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Mechanical, thermal and morphological properties of water-crosslinked wood flour reinforced linear low-density polyethylene composites

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Abstract

Wood flour (WF) reinforced linear low-density polyethylene (LLDPE) composites were prepared. Water-crosslinking technique was used to improve the physical properties of wood composite. Composites were compounded in a twin-screw extruder and treated with a coupling agent (vinyltrimethoxysilane, VTMOS), and then moisture-crosslinked in hot water. Composite after water-crosslinking treatment exhibited better mechanical properties than the non-crosslinked one because of the improved chemical bonding between the wood fiber and the polyolefin matrix. As the wood flour content reaches to 30 wt% and after water-crosslinking for 4 h, tensile strength and flexural strength are increased by 87% (14.7–27.5 MPa) and 137.5% (11.2–26.6 MPa) with respect to that of non-crosslinked ones. Scanning electron microscopy (SEM) of the fracture surfaces of water-crosslinked composites showed superior interfacial strength between the wood fiber and the polyolefin matrix. Thermal analyses of water-crosslinked composites indicate that thermal degradation temperature and heat deflection temperature of composite increase with the increasing water-crosslinking time. The heat deflection temperature of the composite can be raised from 55.7 to 88.5 °C.

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1. Introduction

Wood fiber composites have been extensively studied over the last two decades [1,2]. Natural wood flours have the potential for use as reinforcing fibers in thermoplastic resins. The primary advantages of these flours are their low cost, low density and resistance to breakage during processing [1]. Adding wood flour to thermoplastic resins can yield composite materials with increased strength and stiffness. However, in several cases, the wood flour requires their surfaces to be modified to enhance the strength of composites [2–8].

Due to the hydrophilicity of wood fiber and the nonpolar character of the polyolefin matrix, both wood fiber and polymeric matrix have to be chemically modified to improve interfacial compatibilization. Adding a suitable interface modifier will promote the stability of the morphology in incompatible polymer–fiber composites [6]. Such modifiers improve the composite morphology by more finely dispersing the discontinuous fiber in the dominant polymer matrix. In the present work, silane coupling agent was used as an interface modifier, which was chemically bonded to both the wood flour and the polymer matrix [7].

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Scott et al. first proposed water-crosslinking reaction of PE in 1972 [9] and the reaction received much intention recently [10–18]. Shieh et al. [19–24] studied the watercrosslinking reaction of different grades of polyethylene. The flame-retardant properties [25] and photoacoustic properties [26] have also been discussed. The advantage of this process are energy saving, low cost and higher productivity. Crosslinked polyethylene possesses better physical properties than general polyethylene [27], and also has become widely adapted for a number of industrial applications. Crosslinking with water is achieved by grafting polyethylene with silane followed by the hydrolysis to Si-OH groups and subsequently condensation to form Si-O-Si bonds [18]. The grafting of vinyltrimethoxysilane onto the polyethylene polymer chain is becoming more popular due to the low investment cost and high production rate of that process. This process is through free radical initiators and can subsequently condense through water, leading to the formation of crosslinking [3].

The purpose of this study is to investigate the effects of varied crosslinking time on the mechanical properties of the wood fiber/LLDPE composite. Since wood composite is usually used outdoor and under the environmental aging

Step 1

conditions, hence, the sunlight and moisture would further promote the water-crossling reaction of wood fiber/ LLDPE composite, consequently, improve some physical properties of this wood composite. The mechanism is described in reaction Scheme 1. To authors knowledge, this unique phenomenon has not been reported until now. Thermal degradation properties and heat deflection temperature of water-crosslinked wood composite were also investigated in this study.

2. Experimental procedure

2.1. Materials

Linear low density polyethylene (LLDPE) with a melt index of 2.0 was supplied by the Taiwan Polymer Corporation, Taiwan No. LL120. Wood flour is from maple tree (Acer spp), fiber length is about 150 μ m, fiber diameter is 20–30 μ m, apparent density 0.10–0.12 g/cm³, specific surface 3200 cm²/g, 180 mesh powder, was supplied by Zell-Wildshausen (Germany), its product name is CELLU-FLEX. Vinyltrimethoxysilane (VTMOS), No. Q9-6300, is produced by Dow Corning company, USA. Dicumyl



Step 2



Step 3



Scheme 1. The water-crosslinking reaction mechanism of wood fiber/LLDPE composite investigated in this study.

peroxide (DCP), No. PEROXIMON DC, was supplied by ELF ATOCHOEM, France. Di-*n*-butyltin dilaurate (DBTDL), No. T12, was supplied by Air Products Co., USA, is a catalyst to improve the water-crosslinking reaction.

2.2. Sample preparation

Wood flour was dried in an air oven at 100 °C for 4 h, until the moisture content was below 1.0 wt%. Wood flour with VTMOS silane coupling agent 2 phr (part per hundred parts of resin) surface treatment, 0.2 phr DCP and



Scheme 2. The screw configuration and the arrangement of kneading and conveying blocks of twin extruder.



Fig. 1a. FTIR spectra of 10 wt% wood fiber reinforced LLDPE composites for various water-crosslinking times.



Fig. 1b. FTIR spectra of 20 wt% wood fiber reinforced LLDPE composites for various water-crosslinking times.



Fig. 1c. FTIR spectra of 30 wt% wood fiber reinforced LLDPE composites for various water-crosslinking times.

0.15 phr T12 (DBTDL) were mixed by Hancel mixer, then was mixed with LLDPE pellets in a plasticizing extruder. The extruder is a twin screw co-rotating type extruder: with L/D = 43.5, and a low shear rate configuration (Scheme 2), a gravimetric feeder and side stuffer (section 6) were used for loading wood flour. The vacuum (section 9) was used during the extrusion process. The rotation speed is 80 rpm and barrel temperatures are 100, 115, 130, 135, 145, 160, 170, 155, 145, 140 and 140 °C from section 1 (primary feed) to die. Extruded material was cut into small pellets in a granulator. Dumb-bell shaped specimens were then injection moulded using a Battenfeld, Ba750 CD^{PLUS} injecting molding machine from dried pellets at a mould temperature of 160-190 °C. The maximum injection pressure was 100 bar and the hold pressure was 10 bar.

Some of the specimens were subsequently subjected to water-crosslinking with different crosslinking times. They were placed in isothermal water bath at 70 °C for 0.5, 1, 2, 4 h to proceed water-crosslinking reaction.

2.3. Measurement

FTIR spectra of wood flour reinforced LLDPE composites were recorded between 400 and 4000 cm⁻¹ with a Nicolet Avatar 320 FT-IR spectrometer, Nicolet Instrument Corporation, Madison, WI, USA. Samples were placed on the ATR attachment and a minimum of 32 scans were averaged with a resolution of 2 cm^{-1} within the 400– 4000 cm⁻¹ range. The characteristic absorption peaks of functional group were detected and monitored during the water-crosslinking reaction.



Fig. 2a. Tensile strength of wood fiber reinforced LLDPE composites with or without silane treatment.



Fig. 2b. Tensile strength of silane treated wood fiber reinforced LLDPE composites with various wood fiber contents for various water-crosslinking times.

The mechanical properties of dumb-bell shaped specimens were measured on an Instron Model 4468 machine. Tensile test procedures followed the ASTM D638-98 method [28] with a crosshead speed 20 mm/min. The dimensions of the samples were $25.0 \times 10.0 \times 1.4$ mm (length × width × thickness). Six specimens were tested in each case. Flexural tests were following the ASTM D790-98 method [29] with a span-to-depth ratio of 40 and crosshead speed of 1.0 mm/min. Notched impact strength was tested according to ASTM D256-97 method [30] and a TMI Testing Machine (TMI Co. USA) was used (the dimensions of these samples were 63.0 mm × 12.7 mm × 3.2 mm (length × width × thickness)). All tests were performed at ambient temperature of 25 ± 2 °C.

Impact fractured surfaces of the composites were used for scanning electron microscope (SEM) studies using a TOP-CON microscope (Model SM-300, Japan). The fractured surfaces were sputter coated with gold prior to scanning.

Heat deflection temperature (HDT) was measured by a TOYOSEIKI S-6 M HDT tester, and followed the ASTM D648-98 C method [31]. The loading pressure was 4.6 kgf/ cm^2 , and the heating rate was 120 K/h.

Thermo-oxidative degradation of these composites was measured by a TGA instrument (Du-Pont-951) from room temperature to 600 °C with a heating rate of 10 K/min under the air atmosphere. The measurements were conducted using 6-10 mg samples. Weight-loss versus temperature curves were recorded.



Fig. 3a. Tensile elongation of wood fiber reinforced LLDPE composites with or without silane treatment.



Fig. 3b. Tensile elongation of silane treated wood fiber reinforced LLDPE composites with various wood fiber contents for various water-crosslinking times.

3.1. Spectroscopy analysis

Figs. 1a, 1b and 1c show the FTIR spectra for 10, 20, and 30 wt% wood fiber reinforced composites, respectively for various water-crosslinking times. The spectra are shifted vertically for clarity. It is well known that the changes in IR absorption peak heights may be due to actual changes in the chemical composition of composite. From Figs. 1a, 1b and 1c, it can be seen that the absorption band of Si–O–Si appears at 1020 cm^{-1} , and the peak become stronger with a longer water-crosslinking time. Another absorbance band appears at 1580 cm^{-1} , apparently associated with $R-CH_2-R'$ bonds introduced on the main chain of LLDPE during the grafting process, it represents the increase of water-crosslinking time can generate more $-CH_2CH_2Si-O-Si$ bonding on the LLDPE main chain.

3.2. Tensile properties

Fig. 2a illustrates the tensile strengths of wood flour reinforced LLDPE composites with and without silane coupling agent treatment. Composites with high wood fiber content and treated with interface modifiers exhibited better tensile strength than the untreated ones. Fig. 2b shows the tensile properties of wood flour reinforced LLDPE



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Fig. 4a. Flexural strength of wood fiber reinforced LLDPE composites with or without silane treatment.



Fig. 4b. Flexural strength of silane treated wood fiber reinforced LLDPE composites with various wood fiber contents for various water-crosslinking times.

composites with 10, 20 and 30 wt% wood fiber content for various water-crosslink times. Composites treated with water-crosslinking reaction exhibited better tensile strength than the untreated one (after 4 h water-crosslinking treatment, the tensile strength of 30 wt% wood composite increased from 14.7 to 27.5 MPa , which corresponds to an 87% increase). The increase in tensile strength is due to the crosslinking network formation between the fibers and the polymer matrix, i.e. LLDPE polymer chains. Results suggest that modifying the polymer or fiber surface could enhance the compatibility of hydrophobic polymer and hydrophilic cellulose fiber. Longer water-crosslinking time could improve the tensile strength of wood composite.

Results of tensile elongation are illustrated in Figs. 3a and 3b. Although the silane coupling agent treatment and water-

crosslinking reaction could improve the tensile strength of composite, tensile elongation property of composite will be reduced, due to the crosslinking network (chemical bonding) between the flexible LLDPE matrix and stiff wood fiber or between the LLDPE inter-molecular chains.

3.3. Flexural properties

Figs. 4 and 5 show the flexural strengths and flexural moduli of wood flour reinforced LLDPE composites with wood fiber content of 10 wt%, 20 wt% and 30 wt% and for different water-crosslinking times. Adding wood flour to the LLDPE matrix markedly increased the initial flexural strength and flexural modulus of the composites. The results of flexural strength testing are similar to that



Fig. 5a. Flexural modulus of wood fiber reinforced LLDPE composites with or without silane treatment.



Fig. 5b. Flexural modulus of silane treated wood fiber reinforced LLDPE composites with various wood fiber contents for various water-crosslinking times.

of tensile strength testing, composites with high wood fiber content and treated with interface modifiers exhibited better flexural strength than the untreated ones. Longer watercrosslinking time could significantly improve the flexural strength (from 11.2 to 26.6 MPa, which corresponds to an increase of 137.5% after 4 h water-crosslinking treatment) and flexural modulus (from 213.8 to 614.6 MPa, which corresponds to an increase of 187.5% after four hours water-crosslinking treatment).

3.4. Impact properties

Figs. 6a and 6b show the notched impact strength of wood flour reinforced LLDPE composites. The results of

impact property testing are similar to that of tensile elongation testing. Composites with high wood fiber content possesses low impact strength. Wood flour is a kind of stiff organic filler, comparing to LLDPE, so adding wood flour could decrease the impact strength of composite. Composite treated with interface modifiers exhibited better impact strength than the untreated ones since the debonding behavior between the interface of wood flour and LLDPE matrix absorb larger impact energy in modified composites than the unmodified ones. Longer water-crosslinking time show no effect on the impact strength of wood composite. Crosslinking reaction can limit the shear deformation behavior of polymer matrix and slightly decrease the impact strength of wood flour reinforced LLDPE compos-



Fig. 6a. Izod impact strength of wood fiber reinforced LLDPE composites with or without silane treatment.



Fig. 6b. Impact strength of silane treated wood fiber reinforced LLDPE composites with various wood fiber contents for various water-crosslinking times.

ite, however, crosslinking reaction can also strengthen the interface between wood flour and LLDPE matrix, that help the impact energy transfer from matrix to reinforcement, then the impact strength could increase. These two effects compete each other, consequently, the impact strengths of composites have no significant change after water-crosslinking reaction.

3.5. Fractured surface morphology

Figs. 7a and 7b show the morphology of the fracture surface of water-crosslinked wood composite. Form Fig. 7a, one can find that there still some LLDPE resin attached on the surface of wood flour. From Fig. 7b, it can be seen that fibers were pulled out and broken during the fracture of the composite, but there are still some strong adhesion bonding between the polymer matrix and the wood fiber. This finding suggests that the adhesion between the matrix and fiber is very good. Accordingly,



Fig. 7a. SEM microphotograph of the fracture surfaces of 2 h watercrosslinked wood fiber (30tw%)/LLDPE composites ($\times 200$).



Fig. 7b. SEM microphotograph of the fracture surfaces of 2 h watercrosslinked wood fiber(30 wt%)/LLDPE composites (×1500).



Fig. 7c. SEM microphotograph of the fracture surfaces of 30 wt% virgin wood fiber/LLDPE composites (×200).

the interfacial strength is improved. Comparing with the fracture surface of untreated wood flour composite, as shown in Fig. 7c, the surface of wood flour is very clean and with no LLDPE resin attached indicating that there is no bonding between wood flour and LLDPE matrix.

3.6. Heat deflection temperature (HDT)

Figs. 8a and 8b illustrate the heat deflection temperature of wood flour/LLDPE composites. The figures reveal that the heat deflection temperature of the composite increases with the wood flour content. As the wood flour content approached 30 wt%, the heat deflection temperature of the composite increases from 55.7 to 79.1 °C. Composite with silane treatment exhibits a higher heat deflection temperature, for example, the heat deflection temperature of 30 wt% treated wood flour/LLDPE composite is 83.2 °C (increase by 49.4%). From Fig. 8b, it can be seen that the composite treated for longer water-crosslinking time exhibits higher heat deflection temperature, since better chemical bonding exists between the wood fiber and the polyethylene matrix. After 4 h water-crosslinking reaction, the heat deflection temperature of the 30 wt% wood flour composite increased from 55.7 to 88.5 °C (an increase by 58.9%).

3.7. Thermal degradation properties

Figs. 9a, 9b and 9c summarize the TGA curves of 10, 20 and 30 wt% wood fiber reinforced LLDPE composites respectively. It reveals that the onset temperature of thermal degradation increased when the water-crosslinking time increased. The thermal stability of composite is greatly improved by water-crosslinking reaction, compared with the pure LLDPE resin. For example, the temperatures of the 10% weight loss for pristine LLDPE and the 10 wt% wood flour/LLDPE composite with 4 h water-crosslinking reaction are 420.4 and 459.2 °C, respectively. The results suggest that the crosslinking reaction can raise the temperament limit of composite in practical application.



Fig. 8a. Comparison of the heat deflection temperature of wood fiber reinforced LLDPE composites.



Fig. 8b. Comparison of the heat deflection temperature of silane treated wood fiber reinforced LLDPE composites.



Fig. 9a. TGA curves of 10 wt% wood fiber reinforced LLDPE composites during various water-crosslinking times.



Fig. 9b. TGA curves of 20 wt% wood fiber reinforced LLDPE composites during various water-crosslinking times.



Fig. 9c. TGA curves of 30 wt% wood fiber reinforced LLDPE composites during various water-crosslinking times.

4. Conclusions

This study demonstrated that wood flour could be successfully used as a reinforcing fiber material in a linear low-density polyethylene. Silane coupling agent improves the compatibility between wood fiber and LLDPE resin. Water-crosslinking technique is an effective method to improve the physical properties of wood composite.

Tensile strength, flexural strength and flexural modulus are significantly increased with increasing wood flour content and water crosslinking time, however, tensile elongation and notched impact strength decreases with the increasing of wood flour content and water crosslinking time. The morphology (SEM) indicates that the composites treated with silane modifiers and water-crosslinking process exhibit much better bonding between fiber and matrix. Heat deflection temperature increases with the increasing of wood fiber content and water-crosslinking time. Thermal degradation temperature raises as the water-crosslinking time increases.

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