Preparation and Performance Evaluation of PLA/Coir Fibre Biocomposites

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Alkali-treated coir fibers were modified by silane coupling agent in a microwave oven. The use of microwave-assisted chemical treatments efficiently promoted the esterification reaction to improve the interfacial adhesion between the coir fibers and PLA matrix. Effects of the treated coir fiber content (1 wt.% to 7 wt.%) on the surface morphology and tensile, impact, and thermal properties of PLA/coir fiber biocomposites (AKWCF/PLAs) were evaluated. At a coir fiber content of 1%, the AKWCF/PLAs showed a remarkable increase of 28% in the percentage impact strength, while the tensile strength and breaking strength decreased with increasing coir fibre content. The thermal stability of the AKWCF/PLAs worsened and the degree of crystallinity increased with increasing fiber content. The decreased cold crystallization temperatures of AKWCF/PLAs further confirmed the role of coir fibers treated with the new combined method as an effective nucleating agent.

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INTRODUCTION

The development of degradable biocomposites is expected to ease the current pressures caused by global environmental pollution and resource depletion (Mohanty *et al.* 2000; Gross and Kalra 2002). Polylactic acid (PLA) is a type of biodegradable polymer that currently represents one of the important directions of research and application (Lim *et al.* 2008; Luckachan and Pillai 2011; Babu *et al.* 2013). However, the application of PLA polymer has been limited due to its brittle physical properties (Cohn and Salomon 2005).

Natural fibres, such as flax, sisal, hemp, jute, kenaf, bamboo, and coir, have been used as reinforcements to improve the overall performance of PLA biocomposites (Bodros *et al.* 2007; Graupner *et al.* 2009; Faruk *et al.* 2014; Siengchin 2014; Qian *et al.* 2015; Ramamoorthy *et al.* 2015; Orue *et al.* 2016; Pickering *et al.* 2016). Coir fibre has drawn significant attention due to its abundance, renewability, low thermal conductivity, and high toughness, *etc.* (Babu *et al.* 2013). The PLA biocomposite reinforced with coir fiber is an ideal candidate for environmentally friendly materials and can offer other benefits, *e.g.*, enhanced mechanical and thermal properties, excellent biodegradability, and conservation of resources (Shibata *et al.* 2003; Tayommai and Ahtong 2010). Therefore PLA biocomposite is expected to be widely used in several applications, such as food packaging, water and milk bottles, degradable plastic bags, *etc.* (Jonoobi *et al.* 2010). However, coir fibre is a polar, hydrophilic fibre because of the hydroxyl groups on its surfaces (Pickering *et al.* 2016). This property prevents the fibres from interacting with nonpolar-hydrophobic polymers, including PLA. Thus, it is necessary to improve the compatibility and interfacial bonding between coir fibres and the PLA matrix by surface or structure modification of

natural fibres using chemical and physical methods, such as alkali treatment, acetylation, application of coupling agents, or microwave radiation (Mohanty *et al.* 2000; Oksman *et al.* 2003; John *et al.* 2008; Faruk *et al.* 2012; Faruk *et al.* 2014; Ramamoorthy *et al.* 2015; Pickering *et al.* 2016).

The microwave irradiation method has been found to be economical, energy efficient, rapid, and environmentally friendly (Woldesenbet *et al.* 2012). It is found that the microwave-assisted process enhances the esterification reaction between silane coupling agents and fibers compared to that of the conventional heating (Li *et al.* 2014). Several researchers also have reported that an alkali treatment results in a higher amount of cellulose exposed on the fibre surface, thereby increasing the number of possible reaction sites for silane coupling agents (Bismarck *et al.* 2001; Rout *et al.* 2001b; Choudhury *et al.* 2007; Rahman and Khan 2007).

Over the past decade, researchers have explored microwave-assisted pretreatment of natural fibers as an alternative to conventional heating. Hashemi *et al.* (2010) investigated the effect of the polypropylene (PP) composites reinforced by bagasse fibers. The fiber coating was performed by mixing of silane coupling agents with fibers and cured in a microwave oven in the presence of catalyst. It was observed that fiber adhesion and dispersion to matrix were improved by the combined treatment. As a result, tensile strength and tensile modulus of treated PLA biocomposites were improved relative to those of the untreated counterparts. Akhtar *et al.* (2015) treated oil palm empty fruit bunches by using microwave-assisted dilute acid/alkali method. Their results showed this pretreatment was an efficient and rapid method of removing lignin and hemicelluloses. Applications of microwave-assisted pretreatment have been reported on switchgrass (Hu *et al.* 2008) and rice straw (Ma *et al.* 2011).

This study conducted an initial investigation on how the content of treated coir fibres affects the reinforcement of AKWCF/PLAs. Here, the coir fibres received a combined treatment of alkali, a silane coupling agent, and a microwave irradiation. It was anticipated that this new pretreatment of coir fibres would be effective for enhancing the fibre matrix adhesion, mechanical properties, and thermal stability of PLA-based biocomposites. The mechanical properties of the AKWCF/PLAs were studied using tensile testing and impact testing. Furthermore, the thermal properties were studied using dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The morphology was also studied using scanning electron microscopy (SEM).

EXPERIMENTAL

Materials and Fibre Treatments

Poly lactic acid 4032D from Natureworks LLC. (Minnetonka, USA) with a density of 1.24 g/cm^3 and melting point of 160 °C was used as the matrix. Brown coir fibres with a density of 1.15 g/cm^3 and fibre diameter in the range of 150 µm to 250 µm were supplied by Tianjin Jia Add Green Products Technology Co., Ltd. (Tianjin, China).

First, all coir fibres were pre-washed with distilled water and dried at 60 °C until they reached constant weight. Next, the coir fibres were chopped into lengths of approximately 4 mm to 6 mm and sieved through a 40-mesh sieve. Then, coir fibres (300 g) were added to a 1 L solution containing 160 mL (30%; w/w) of hydrogen peroxide and 0.5 g of sodium hydroxide at 85 °C and magnetically stirred for 1 h. These fibres were then

removed from the solution and washed thoroughly with distilled water again and oven-dried at 60 °C until they reached constant weight. The treated fibres (250 g) were immersed in a 1 L solution containing 600 mL of ethanol, 400 mL of distilled water and 10 mL of silane coupling agent KH560 (Zhonghao Chenguang Research Institute of Chemical Industry, Zigong, China), placed in a microwave oven (2450 MHz, 800 W, 5 min). Lastly, the treated fibres were washed thoroughly with distilled water again and oven-dried at 60 °C until they reached constant weight.

Sample preparation

The prepared compositions and processing conditions are summarized in Table 1. The compounding was performed in a DSE-25 counter-rotating twin-screw extrusion machine (Brabender, Duisburg, Germany) with a screw diameter of 25 mm and an L/D ratio of 30 in the mixing mode screw configuration. The barrel temperature was in the range of 160 °C to 190 °C, and the screw speed was fixed at 30 rpm. The extruded material was cooled in air and then granulated in a cutting mill to produce composite pellets with dimensions of 4 mm to 5 mm. In addition, all obtained pellets were then injected into an injection moulding machine SY-200-1 (Yiyang Plastic Machinery Co., Ltd., Wuhan, China) in which the screw diameter was 22 mm. The injection time was 5 s and the cooling time was 20 s at 180 °C. The AKWCF/PLAs presented a compact morphology with no evidence of macroscopic pores or voids. Neat PLA samples and AKWCF/PLAs were placed in a desiccator at room temperature for at least 48 h.

Table 1. Composite Compositions

Code	PLA (wt.%)	Coir Fibres (wt.%)	Extrusion	
			Temperature Profile (°C)	Mortar (rpm)
Neat PLA	100	0	160,170,180; 190; 185,180	30
1 wt.% AKWCF/PLA	99	1	160,170,180; 190; 185,180	30
3 wt.% AKWCF/PLA	97	3	160,170,180; 190; 185,180	30
5 wt.% AKWCF/PLA	95	5	160,170,180; 190; 185,180	30
7 wt.% AKWCF/PLA	93	7	160,170,180; 190; 185,180	30

Methods

Differential scanning calorimetry

The DSC measurements were performed on a DSC1 Star (Mettler-Toledo, Zurich, Switzerland) under nitrogen flow. Approximately 5 mg of the polymer was placed on an aluminium pan for sampling. The heating temperature was ramped from 30 °C to 210 °C at a rate of 10 °C/min. The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m), degree of crystallinity (X_c), and enthalpy of melting (ΔH_m) were determined.

Thermogravimetric analysis

The thermal stability of neat PLA and AKWCF/PLAs was analysed at up to 500 °C under a purging nitrogen gas with a flow rate of 200 mL/min using TGA/SDTA851e (Mettler-Toledo, Zurich, Switzerland). Approximately 6 mg to 10 mg of each specimen

was loaded for each measurement at a heating rate of 10 °C/min. The TGA and differential thermal analysis (DTA) curves were recorded.

Thermal and dynamic mechanical properties

The dynamic mechanical properties of the neat PLA and AKWCF/PLAs were determined using a DMA Q800 dynamic mechanical analyser (TA Instruments, New Castle, DE, USA) in 3-point bending mode. The measurements were performed at a constant frequency of 1 Hz over a temperature range from -50 °C to 150 °C at a heating rate of 3 °C/min. The test specimen dimensions were approx. 60 mm × 10 mm × 4 mm (length × width × thickness). The presented data are based on three measurements.

Mechanical tests

Then, the tensile properties of both neat PLA and AKWCF/PLAs with different fibre mass content were measured according to China's National Standard GB/T1040 (2006) using an RGM-4005 electronic tensile machine (Shenzhen Instrument Co., Ltd., Shenzhen, China) with a load cell of 5 kN. The mould had a dog bone shape with dimensions of 150 mm × 20 mm × 4 mm (length × width × thickness). All of the tensile tests were conducted at room temperature with a strain rate of 5 mm/min. The mean values of the tensile properties of each composite were obtained from five test specimens.

Impact tests were performed on an XCJ-40 impact testing machine (Chengde Jinjian Testing Instrument Co., Ltd., Chengde, China). The dimensions of the specimens were 80 mm × 10 mm × 4 mm (length × width × thickness). The impact strengths of the samples were tested according to China's National Standard GB/T1843 (2008).

Electron microscopy

The surface morphology of coir fibres and fractured impact specimens of AKWCF/PLAs was analyzed by a Hitachi SU8020 (Tokyo, Japan) at 15 kV and a magnification of 10,000. It was used to correlate the material structure with the mechanical properties through investigating the interfacial bonding between the coir fibres and PLA matrices.

RESULTS AND DISCUSSION

DSC Analysis

The resulting degree of crystallinity (X_c) was calculated based on the following equation,

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times \frac{100\%}{w} \tag{1}$$

where ΔH^0_m is the heat of fusion for a 100% crystalline PLA material ($\Delta H^0_m = 93$ J/g) and w is the weight fraction of the PLA matrix in the AKWCF/PLA. The thermal properties of all samples were measured in triplicate.

The DSC-derived thermal characteristics are shown in Fig. 1 and Table 2. With the addition of coir fibres, the glass transition temperature (T_g) and crystallinity degree (X_c) of AKWCF/PLAs increased, while the crystallization temperature (T_c) decreased relative to the values associated with neat PLA. The increase in the T_g of PLA in the presence of coir

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fibres could have been explained by the coir fibres that played a role as cross-linking points in the AKWCF/PLAs. A growing number of cross-linking points led to a lower free volume of the PLA polymer. Accordingly, the movements of the molecular chain were restricted at a higher level, which implied that the molecular chains must absorb more heat from the environment to break loose. The T_g of AKWCF/PLAs increased gradually but only minimally. Neat PLA had a T_c of 110 °C, and the T_c of AKWCF/PLAs was approximately 106 °C, which showed that the latter shifted toward a lower temperature with the addition of coir fibres due to reactive blending. This result confirmed that the coir fibres created favourable conditions for PLA crystallization and thus increased the crystallization rate. The X_c of AKWCF/PLA increased continuously with increased coir fibre content, which indicated that the addition of coir fibres was favourable for PLA crystallization and consequently that the crystallization rate was accelerated. In summary, the coir fibres were confirmed to act as an effective nucleation agent during the melt crystallization process of the blends.

Table. 2. Thermal Properties of Neat PLA and AKWCF/PLA

| Sample	T_g (°C)	$T_{o,c}$ (°C)	$T_{p,c}$ (°C)	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	$\Delta H_{c,PLA}$ (J/g)	$\Delta H_{m,PLA}$ (J/g)	X_c (%)
Neat PLA	63.33	101.17	117.67	110.00	158.83	176.67	4.21	4.97	5.35
1 wt.% KCFB	63.50	96.83	114.50	106.83	156.17	175.17	4.41	5.08	5.52
3 wt.% KCFB	63.67	98.50	113.83	106.67	155.17	173.00	4.17	5.04	5.59
5 wt.% KCFB	64.33	97.50	113.50	106.17	155.00	172.00	4.30	5.00	5.66
7 wt.% KCFB	64.83	97.67	113.17	106.00	153.17	169.50	3.66	4.64	5.36
Note: T_g -glass transition temperature, $T_{o,c}$ -crystallization onset temperature, $T_{p,c}$ - crystallization quench temperature, T_c - crystallization peak temperature, T_{m1} -low melting temperature, T_{m2} - high melting temperature, $\Delta H_{c,PLA}$ - crystallization enthalpy, $\Delta H_{m,PLA}$ -melting enthalpy, and X_c - crystallinity									
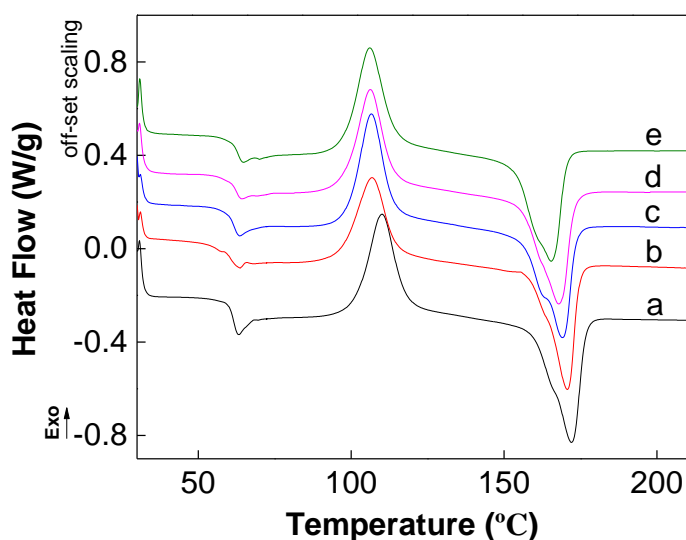
Fig. 1. DSC thermograms of PLA and its biocomposites: (a) Neat PLA, (b) 1 wt.% AKWCF/PLA, (c) 3 wt.% AKWCF/PLA, (d) 5 wt.% AKWCF/PLA, and (e) 7 wt.% AKWCF/PLA

TGA Results

   The results of the thermogravimetric analyses for untreated and treated coir fibres are shown in Fig. 2 (TG and DTG curves) and summarized in Table 3. As evident from the derivative thermogram (DTG), it was clear that the untreated coir fibres exhibited three-step decomposition (Rosa *et al.* 2009a,b) and that treated coir fibres exhibited two-step decomposition. There was a similarity between the materials in that the first maximum decomposition temperature occurred at approximately 73 °C due to the evaporation of water. The start of the second decomposition step of untreated coir fibres ranged from 150 °C to 323 °C, which corresponded to the degradation of small molecules such as pectin, wax, and hemicellulose. Unlike the untreated coir fibres, there was no peak within this temperature range for the treated coir fibres because these small molecules were removed after the alkali solution and microwave pretreatment. The subsequent peaks of the two curves for the untreated and treated fibres appeared at 366 °C and 329 °C, respectively, which corresponded to the thermal degradation of cellulose.

Table 3. TGA Peak Data for Untreated and Treated Coir Fibres

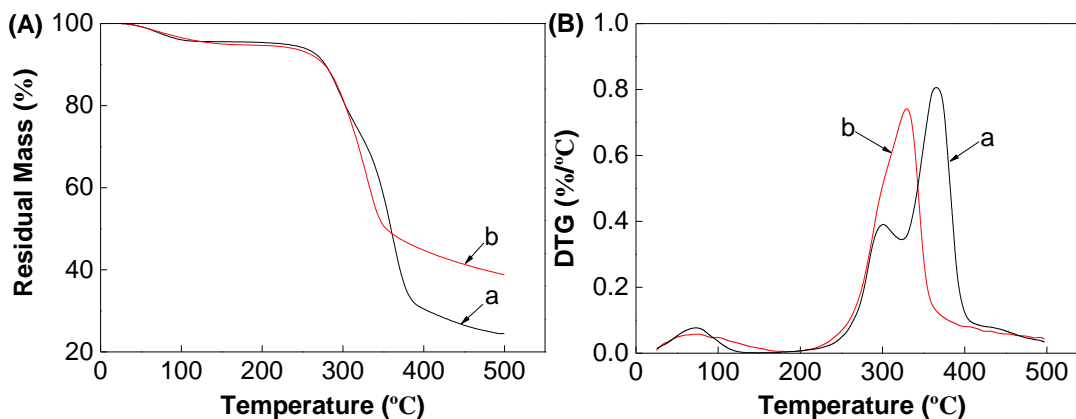| Code	Transition Temperature Range (°C)	Temperature of Maximum Rate of Weight Loss (°C)	Weight Loss (%)
Untreated Fibre	25 to 150	73	2
Untreated Fibre	150 to 323	300	16
Untreated Fibre	323 to 500	366	51
Treated Fibre	25 to 182	75	2
Treated Fibre	182 to 500	329	37

Fig. 2. TGA and DTGA curves of untreated and treated coir fibres: (a) Untreated coir fibres and (b) treated coir fibres

   As depicted in Fig. 3 and Table 4, the neat PLA showed a degradation peak at 388 °C, while in the AKWCF/PLAs, the authors observed a peak shift to lower temperatures of 379 °C, 379 °C, 377 °C, and 363 °C for fibre contents of 1 wt.%, 3 wt.%, 5 wt.%, and 7 wt.%, respectively. Evidently, increasing the fibre content decreased the thermal stability of AKWCF/PLAs due to the lower degradation temperature of coir fibres (Rosa *et al.* 2009a). Similar results were found by de Rosa and Albano, who investigated the properties of PLA biocomposites reinforced with *Phormium* fibres and sisal fibres (Albano *et al.* 1999; De Rosa *et al.* 2011).
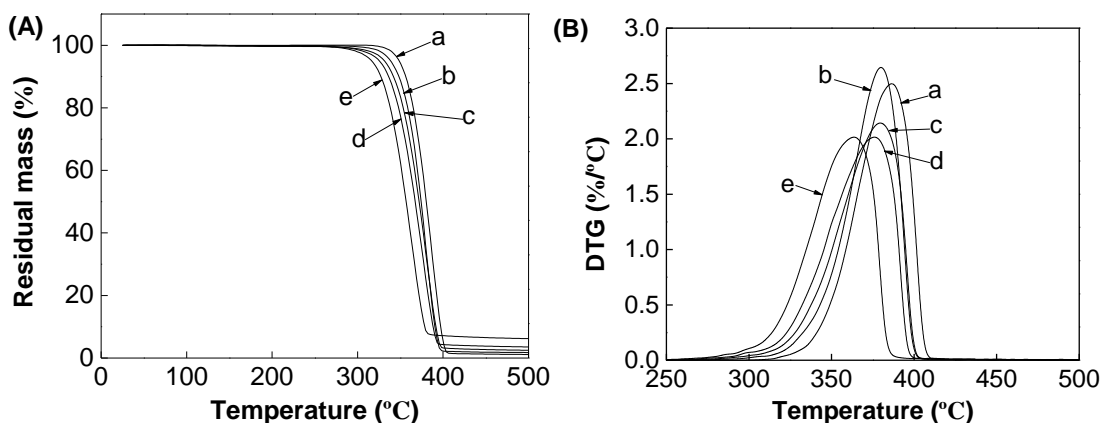
Fig. 3. TGA and DTGA curves of (a) neat PLA, (b) 1 wt.% AKWCF/PLA, (c) 3 wt.% AKWCF/PLA, (d) 5 wt.% AKWCF/PLA, and (e) 7 wt.% AKWCF/PLA

Table 4. TGA Peak Data for Neat PLA and AKWCF/PLA

Code	Transition Temperature Range (°C)	Temperature of Maximum Rate of Weight Loss (°C)	Weight Loss (%)
Neat PLA	302 to 417	388	68
1 wt.% AKWCF/PLA	250 to 417	379	64
3 wt.% AKWCF/PLA	250 to 411	379	66
5 wt.% AKWCF/PLA	250 to 411	377	69
7 wt.% AKWCF/PLA	250 to 400	363	64

DMA Analysis

Figure 4 shows a plot of the storage modulus (E') and loss factor (tan δ) against temperature for the neat PLA and AKWCF/PLAs; the T_g was calculated from the tanδ peak temperature and is summarized in Table 5. As observed from the storage modulus curves of Fig. 4a, at room temperature (25 °C), the E' values for all AKWCF/PLAs were higher than that of the PLA matrix. This finding indicated that the treated coir fibres played a role as a nucleating agent, which resulted in an effective stress transfer from the coir fibres to the PLA matrix. Furthermore, it was observed that the E' value of the AKWCF/PLAs gradually increased with increased content of treated coir fibres with temperature, which implied an increase in the thermal stability of AKWCF/PLAs and efficient interfacial adhesion between the fibres and the matrix. Within the range of 50 °C to 70°C, all of the AKWCF/PLAs showed a sharp drop in the E' value due to the glass transition of PLA and then a noticeable increase in the E' value after surpassing 90 °C. This effect was a result of cold crystallization of amorphous PLA. Table 5 shows the temperature at which cold crystallization began for the AKWCF/PLAs. The downward trend of T_c indicated that the addition of treated coir fibres was favourable for inducing crystallization of the AKWCF/PLAs. The same trend was recorded by the DSC analysis. In all of the cases, the pretreatment of coir fibres was shown to be effective.

The parameter tanδ is important and related to the dynamic behaviour of AKWCF/PLAs. As shown in Fig. 4b, the tanδ peaks of the AKWCF/PLAs reinforced with

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treated coir fibres all shifted to higher temperatures relative to that of the PLA matrix. The result indicated some type of interaction between the fibres and PLA matrix due to the silane coupling agent. It was possible that the silane coupling agent acted as a compatibilizer for the AKWCF/PLA system.

Table 5. Dynamic Mechanical Properties of Neat PLA and AKWCF/PLA

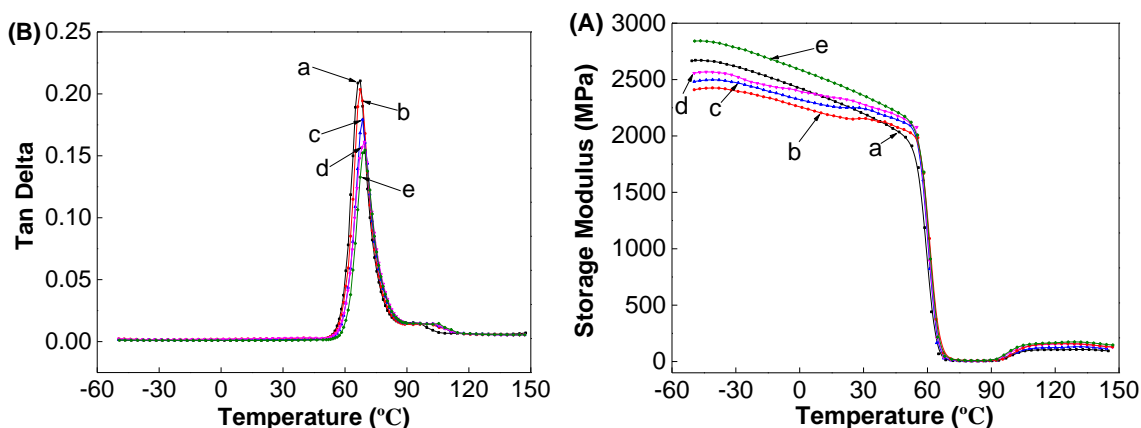| Code	T_g (°C)	$T_{c,onset}$ (°C)	Storage Modulus at 25 °C (GPa)
Neat PLA	66.6	93.6	2.2
1 wt.% AKWCF/PLA	67.4	93.5	2.3
3 wt.% AKWCF/PLA	68.5	92.6	2.3
5 wt.% AKWCF/PLA	69.5	91.1	2.4
7 wt.% AKWCF/PLA	69.7	90.7	2.4

Fig. 4. DMA curves of (a) neat PLA, (b) 1 wt.% AKWCF/PLA, (c) 3 wt.% AKWCF/PLA, (d) 5 wt.% AKWCF/PLA, and (e) 7 wt.% AKWCF/PLA

Mechanical Properties

The tensile, break, and impact strength curves, and the elongation to break of neat PLA and the AKWCF/PLAs are shown in Fig. 5. Details of the mechanical properties are listed in Table 6. Neat PLA was relatively rigid and brittle, with a tensile strength of approximately 71.2 MPa, a break strength of approximately 59.0 MPa, elongation at break of approximately 14.04%, and impact strength of approximately 2.65 kJ/m^2. The tensile and break strength curves of AKWCF/PLAs are shown in Figs. 5(a and b). The tensile and break strength values of AKWCF/PLAs were lower than the values of neat PLA. Moreover, both strengths decreased with the addition of the treated coir fibres. As is well known, silane coupling agents are theorized to interact with PLA molecules. This reaction can enhance interfacial adhesion and thus effectively improve the compatibility of AKWCF/PLAs. In addition, studies have shown that fibre strength can be decreased by a chemical treatment (Rout and Prasad 2001a; Dong *et al.* 2014; Rajesh *et al.* 2014). It was highly likely that this effect played a major role in affecting the mechanic properties and causing the strength of the AKWCF/PLAs to decrease.

Table 6. Mechanical Properties of Neat PLA and AKWCF/PLA

Code	Coir Fibres (wt.%)	Tensile Strength (MPa)	Break Strength (MPa)	Elongation at Break (%)	Impact Strength (kJ/m²)
Neat PLA	0	71.23	58.96	14.04	2.65
1 wt.% AKWCF/PLA	1	65.19	54.65	10. 80	3.39
3 wt.% AKWCF/PLA	3	64.36	48.23	10. 82	3.32
5 wt.% AKWCF/PLA	5	62.26	43.71	11. 85	3.23
7 wt.% AKWCF/PLA	7	60.57	31.02	11. 91	3.18
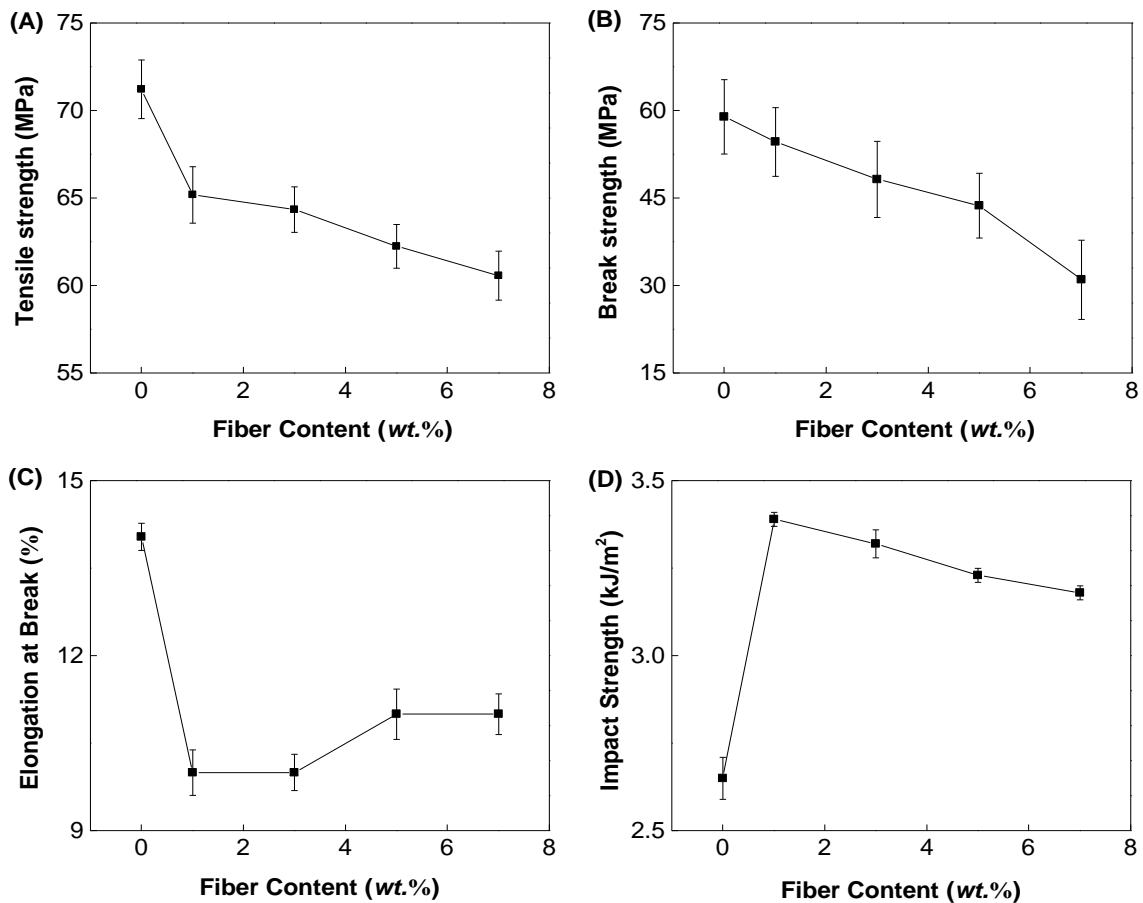
Fig. 5. Tensile and impact properties of neat PLA and AKWCF/PLA: (a) tensile strength, (b) break strength, (c) elongation at break, and (d) impact strength.

In Fig. 5(c), the increasing coir fibre content also shows a positive effect on the elongation to break for AKWCF/PLAs, which was expected because the coir fibres also exhibited much greater elongation at break (15% to 40%). Figure 5(d) shows that the impact strength of AKWCF/PLAs improved continuously with the addition of coir fibres. This result indicated that more impact energy was absorbed by the coir fibres. At coir fibre

content of 1%, the AKWCF/PLAs exhibited a remarkable increase of 28% in the percentage impact strength. Furthermore, the impact strength decreased with increased coir fibre content, which indicated that coir fibres may have been reunited under the high content.

Morphological Structures

The effects of the treated fibre surface and adhesion between the treated fibres and PLA matrix were investigated by SEM. Figures 6a through 6b show an SEM micrograph comparison of untreated and treated coir fibre surfaces. Figures 6c through 6d show SEM micrographs of the fracture surfaces of AKWCF/PLAs.
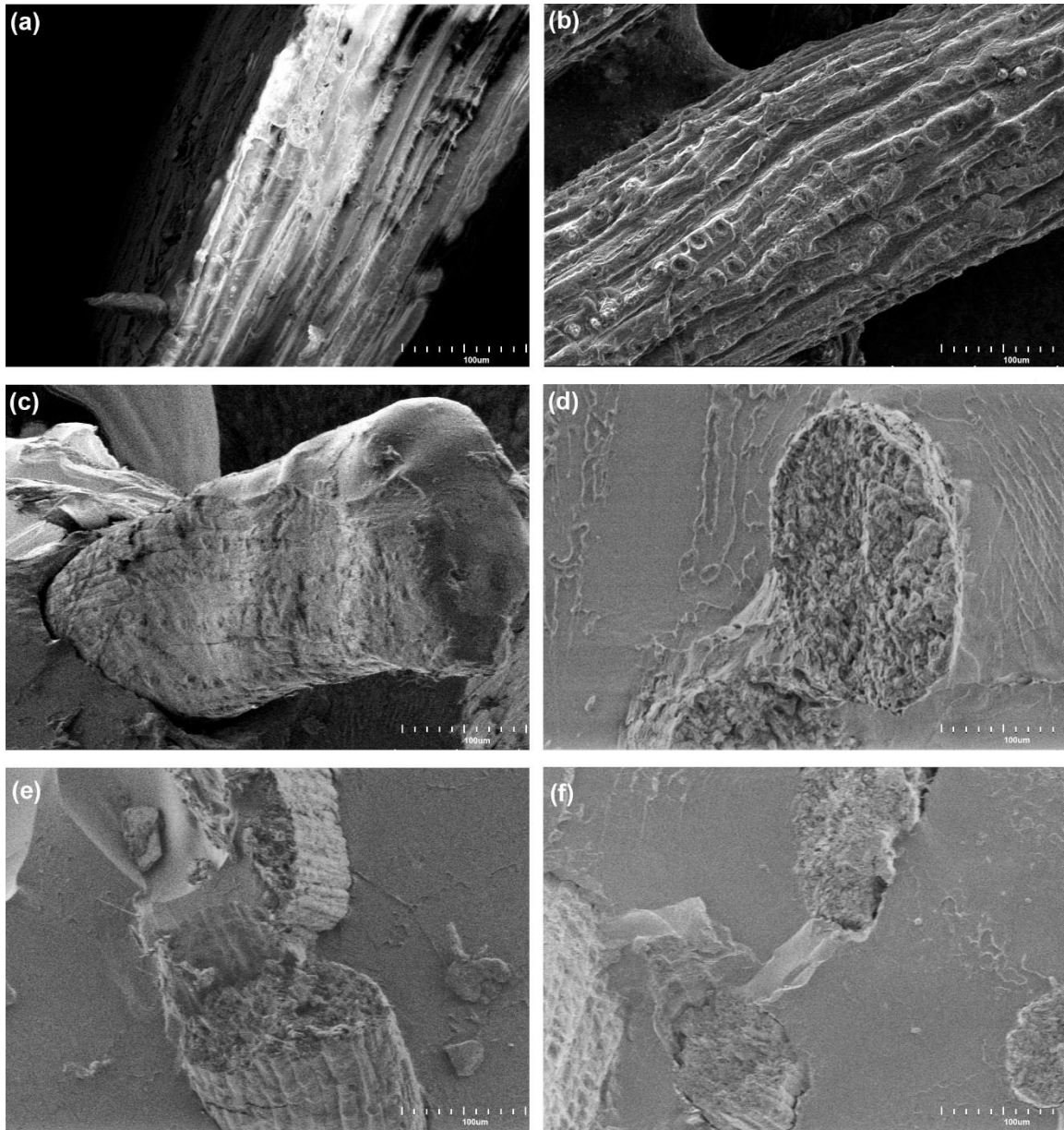

Fig. 6. SEM micrographs of (a) untreated coir fibres, (b) treated coir fibres, (c) 1 wt.% AKWCF/PLA, (d) 3 wt.% AKWCF/PLA，(e) 5 wt.% AKWCF/PLA, and (f) 7 wt.% AKWCF/PLA

Natural coir fibres (Fig. 6a) contain polar molecules, such as water, hemicellulose, and lignin (Zhu *et al.* 2005), which are efficient absorbers of microwaves. Under microwave irradiation, these molecules volatilize sufficiently rapidly so that a large micro gap and hole were formed on the surface of fibres. In addition, an alkali treatment also removed small molecules of fibres, such as lignin, pectin, wax, and hemicellulose, which led to the formation of pits on the surface (Jiang *et al.* 2012). As a result, Fig. 6b displays the rough surface of treated coir fibres.

From Fig. 6c to Fig. 6f, the impact fracture surfaces of AKWCF/PLAs are showed with the fibres pulled out. It can clearly be observed that the pulled-out fibre surface enclosed a layer of PLA and the gaps between the fibre and matrix in the composite materials were narrowed. The main reason was that a thin layer coating of silane chains on coir fibers facilitates the filler dispersion into PLA matrix and also functionality of silane was to change hydrophilic nature of fibers to hydrophobic. So the interfacial adhesion between the PLA matrix and coir fibre can be improved. It indicated that the pretreatment of coir fibres was effective to some extent, based on the impact tests and DMA analyses.

CONCLUSIONS

In this study, the AKWCF/PLAs had better impact strength than that of neat PLA and showed a remarkable increase in the percentage (28%), at the treated coir fibre content of 1%. The DMA results also showed that AKWCF/PLAs had higher storage modulus than that of neat PLA. These results were supported by SEM analyses and revealed better interfacial adhesion between treated coir fibres and the PLA matrix. The T_c and X_c values of AKWCF/PLAs were improved (as quantified by a DSC analysis) relative to that of the neat PLA; however the thermal stability of PLA was reduced with the addition of treated coir fibres. This research indicated that the pretreatment of the coir fibre surface was effective in improving the compatibility and interfacial bonding between treated fibres and the PLA matrix and that the treated coir fibres acted as an effective reinforcing agent.

ACKNOWLEDGMENTS

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