

THE EFFECT OF ACETIC ACID ON PROPERTIES OF COCONUT SHELL FILLED LOW DENSITY POLYETHYLENE COMPOSITES

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ABSTRACT

Natural lignocellulosics have an outstanding potential as reinforcement in thermoplastics. Coconut shell is one of natural lignocellulosic material. In this study, coconut shell (CS) was use as filler in low density polyethylene (LDPE) composites. The effect of surface treatment of coconut shell (CS) with acetic acid (acetylation) on mechanical properties, thermal properties and morphology were studied. The acetylation treatment has improved the tensile strength, elongation at break and Young's modulus of LDPE/CS composites. Thermogravimetric analysis (TGA) results show that the acetylated composites has better thermal stability compared to untreated composites at 600 °C. Differential scanning calorimetry (DSC) analysis showed that the esterification treatment increases the crystallinity of LDPE/CS composites. It was found that coconut shell acts as a nucleation agent in the presence of acrylic acid. The scanning electron microscopy (SEM) study of the tensile fracture surface of acetylated composites indicates that the presence of acetic acid increased the interfacial interaction.

Keywords: low density polyethylene, coconut shell, acetic acid, composites

INTRODUCTION

The use of natural plant fibres as reinforcement in polymer composites for making low cost engineering materials has generated much interest in recent years. The advantages of natural plant fibres over traditional glass fibres are acceptable as good specific strengths and modulus, economical viability, low density, reduced tool wear, enhanced energy recovery, reduced dermal and respiratory irritation and good biodegradability [1]. However, natural plant fibre reinforced polymeric composites, also have some disadvantages such as the incompatibility between the hydrophilic natural fibres and hydrophobic thermoplastic and thermoset matrices requiring appropriate use of physical and chemical treatments to enhance the adhesion between fibre and the matrix [2].

Chemical modification will be defined as a chemical reaction between some reactive part of a lignocellulosic cell wall polymer and a simple single chemical reagent, with or without catalyst, to form a covalent bond between the two [3]. The most important chemical modification involves coupling methods. The coupling agent used contains a chemical group, which can react with the fiber and the polymer [4]. Esterification is one of the chemical modifications undergone by the natural fiber. Most of the researches conducted on acetylated natural fiber have focused on improving the mechanical properties polymer composites [5-7]. Esterification by means of acetylation

is a chemical modification procedure, which has been studied extensively for lignocellulosic compounds [8-11]. Chemical modification with acetic and propionic anhydrides, substitutes the cell wall hydroxyl groups with acetyl and propionyl groups, rendering the surface more hydrophobic, and thus, more compatible to the polymer matrix. According to Rowell [8], the hydroxyl groups that react with the reagent, are those of lignin and hemicelluloses (amorphous material), while the hydroxyl groups of cellulose (crystalline material), being closely packed with hydrogen bonds, prevent the diffusion of the reagent and thus result in very low extents of reaction, if any. It has been shown that esterification improves the dispersion [12-14] of lignocellulosic materials in a polymer matrix [12,15-16], as well as the interface of the final composite [12,16].

Coconut shell is one of the most important natural fillers produced in tropical countries like Malaysia, Indonesia, Thailand, and Sri Lanka. Many works have been devoted to use of other natural fillers in composites in the recent past and coconut shell filler is a potential candidate for the development of new composites because of their high strength and modulus properties. Composites of high strength coconut filler can be used in the broad range of applications as, building, materials, marine cordage, fishnets, furniture, and other household appliances [17].

Thermal analysis (TA) means analytical experimental techniques which measure the thermal

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behavior of a composites material as a function of temperature. The manufacturing temperature and variety of applications in industry of composites are influenced by the thermal characteristics of the coconut shell particles and LDPE polymer in this study. Therefore, the thermal and viscoelastic properties of LDPE/CS composites were studied by using a thermal analyzer. Thermogravimetric analysis (TG) can measure the moisture content, thermal breakdown and thermal stability of LDPE/CS materials. DSC is the simplest and most widely used TA technique. Therefore, DSC can be used to measure the melting temperature (T_m) and glass transition temperature (T_g) of LDPE/CS composites in order to obtain information related with the crystallinity.

The aim of this study was to investigate the effects of chemical modification of coconut shell with acetic acid (acetylation) and filler content on mechanical properties, thermal properties and morphology of LDPE/CS composites. The thermal decomposition and thermal stability of LDPE/CS composites was examined using TGA. The melting temperature (T_m), and $\Delta H_{f, com}$ of the LDPE/CS composites were examined by DSC.

EXPERIMENTAL SECTION

Materials

Low density polyethylene used in this study was of injection molding grade, from The Polylefin Company (Singapore) Pte. Ltd (code F410-1) with MFI value of 5 g/10 min at 111 °C and density 0.923 g/cm³. Acetic acid was obtained from ChemAR, and coconut shell was obtained from local grocer, Perlis, Malaysia.

Instrumentation

A ball mill and Endecotts sieve was used for preparation of coconut shell. Preparation of composites was done using Z-Blade mixer and electrically heated hydraulic press. Characterization of the composite were done using Instron 5582 for measuring of tensile properties, SEM model JEOL JSM 6460 LA, Perkin Elmer Pyris Diamond TGA analyzer and Perkin Elmer DSC-7 analyzer.

Procedure

Preparation and acetylation of coconut shell

Coconut shell was cleaned from waste and crushed into small pieces. After soaked in water for 2 weeks, coconut shell pieces dried in a vacuum oven at 80 °C for 24 h to remove moisture and then ground to a powder.

Coconut shell powder was soaked in an acetic acid aqueous solution and stirred for 1 h, with filler to solution

ratio at 1 : 20 (w/v). Then coconut shell powder was filtered out, washed with water, and dried in an oven at 80 °C for 24 h. Milling and sieving was done to produce the average filler sizes of 44 μ m (density, 2.2 g/cm³).

Preparation of composite

Composites were prepared by mixing that was done at 180 °C and 50 rpm using Z-Blade mixer. LDPE was first charged to start the melt mixing. After 12 min, the filler was added and mixing continued until 25 min. At the end of 25 min, the composites were taken out and sheeted through a laboratory mill at 2.0 mm nip setting. The sample of composites was taken compression molded in an electrically heated hydraulic press. Hot-press procedures involved preheating at 180 °C and 150 kg/cm² for 6 min followed by compressing for 4 min at the same temperature and subsequent cooling under pressure for 4 min.

The formulation of LDPE/CS composites used in this study is shown in Table 1.

Measurement of Tensile Properties

Tensile tests were carried out according to ASTM D-638. Dumbbell specimens, 1 mm thick, were cut from the molded sheets with a Wallace die cutter. A cross head speed of 50 mm/min was used and the test was performed at 25 \pm 3 °C.

Morphology Study

Studies on the morphology of the tensile fracture surface of the composites were carried out using SEM. The fracture ends of the specimens were mounted on aluminum stubs and sputter coated with a thin layer of palladium to avoid electrostatic charging during examination.

Thermogravimetry Analysis

Thermogravimetry analysis of the composites was carried out with TGA analyzer. The sample weight about 15-25 mg were scanned from 50 to 600 °C using a nitrogen air flow of 50 ml/min and heating rate of 20 °C/min. The sample size was kept nearly the same for all tests.

Differential Scanning Calorimetry

Thermal analysis measurements of selected systems were performed using DSC. Samples of about 4 mg were heated from 25 to 250 °C using a nitrogen air flow of 50 mL/min and the heating rate of 10 °C/min. The melting and crystallization behavior of selected composites were also performed. The crystallinity (X_{com}) of composites was determined using the following relationship:

$$X_{com} (\% \text{ crystallinity}) = \frac{\Delta H_f}{\Delta H_f^0} \times 100\% \quad (1)$$

Table 1. Formulation of LDPE/CS composites with acetylation treatment

Materials	Composite 1 (without acetylation)	Composite 1 (with acetylation)
LDPE (phr)	100	100
Coconut Shell/CS (wt%)	0, 15, 30, 45, 60	15, 30, 45, 60
Acetic Acid (wt%)	-	50

Table 2. Chemical composition of coconut shell

Composition	Wt(%)
Cellulose	26.6
Lignin	29.4
Pentosans	27.7
Solvent Extractives	4.2
Uronic Anhydrides	3.5
Moisture	8.0
Ash	0.6

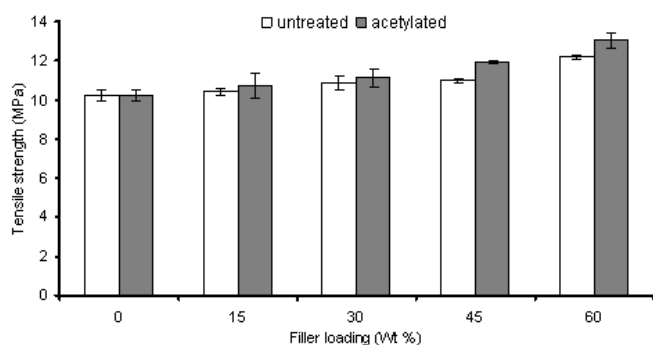
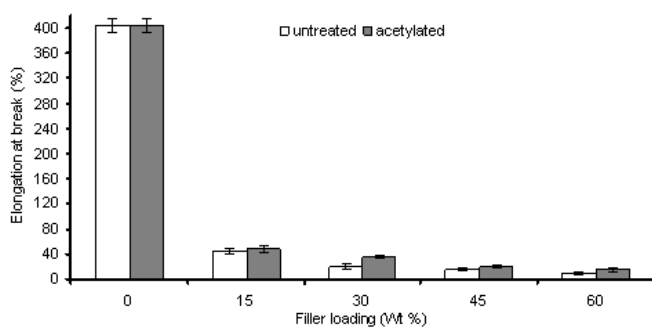
$$X_{LDPE} = \frac{X_{com}}{W_{fLDPE}} \times 100\% \quad (2)$$

where W_{fLDPE} is the weight fraction of LDPE in the composites.

RESULT AND DISCUSSION

The effect of filler loading on the tensile strength of untreated filler and acetylated filler on LDPE/CS composites are shown in Fig. 1. It can be seen that the tensile strength of the composites increases with increasing filler loading. The tensile strength of the composites increases due to the ability of the filler to support stress transferred from the matrix. Coconut shell as a filler has a high toughness and high lignin content. The bio-flour materials are mainly composed of a complex network of three polymers: cellulose, hemicellulose and lignin [20]. According to Kim et al. [21], lignin not only holds the bio-flour together, but also acts as a stiffening agent for the cellulose molecules within bio-flour cell wall. Therefore, the lignin and cellulose content of CS has an influence on the strength of CS and the tensile strength of composites. Kazayawoko et al. [22] and Ichazo et al. [23] found that lignin and waxes producing a rough surface and causing a fibrillation in the fibers of cellulose. This will enlarging the surface area of contact with the polymeric matrix which produces better fiber-matrix adhesion and increase mechanical properties. At similar filler loading, acetylated composites exhibit higher tensile strengths than untreated composite. This indicates that the chemical modification of coconut shell with acetylation has resulted in an improvement of the interfacial bonding and dispersion between the filler and matrix as shown later in SEM morphology. The presence of hydroxyl group on the surface of the CS fibers can promote the establishment of strong interaction between the acetic acid and the fillers, while the non polar part of acetic acid interacts with the polymer matrix.

The effect of acetylation on elongation at break is shown in Fig. 2. When the filler loading increased, more weak interfacial regions between the filler and the matrix are formed. The filler causes a dramatic decrease in the elongation at break, even when it is present in very low amount. This well-known decrease in elongation at break upon addition of rigid fillers arises from the fact that the actual elongation experienced by

**Fig. 1.** Effect of filler loading on tensile strength of untreated and acetylated LDPE/CS composites**Fig. 2.** Effect of filler loading on elongation at break of untreated and acetylated LDPE/CS composites

where ΔH_f and ΔH_f^0 are enthalpy of fusion of the system and enthalpy of fusion of perfectly (100%) crystalline LDPE, respectively. For ΔH_f^0 (LDPE) a value of 285 J/g was used for 100% crystalline LDPE homopolymer [18]. X_{com} , which is calculated using this equation, however, it only gives the overall crystallinity of the composites based on the total weight of composites including noncrystalline fractions, and it is not the true crystallinity of the LDPE phase. The value of crystallinity for LDPE phase (X_{LDPE}) of the LDPE fraction was normalized using Equation (2) as follows [19]:

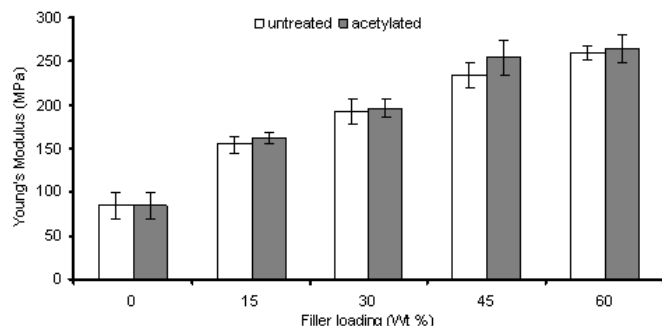


Fig 3. Effect of filler loading on Young's Modulus of untreated and acetylated LDPE/CS composites

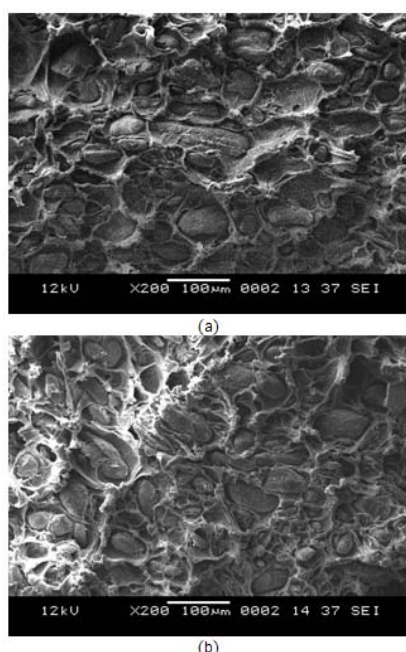


Fig 4. Scanning electron micrograph of the tensile fracture surface of untreated LDPE/CS composites (a) 30 wt% and (b) 60 wt% at a magnification of 200x

the polymeric matrix is much higher than that measured for the specimen [24]. Habibi et al. [25] in their research found that the elongation at break decreased upon fiber addition for both sets of composites regardless the nature of the fiber. The lignocellulosic fibers are responsible for the decrease of the deformation capability. The LDPE matrix provides ductility whereas the lignocellulosic fibers exhibit brittle behavior with a subsequent loss of toughness of the composite material. The elongation at break mainly depends on the fiber content. The acetylated composites exhibit higher elongation at break than untreated composites. The improvement in tensile strength (Fig. 1), elongation at break (Fig. 2), and Young's modulus (Fig. 3) of treated composites is a clear indication of improved adhesion at the interface between coconut shell and LDPE after

acetylation. Salmah et al. [4] also reported a similar result on The Effects of chemical modification of paper sludge filled PP/EPDM composites. Fig. 3 shows the effect of filler loading on Young's modulus of untreated and acetylated LDPE/CS composites. It is clear that the Young's' modulus increases with increasing coconut shell loading. It is known that filler, which has a higher stiffness than the matrix can increase the modulus of the composites, but generally cause a dramatic decrease in the elongation at break. At a similar filler loading, Young's modulus of acetylated composites exhibits the highest value than that of untreated composites. This result provides evidence that the stiffness of the LDPE/CS composites increases with the introduction of chemical treatment.

The scanning electron microscope was used to compare the tensile fracture surface of coconut shell filled LDPE composites containing 30 and 60 wt% of coconut shell. SEM micrograph of the fracture surfaces of untreated and acetylated composites are shown in Fig. 4. The micrograph of the untreated composite in Fig. 4 (a) and (b) indicates poor wetting of coconut shell by the LDPE matrix. The agglomeration of coconut shell particles in composites indicating interaction between those particles and it cause a low adhesion between coconut shell and LDPE matrix. As the amount of filler content increase, the tendency for filler-matrix interaction increases. Consequently, composites with higher filler content exhibit higher tensile properties such as tensile strength (Figure 1) and Young's modulus (Fig. 3).

The tensile fracture surfaces of acetylated composites are shown in Fig. 5. Fig. 5 (a) and (b) shows that there is less evidence of filler pull out and better interfacial adhesion between the filler and the matrix. The composite with acetylation has more homogeneous dispersion of filler and better wetting by compared to composites without acetylation.

The comparison of thermogravimetric analysis curve of untreated and acetylated LDPE/CS composites at 30 and 60 wt% of coconut shell is shown in Fig. 6. It can be seen as CS loading increased, the thermal stability and decomposition temperature of acetylated LDPE/CS composites decreased and the ash content of acetylated LDPE/CS composites increased. The graph exhibits that mass change occur from approximately 250–500 °C, which is due to the decomposition of three major constituents of the CS filler, namely cellulose, hemicellulose and lignin. According to Kim et al. [27], lignocellulosic materials are chemically active and decompose the chemically in the range of 150–500 °C, hemicellulose mainly between 150 and 350 °C, cellulose between 275 and 350 °C and lignin between 250–500 °C. At 500–600 °C, the ash content of LDPE/CS composites with 60 wt%

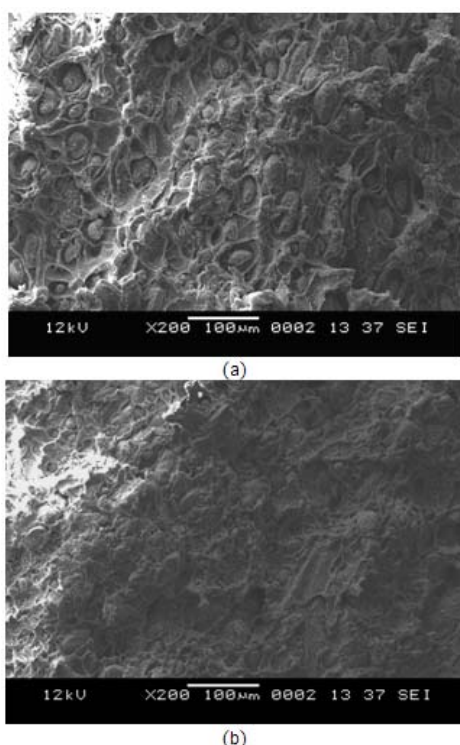


Fig 5. Scanning electron micrograph of the tensile fracture surface of (a) 30 wt% and (b) 60 wt% acetylated LDPE/CS composites at a magnification of 200x

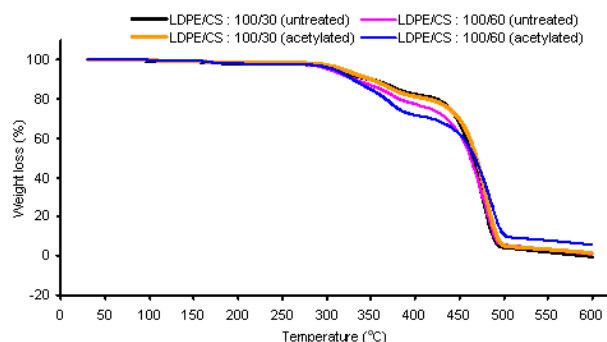


Fig 6. Comparison of thermogravimetric analysis curve of untreated and acetylated LDPE/CS composites at 30 and 60% coconut shell

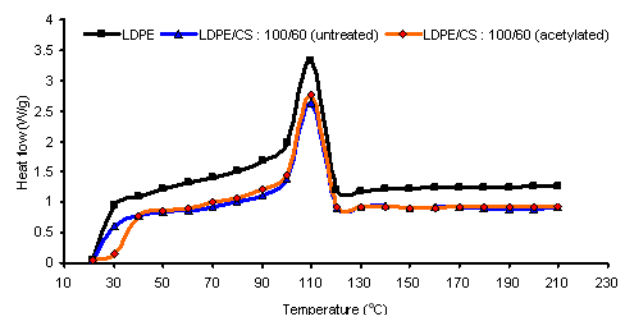


Fig 7. Comparison of differential scanning calorimetry (DSC) curve of untreated and acetylated LDPE/CS composites at 60 wt% coconut shell.

Table 3. Percentage weight loss of untreated and acetylated LDPE/CS composites at different filler loading and temperature

Temperature (°C)	Weight Loss (%)			
	LDPE/CS (30 wt%)		LDPE/CS (60 wt%)	
	(untreated)	(acetylated)	(untreated)	(acetylated)
100	0.089	0.045	0.090	0.083
150	0.528	0.378	0.532	0.438
200	1.490	1.189	1.790	1.996
250	1.665	1.165	2.060	2.106
300	3.277	2.416	4.448	3.847
350	9.792	9.717	13.049	15.135
400	17.496	18.415	22.471	28.189
450	31.503	30.129	37.647	37.841
500	95.621	94.701	94.117	89.053
550	97.994	96.799	96.601	91.945
600	99.701	98.587	99.057	94.143

coconut shell is higher than 100 LDPE/CS composites with 30 wt%.

From Table 3, it can be seen that the degradation temperature corresponding to the major total weight loss decreased with esterification treatment of the composites. The improved thermal stability of acetylated composites may be due to the fact that lignin, which is very poor in thermal stability, was separated from the coconut shell by acetylation. The acetylated composites have the highest thermal stability compared to untreated

composites. A similar observation was also reported Salmah et al. [4], who studied the effect of chemical modification of paper sludge filled polypropylene (PP)/ethylene propylene diene terpolymer (EPDM) composites.

Fig. 7 shows the differential scanning calorimetric (DSC) curve of untreated and acetylated LDPE/CS composites at 60 wt% of coconut shell. Table 4 summarizes the thermal parameter DSC of untreated and acetylated LDPE/CS composites at different filler

Table 4. The thermal parameter DSC of untreated and acetylated LDPE/CS composites at different filler loading

Composites	Melting Temperature T_m (°C)	$\Delta H_{f(\text{com})}$ (J/g)	X_{Com} (% crystallinity)	X_{LDPE} (%)
LDPE/CS:100/30 Untreated	109.86	65.45	22.96	29.85
Acetylated	109.32	69.14	24.25	31.53
LDPE//CS:100/60 Untreated	110.14	57.64	20.22	32.35
Acetylated	109.98	68.88	24.16	38.66

loading. It can be seen from Table 4 that the value of $\Delta H_{f(\text{com})}$ and X_{com} decreased with increasing coconut shell loading. This is due to the decrease in LDPE concentration at high coconut shell loading. At a similar filler loading, acetylated composites exhibit higher value $\Delta H_{f(\text{com})}$, X_{com} , and X_{LDPE} than untreated composites. The increase in crystallization of acetylated LDPE/CS composites might be due to the enhancement of coconut shell as a nucleation agent. However, the melting temperature decreases with acetylation treatment.

CONCLUSION

The acetylation treatment of LDPE/CS composites has improved the tensile strength, elongation at break, and Young's modulus compared to composites without acetylation. The higher tensile strength, elongation in break and Young's modulus was found on 60% filler loading. Scanning electron microscope showed that the interfacial interaction and adhesion between coconut shell and LDPE matrix were improved with chemical modification of coconut shell with acetic acid. The results from thermal properties show that the increasing of coconut shell loading increased the thermal stability and decrease crystallinity of LDPE/CS composites. TGA exhibit that the acetylation treatment increases thermal stability of LDPE/CS composites compare untreated composites. DSC analysis indicates that the acetylation treatment increases crystallinity of LDPE/CS composites.

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