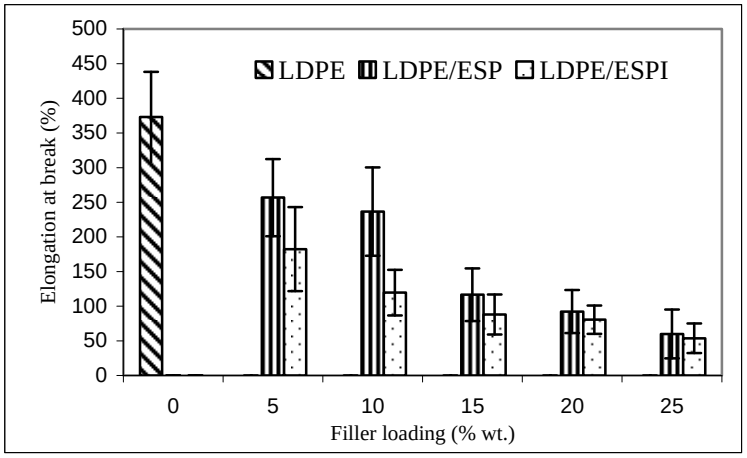

Figure 2: Effect of filler loading on the elongation break of ESP-filled LDPE composites

Figure 2 shows the effect of filler loading on the elongation at the break of ESP and ESP_I-filled LDPE composites. It can be seen that the elongation at the break for the composites decreases with increasing filler loading. Increased filler loading in the LDPE matrix resulted in the stiffening and hardening of the composite. This reduced its resilience and toughness, and led to lower elongation at the break.[14] The reduction of the elongation break with the increasing filler loading indicates the incapability of the filler to support the stress transfer from polymer filler to matrix. From Figure 2, we can see that the elongation at the break for ESP is higher than for ESP_I. This is due to the addition of isopthalic acid in the composites. The stiffness of the composites increased gradually with an associated decrease in elongation at the break.

Figure 3 shows the effect of filler loading on the Young's modulus of ESP and ESP_I-filled LDPE composites. Young's modulus for the composites increases with the increasing filler loading. The increased modulus corresponds to more filler where its intrinsic properties as a request agent exhibit high stiffness (modulus) compare to polymeric material.[14] This is because at a high filler loading, the composite will be able to withstand greater loads. This behaviour is similar to a result reported by Ardhyananta et al.[15] Young's modulus for ESP_I composites is low than for ESP composites, due to the presence of isopthalic acid, which toughens the composites and thus decreases Young's modulus.

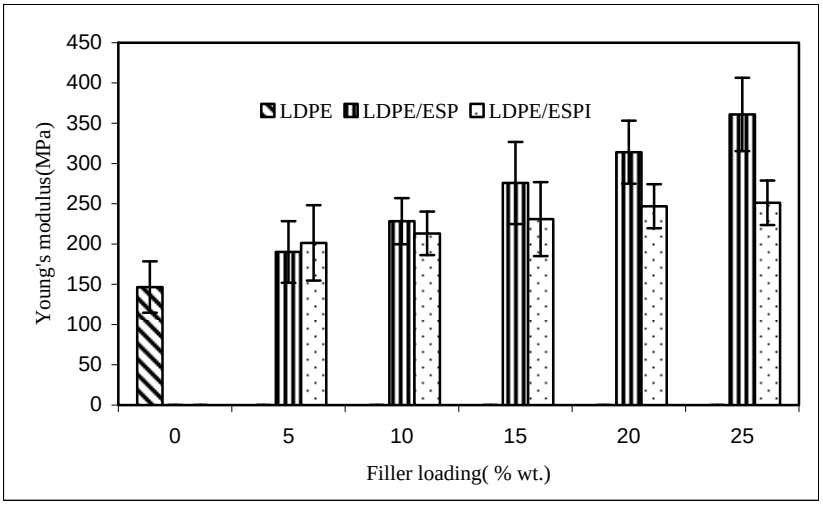

Figure 3: Effect of filler loading on the Young's modulus of ESP-filled LDPE composites.

3.2 Morphology Properties

Figure 4(a) shows the tensile fracture micrograph of the LDPE/ESP5 and Figure 4(b) shows the micrograph of the LDPE/ESP$_I$5 composites. Figure 4(a) shows a rougher surface than does Figure 4(b), and there are plastic deformations of the matrix, which indicate ductile failure mode. Figure 4(c) shows the micrograph of the LDPE/ESP15 composites, and Figure 4(d) shows the micrograph of the LDPE/ESP$_I$15 composites. It shows a rougher surface where there are many voids and plastic deformations. Many holes can be seen clearly on the surface due to the detachment of filler from the matrix surface. Figure 4(e) shows the micrograph for LDPE/ESP25 and Figure 4(f) shows the micrograph for LDPE/ESP$_I$25. As the filler loading increases, the formation of the microfiller (agglomeration) is found due to the difficulties of achieving a homogeneous dispersion of filler at high filler loading. The micrograph shows a lack of matrix fibrils, poor interfacial bonding and voids between the matrix and the filler. The lower filler loading shows better dispersion and less pull out of filler from matrix compared to the higher filler loading. Consequently, LDPE/ESP5 composites exhibit better tensile strength and elongation at break. For the micrograph of modified composites, it can be seen that the fibres were pulled out as in the unmodified case during the fracture of the composite, but it showed less plastic deformation than did the unmodified composites.

The micrograph shows that the modified composites are more compatible than the unmodified composites. The modification improves the compatibility by more finely dispersing the filler in the polymer matrix. This finding suggests that the adhesion between the matrix and the filler is very good. Accordingly, the interfacial strength is improved.[16]

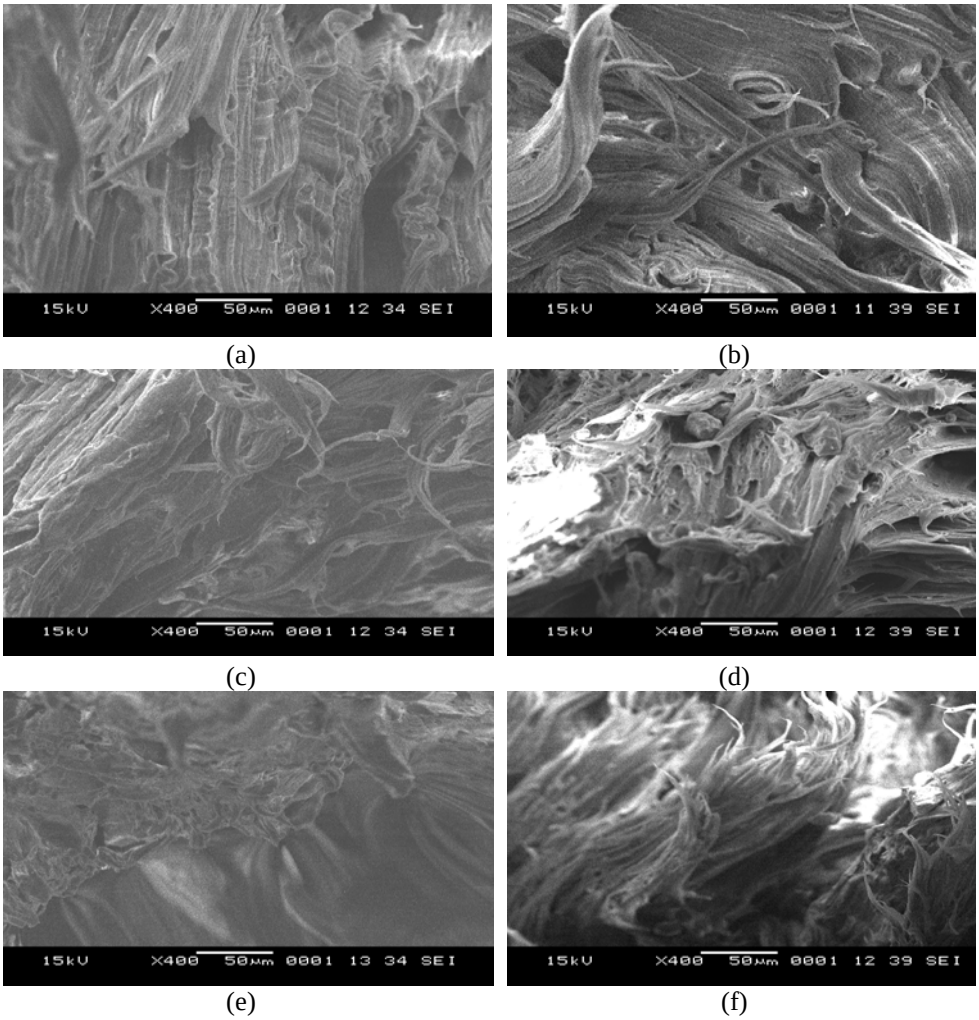

Figure 4: SEM micrographs of tensile fracture surfaces of LDPE/ESP composites. (a) LDPE/ESP5; (b) LDPE/ESP$_t$5; (c) LDPE/ESP15; (d) LDPE/ESP$_t$15; (e) LDPE/ESP25; and (f) LDPE/ESP$_t$25.

3.3 Water Absorption

Figures 5 and 6 show the percentage of water absorption versus time for the LDPE/ESP and LDPE/ESP_I composites with different filler loading, while Figure 7 shows the equilibrium water absorption for LDPE/ESP and LDPE/ESP_I composites. Composites with higher ESP loading show more water absorption. This is due to the higher contents of filler loading in the composites that can absorb more water. As the filler loading increase, the formation of agglomerations increases due to the difficulties of achieving a homogeneous 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 that the percentage of water absorption by LDPE/ESP_I was lower than for ESP. The modified ESP_I has better adhesion between the matrix and the filler, reducing the formation of agglomerates. This can reduce the percentage of water absorption. Modification of the ESP leads to a decrease in the number of free hydroxyl groups on the surface, reducing the percentage of water absorption.

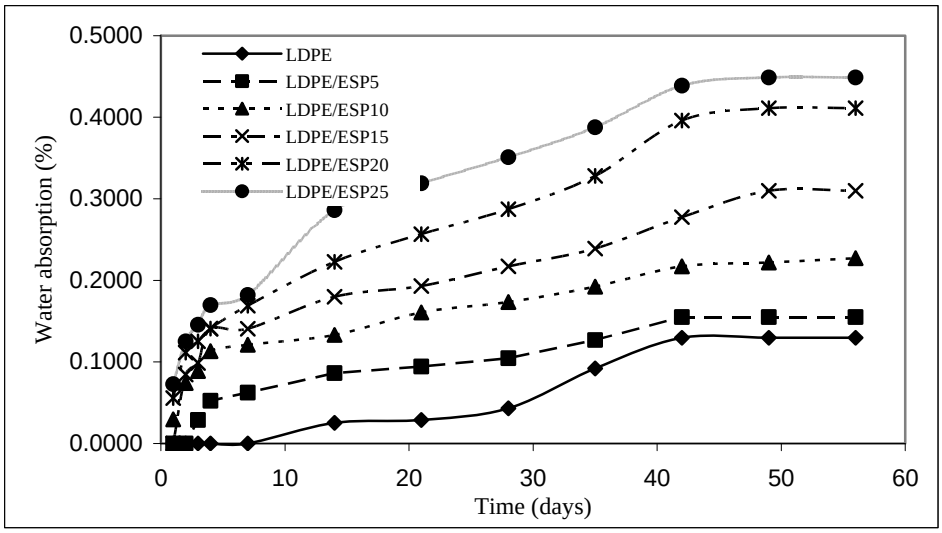

Figure 5: Water absorption versus time of LDPE/ESP composites with different filler loading.

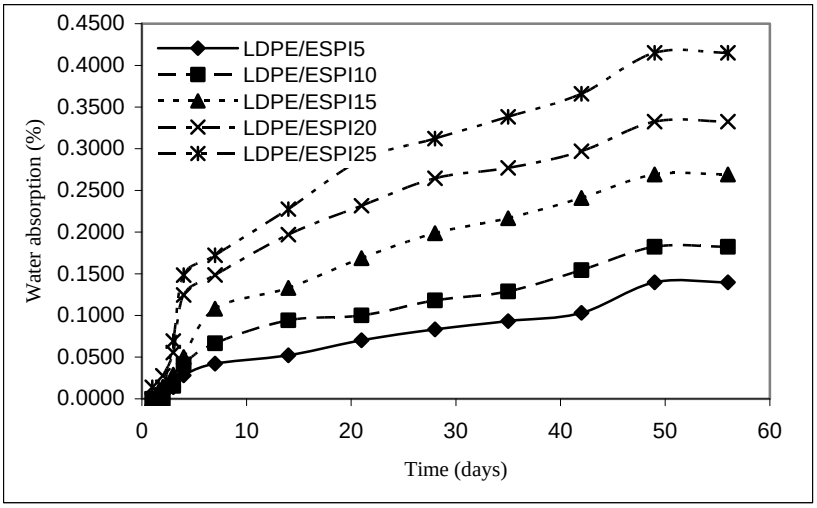

Figure 6: Water absorption versus time of LDPE/ESP_I composites with different filler loading.

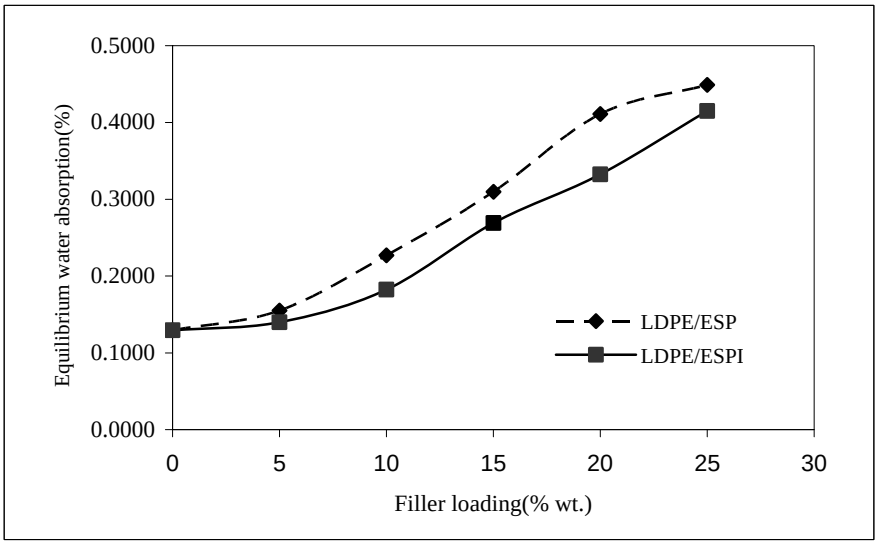

Figure 7: Percentage of equilibrium water absorption versus filler loading for LDPE/ESP and LDPE/ESP_I composites.

4. CONCLUSION

The influences of isopthalic acid as a coupling agent in the mechanical properties, morphology and water absorption in LDPE/ESP composites were investigated. Isopthalic acid enhanced the tensile strength, water absorption resistance, and equilibrium water absorption of the LDPE/ESP composites. Morphological studies on tensile fracture surfaces indicated that LDPE/modified ESP composites have higher strength and better interaction than LDPE/unmodified ESP composites.

5. ACKNOWLEDGMENTS

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