Studies of Different Kinds of Fiber Pretreating on the Properties of PLA/Sweet Sorghum Fiber Composites

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ABSTRACT: In this article, truly degradable composites were prepared using sweet sorghum fibers which are residue of ethanol fermentation industry as reinforcement and renewable resource-based biodegradable polyester, poly (L-lactide) (PLLA) as matrix, they were fabricated by melt-blending. The effect of different kinds of pretreatments (dilute sulfuric acid pretreatment, mild alkaline/oxidative pretreatment, steam explosion pretreatment) on mechanical properties of composites were investigated. Besides the composition of untreated and treated fibers as determined by Van soest method, Fourier transformed infrared (FTIR) spectroscopic and scanning electron microscopic (SEM) were also used to study the change of sweet sorghum fibers before and after pretreatments. Mechanical properties testing indicated that tensile strength and impact strength of PLLA/treated fibers were improved except the dilute sulfuric acid pretreated fibers reinforced PLA composite. The mild alkaline/oxidative pretreated fiber reinforced PLA composite showed highest tensile strength of 46.12 MPa and impact strength of 8.02 kJ/m^2 which was 15.5 and 33% higher than that of the control. The SEM of impact fracture surface and DMTA test were carried out to investigate the interfacial morphology and interfacial adhesion between the fiber and matrix. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1385–1393, 2010

Key words: truly degradable composites; poly(L-lactide); fibers; morphology; mechanical properties

INTRODUCTION

As a result of resources crisis and eco-environmental problems, socio-economic sustainable development, and ecological environment protection have attracted more and more attention by people worldwide. As a consequence, material researchers are seeking more environmental friendly materials instead of common plastics. So wood-plastic composites[1](WPCs) have emerged as a kind of potential environment friendly material, and investigated by many scientist. Biodegradable renewable composites reinforced with plant fiber have been obtained increasing interests, because natural fibers are abundant among the world, as well as they are reproducible. Compared with traditional reinforcing fibers such as glass fibers, natural fibers have lots of advantages such as high specific strength, lower cost, and renewable nature. However, the primary drawback of using natural fibers for reinforcement is the poor interfacial adhesion between polar–hydrophilic natural fibers and nonpolar–hydrophobic plastics. This results in poor mechanical properties of the final product,[2] to improve the adhesion between the two phases, surface treatments are necessary for modifying the surface polarity by physical methods and chemical methods. Treatments using alkaline solutions have been applied by several researches[3–5] and[6] to improve mechanical properties and fiber-matrix adhesion of natural fiber reinforced plastics such as polypropylene/flax, epoxy/flax, and polyester/kenaf. After alkali treatment, the fibers physical structure changes, meanwhile waxy materials and impurities are also removed. This action often leads to improvement of the interfacial bonding between fibers and matrix. Huda et al.[7] found that both silane-treated fiber reinforced composite and alkali treated fiber reinforced composite offered superior mechanical properties compared with untreated fiber reinforced composite. Keener et al.[8] reported that, use of MAPE coupling agent at 3% loading can double the tensile strength and triple the impact properties compared to noncoupled blend of wood and polyethylene. Maldas and Kokta.,[9] and Karnani et al.[10] have also reported improved mechanical properties by using silane and isocyanate coupling agents. The improvement in mechanical properties is believed to be due to a better dispersion of fibers in the matrix, a more effective wetting of fibers by matrix resin and a better adhesion between the two phases.

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In this work sweet sorghum fiber which was the residue obtained after sugar juice extraction of sweet sorghum stalk was used as reinforcement.[11] Sweet sorghum is presently considered as a potential alternative crop for energy and industry in the EU.[12] In china, sweet sorghum is a kind of potential energy plant because of high sugar content and high weatherability. Poly(L-lactide) (PLLA) was used as a completely biodegradable matrix for its great application prospect. In the article, sweet sorghum fiber were treated with dilute sulfuric acid, mild alkaline/oxidative method and steam explosion method respectively, mechanical properties of the three kinds of fiber reinforced PLA composites were investigated compared with that of the control, then the results are discussed. The composing component and surface structure of the untreated and pretreated fibers are also determined to interpret the results.

EXPERIMENTS

Materials

Sweet sorghum, bred by the Chinese Academy of Agricultural Science, was harvested in Beijing, October 2008. Leaves and husks were stripped from the fresh stalks by hand, then the stalks were squeezed by a three-roller mill to remove fresh juice and bagasse was obtained. After that the residue which contained both outer and inner part of stalks was washed to remove sugar and dried in an oven at 80°C for 24. The dried sweet sorghum fiber was ground to pass a 0.25-mm size screen. Poly(lactic acid), PLA-2002D pellets was obtained from Cargill Dow LLD, NatureWorks.

Pretreatment of sweet sorghum fiber

The sweet sorghum fibers were subjected to a series of different pretreatments as follows:

1. Dilute sulfuric acid pretreatment, 30 g sweet sorghum fibers were added into 300 mL 2% dilute sulfuric acid solution, then the mixture was boiled for 1 h followed by washed and air pump filtration. They are dried in an oven at 80°C for 24 h and ground to pass a 0.25-mm size screen.
2. Mild alkaline/oxidative pretreatment, 30 g sweet sorghum was treated with 300 mL 4% sodium hydroxide solution for 12 h at 40°C, then hydrogen peroxide was added to form 1% solution, it is kept at 40°C for another 12 h, then the fibers were washed by deionized water and air pump filtration.They are dried at 80°C in an oven for 24 h and ground to pass a 0.25-mm size screen.
3. Steam explosion pretreatment: The explosive pressure was kept at 1.5 MPa for 5 min, then it is relieved to obtain products. The products were washed and dried at 80°C in an oven for 24 h and ground to pass a 0.25-mm size screen.

Processing preparation of composites

Sweet sorghum fiber/PLA composites were blended using a two rollers counter rotating mixer Haake Rheomix 600 with a mixing chamber volume of 50 cm^3. The process temperature was 170°C. The compounding was carried out with a speed of 60 rpm and maxing time of 10 min at 170°C. All the materials were dried in an oven at 80°C under vacuum for 12 h before using. The weight ratio of PLA to sweet sorghum fibers was maintained at 70 : 30 for all the specimens.

Preparation of specimens for mechanical property tests

The specimens used in the mechanical property test were manufactured by hot compression molding method: the weighed ground pellets of PLA/SSF blends were added into the mold with dimension of 2 × 100 × 150 mm and preheated at 180°C for 4 min; and then the melt blends were molded at a pressure of 5 MPa. After 10 min, the melt specimens were cooled by cold compression at 5 MPa for 5 min, and then the plate was removed from the mold.

The product plates were then cut into pieces with the dimension of 2 × 10 × 80 mm for the tensile mechanical test and impact test. The tensile tests were performed using Lloyd LR30K Plus Materials Testing Machine at a constant extensional strain rate of 1 mm/min at 25°C. Five composite specimens were tested for each set of samples. The impact test was performed using Ceast Resil Impactor at 25°C, and 10 composite specimens were tested for each set of samples.

Analysis of composition of sweet sorghum fiber

The determination of composition (cellulose, hemicellulose, and lignin) of the untreated and pretreated sweet sorghum fiber used the methods according to Van Soest.[13]

Fourier transformed infrared (FTIR) spectroscopic analysis

Before analysis by FTIR spectroscopy, samples and potassium bromide (KBr) were dried in a vacuum drying oven overnight at 50°C. FTIR data were

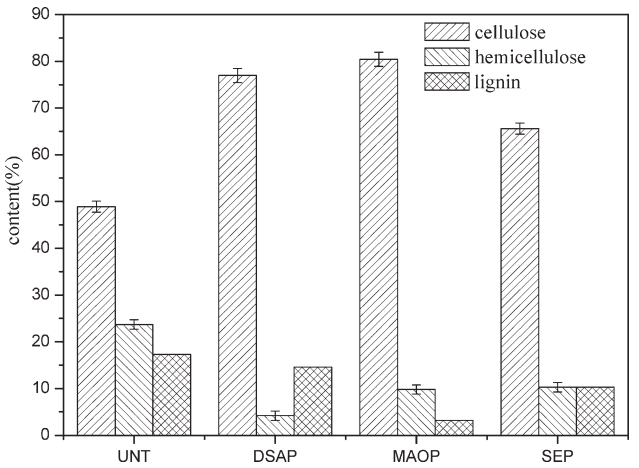

Figure 1 Compositions of fiber with different pretreatments.

obtained with a FTIR Spectrophotometer (Varian 3100) with detector at 4 cm^{-1} resolution by preparing dried KBr powder pellets containing 1% w/w of the investigated samples. Recording was within the range of 4000–1400 cm^{-1} and 32 scans were taken within this interval.

Scanning electron microscopy (SEM)

The topographies of used fiber before and after pretreatments and the fracture surfaces of composites were analyzed using an SEM microscope (HITACHI S-4700). The samples were coated with gold using a vacuum sputter coater.

Dynamic mechanical properties

Dynamic mechanical thermal analysis (DMTA) was performed in single cantilever bending mode using a Pheometric scientific dynamic mechanical analyzer with a frequency of 1 Hz over a temperature range of 30 to 120°C at a heating rate of 2°C/min. The samples were cut from the sheets with typical dimensions of 30 × 6 × 2 mm. The test specimen dimensions were kept as similar as possible to obtain an accurate comparison.

RESULTS AND DISCUSSION

Composites of different kinds of pretreatment

The contents of cellulose, hemicelluloses, and lignin between untreated fibers and treated fiber with different methods were provided in Figure 1.

The fibers with all the pretreatments have lower contents of hemicelluloses and lignin but higher cellulose content comparing with that of the control. For untreated fiber, the contents of cellulose, hemicellulose, and lignin were 48.9, 23.7, and 17.3%, respectively, while the cellulose content of fiber with MAOP is 80.44% which is higher compared with the other two pretreatments. Among the three pretreatments, fiber with DSAP had the lowest hemicelluloses content, while fiber after MAOP obtains lowest lignin content. The composition of F-MAOP is similar as the previous research.[14]

From the data above, it is concluded that all the three pretreatments are available to remove hemicelluloses and lignin apparently. DASP is the most effective method to remove hemicelluloses, while MAOP is highly effective to remove lignin.

Fourier transform infrared analysis (FTIR)

Figure 2(a,b,c) depict the FTIR spectra of F-UNT, F-DSAP,F-MAOP, and F-SEP. FTIR spectroscopy is a useful tool in elucidating the functional groups of organic macromolecules, as well as understanding the bonding interactions of these functional groups.[15] Thus, it is utilized to provide key information of functional groups in the natural fiber before and after pretreatments. The detailed designation of each wavelength band to a specific functional group has been reported previously by others.[16]

Visual observation of FTIR spectra between untreated fiber and pretreated fiber shows that the differences generally present at about 1750 cm^{-1} and 1508 cm^{-1} which are the adsorption peak of carbonyl groups (C=O) stretching[17]and aromatic ring vibrations,[18] it is believed that the former is the characteristic adsorption peak of hemicelluloses, and the latter is characteristic adsorption peak of lignin. In Figure 2(a), the phenomenon of which the frequency bands at 1750 cm^{-1} is almost disappeared proves that the hemicelluloses are almost removed from the natural fiber. Figure 2(b) showed that there is scarcely any absorption peak at about 1750 cm^{-1} and 1508 cm^{-1} after MAOP, it also illustrates that hemicelluloses and lignin are almost removed effectively. As for Figure 2(c), the absorption peak at about 1750 cm^{-1} and 1508 cm^{-1} is smaller than that of F-UNT, which suggested that hemicelluloses and lignin are partly removed from the untreated fiber.

All the conclusions obtained from FTIR are accordance with that of last chapter, in addition it showed that no function groups are generated on the fiber after pretreatments.

Morphology of composites and fibers

The SEM micrographs of untreated fiber and pretreated fiber are shown in Figure 3(a–h). It can be seen from Figure 3(a) that the F-UNT is in short fiber even particulate form, the aspect ratio is small, and there are lots of fragments on the surface of the fiber bundle in the visual field [Fig. 3(b)]. After

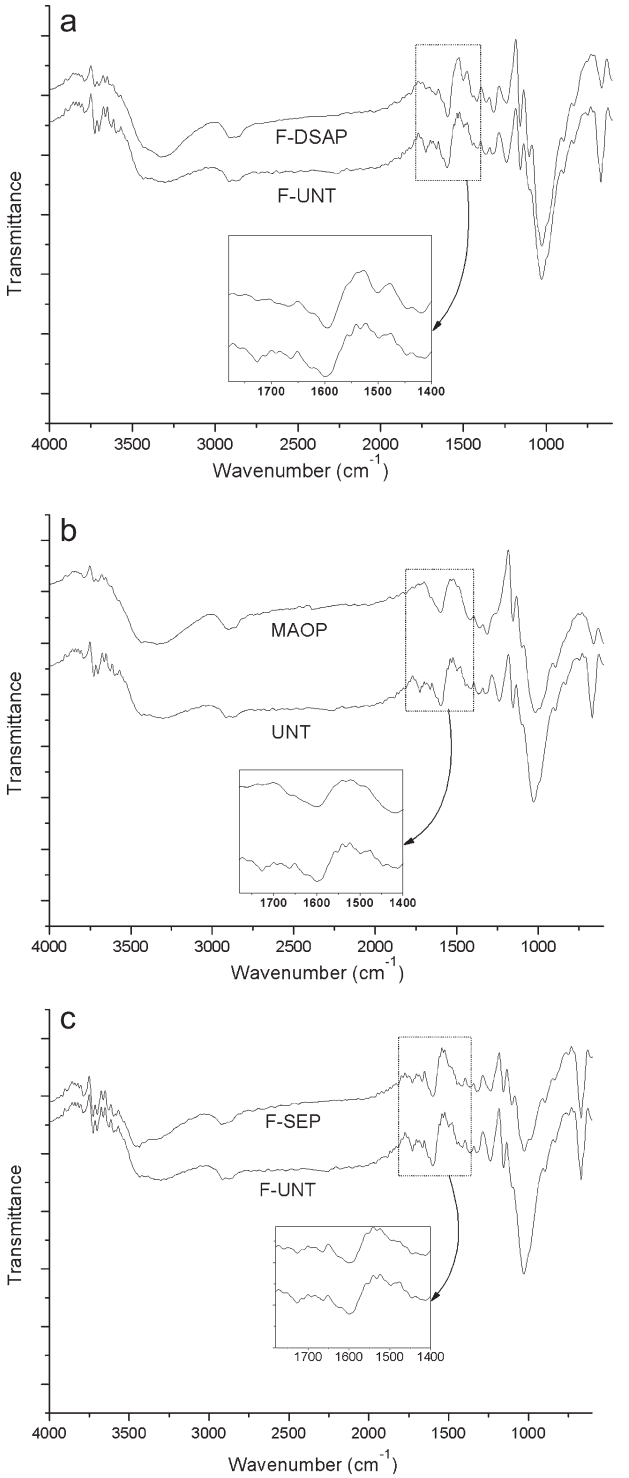

Figure 2 FTIR spectra of F-DSAP (a), F-MAOP (b), and F-SEP (c).

DSAP, the aspect ratio is increased slightly, and the fragments on fiber bundles are partly removed [Fig. 3(c,d)]. The aspect ratio is obviously increased after MAOP compared with F-UNT [Fig. 3(e)]. Figure 3(g) shows that the maximum aspect ratio was achieved with SEP.

The image in Figure 3(f,h) showed that there are a few fragments on the surface of F-DSAP and F-SEP, and the surfaces of F-MAOP [Fig. 3(f)] are rougher than the other three fibers.

The impact fracture surfaces of composites are shown in Figure 4, there is a difference between the adhesion of the untreated and treated flax fibers to the matrix. Many voids and fiber pullouts are observed in Figure 4(a), Figure 4(b) displays the poor interface bonding exactly. The poor adhesion between PLA and fiber is because of different polarities, the surface of cellulose is full of hydroxyl, lead to hydrophilic, while PLA presents lipophilic. As observed in Figure 4(c), after DSAP, the interfacial bonding is almost unchanged. But for the image in Figure 4(d,e), this kind of situation significantly improved. In Figure 4(d) there is a continuous coating of PLA on the F-MAOP. In Figure 4(e), fracture between the matrix and fiber is also continuous, but it is similar to Figure 4(c) that only a small amount of polymer was coated on the surface of fiber.

Dynamic mechanical thermal analysis

The dynamic mechanical thermal analysis is an important characterization method and it provides information such as storage modulus, loss modulus, loss angle, and glass transition temperature. In the article, the four composites, PLA/F-UNT, PLA/F-DSAP, PLA/F-MAOP, and PLA/F-SEP are tested by DMTA to investigate the storage modulus at different temperature, but what is the most important is to see the interaction between PLA and different fiber through the tan-delta peak (α-transition). The storage modulus of different composites versus temperature is shown in Figure 5 and Table I. PLA/F-MAOP and PLA/F-SEP show higher storage modulus whether in Glassy stage or in Rubbery stage than that of PLA/UNT, however, the result of PLA/F-DSAP is just the opposite. The improvement of composites over 80°C is because of the cold crystallization.[19]

From Figure 6 and Table I, it is possible to see that the tan-delta peaks (α-transition) of pretreated fiber reinforced PLA composites are all moved to higher temperature more or less. Tan-delta peak of PLA/F-UNT was measured to be approximately at 62.7°C and that was increased to 64.8, 65.8, and 63.5°C for PLA/F-DSAP, F-MAOP, and F-SEP, respectively, suggesting a constraining effect on the molecular segment motion. This is related to good interfacial interaction and adhesion between the two phases.[20] It is known that the α-transition involves the movement of amorphous chains, and the presence of fiber and/or crystalline regions can act as physical crosslinks, if the interaction between filler

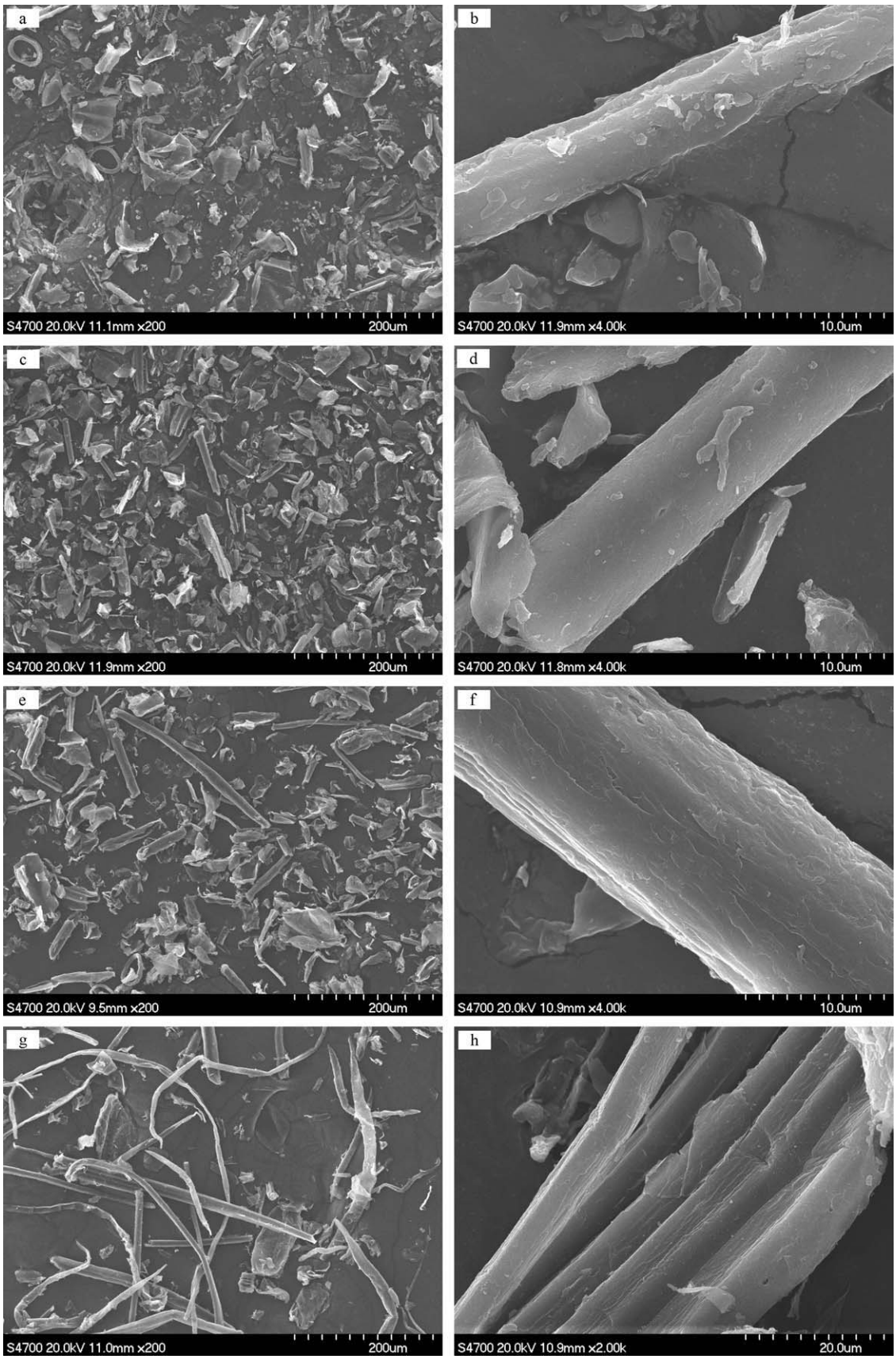

Figure 3 SEM micrographs of F-UNT ×200 (a), F-UNT ×4000 (b), F-DSAP ×200 (c), F-DSAP ×4000 (d), F-MAOP ×200 (e), F-MAOP ×4000 (f), F-SEP ×200 (g), and F-SEP ×2000(h).

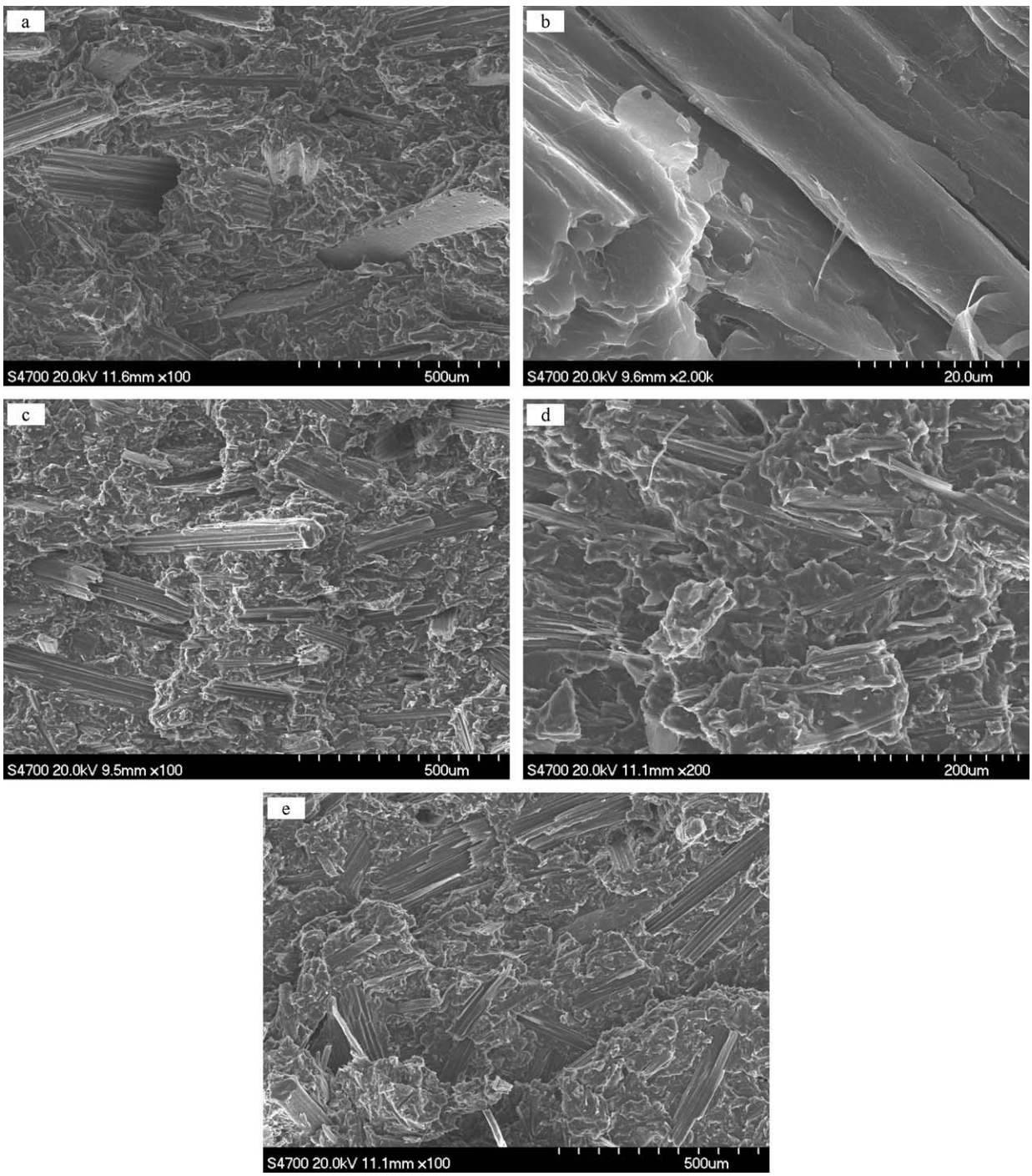

Figure 4 Impact fracture surfaces of different composites. PLA/F-UNT ×100 (a), PLA /F-UNT ×2000 (b), PLA/F-DSAP (c), PLA/F-MAOP (d), and PLA/F-SEP (e).

and matrix increase, the mobility of the amorphous regions will decrease and the modulus will increase.[21,22] As for composites, more energy will consume on the interface if the interfacial action is weak, consequently caused the tan-delta peak increasing. So areas below the tan delta curve can best reflect the movement of macromolecular segment. Figure 6 shows a reduction of loss peak area for pretreated fiber reinforced PLA composites, indicating restricted molecule movement because of improved interaction in filled polymers. The material of PLA/F-MAOP composite shows the minimum area below tan-delta peak, and PLA/F-DSAP composite takes second place, PLA/F-DSAP shows the maximum area among the three pretreated composites, so same results were achieved for the interfacial binding force of the untreated and pretreated fiber reinforced composites.

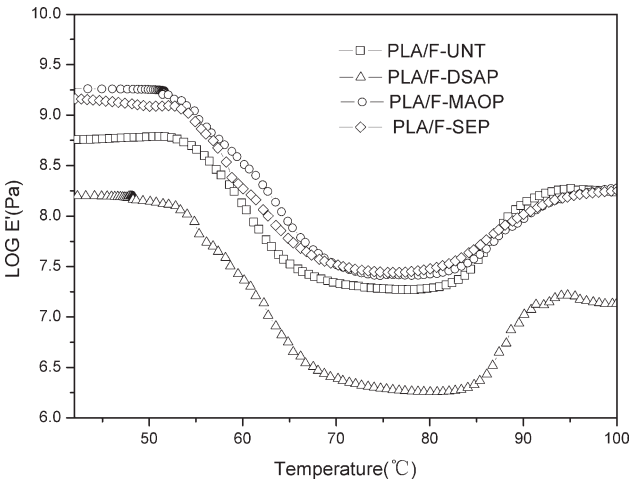

Figure 5 Storage modulus of different composites versus temperature.

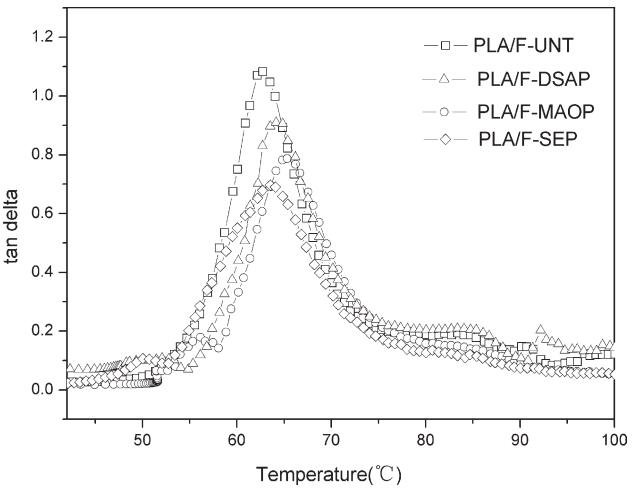

Figure 6 Tan-delta curves of DMTA for different composites.

Mechanical properties

Figure 7 shows tensile strength and elongation as a function of different pretreated fiber reinforced PLA composites. Figure 7 clearly shows that both tensile stress and elongation to break are higher for PLA/F-MAOP and PLA/F-SEP composites compared with PLA/UNT. The tensile strength and elongation at break for the PLA/F-MAOP composite are 46.12 MPa and 5.25% which are 15.5 and 28% higher than that of the control. The tensile strength of PLA/SEP is only 4.3% higher than that of PLA/F-UNT, while the elongation to break is 18.2% higher than that of PLA/F-UNT. Those indicate the composites of F-MAOP and F-SEP have got both strength and toughness improved. As for PLA/F-DSAP, tensile strength is similar to that of PLA/F-UNT, the elongation to break is even lower than that of PLA/F-UNT, which explains that DSAP has negative effect on composite mechanical properties. From the bar graph of Figure 8, impact strength of PLA/F-MAOP and PLA/F-SEP is increased by 33 and 15% compared with PLA/F-UNT, while PLA/F-DSAP is decreased by 6.2%, which also proves that the toughness is improved after MAOP and SEP.

TABLE I
Thermal Characteristics of Different Pretreated Fiber Reinforced PLA Composites

Materials	Storage modulus, E'(GPa) 42°C	75°C	Tan-delta Peak (°C)
PLA/F-UNT	0.572	0.0191	62.7
PLA/F-DSAP	0.158	0.00197	64.8
F-MAOP	1.83	0.0262	65.8
F-SEP	1.49	0.0277	63.5

Because cellulose is the cardinal reinforcement component among all the components in fiber, so it is assumed that the cellulose content is related to the mechanical properties of composites. Combining with the analysis of the composition in the F-UNT, F-DSAP, F-MAOP, and F-SEP, though the cellulose content of F-DSAP is as the same as that of F-MAOP, the tensile strength, elongation at break and impact strength are much lower than that of F-MAOP, which reveal that in this experiment cellulose content is not the key factor to the mechanical performance, some other factors may be more important.

According to Dufresne et al.,[21] in the system of this article, the mechanical performance of composites is expected to depend on the following factors: (1) adhesion between the PLA matrix and natural fiber reinforcements, stress transfer efficiency of the interface; (2) aspect ratio of the reinforcements.

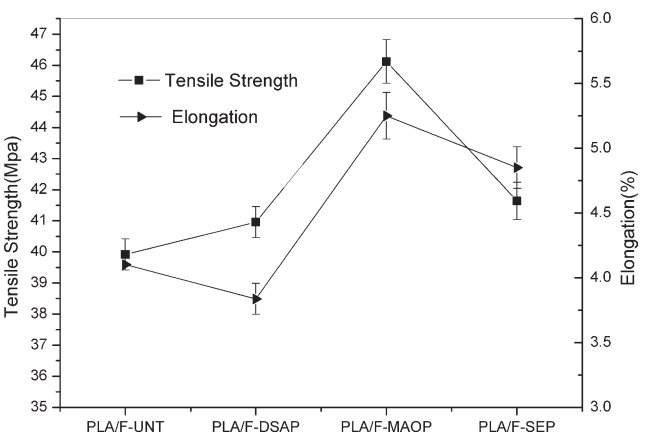

Figure 7 Tensile strength and elongation of different composites.

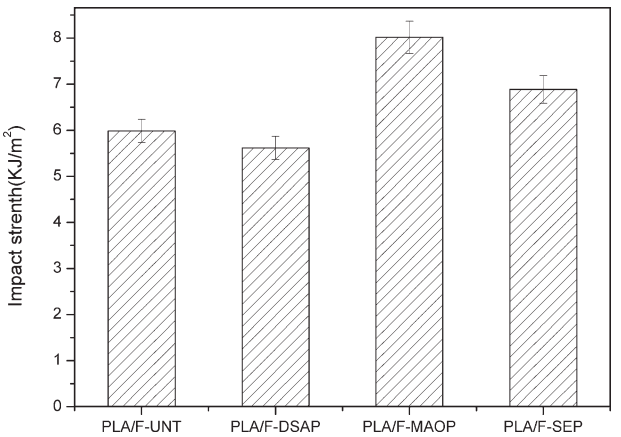

Figure 8 Impact strength of different composites.

The increase in strength of PLA/F-MAOP is an indication of better stress transfer across the interphase, which is because of the rough surface showed in Figure 3(f), alkaline/oxidative pretreatment has removed natural and artificial impurities, thereby producing a rough surface topography.[23] The DMTA result also shows a better adhesive force between filler and matrix. According to Agrawal et al.,[24] the alkali treatments have a lasting effect on the mechanical behavior of natural fibers, especially on fiber stiffness, so it is beneficial for improving mechanical properties of composites.

The fragments on the surface of the fiber inhibit the contact between matrix and reinforcement, so voids and debondings appear when under loading, then PLA/F-UNT showed poor mechanical properties. The aspect ratio of F-MAOP showed some degree of increase compared with F-UNT. The higher aspect ratio contributed to better strength. Though the interfacial bonding of F-SEP and PLA is not strong, F-SEP have the highest aspect ratio among the three pretreated fiber, so the mechanical properties are better than PLA/F-UNT composite and PLA/F-DSAP composite, but worse than PLA/F-MAOP. As for the PLA/F-DSAP, although the interfacial bonding is slightly improved, the aspect ratio is not increased, in addition, according to Lin et al.[25]and Shibazaki et al.,[26] the degree of polymerization (DP) of cellulose decreased after acid treating, which will decrease the mechanical properties of fiber, so the mechanical behavior basically had no changes compared with that of the control.

CONCLUSIONS

This article demonstrated that mechanical properties of a truly biodegradable wood plastic composites which use sweet sorghum fibers as reinforcements and PLA as matrix could be successfully developed by pretreating fiber with different methods. Three methods was carried out to pretreat sweet sorghum fiber including dilute sulfuric acid pretreatment, mild alkaline/oxidative pretreatment, and steam explosion pretreatment. Composition analysis and FTIR analysis were preformed to investigate composing components before and after pretreatment. The result shows cellulose content increases after pretreatment, while the other constituents decreased dramatically, but the tensile test and impact test of composites reveal that the cellulose content is not the critical factor of improving the mechanical properties in the directly blending procedure.

The SEM micrographs and the tan-delta peak in DMTA proved that the different adhesion between fiber and PLA, PLA/F-MAOP composites showed the best interfacial bonding, PLA/F-DSAP composites take the second place, then was the PLA/F-SEP composites, the interfacial adhesion of these three materials are all better than PLA/F-UNT. The aspect ratio was great improved by SEP and was also improved by MAOP in some degree. The PLA/F-MAOP material showed the best tensile strength and impact strength among all the composites, which is 15.5 and 28% higher than that of the control, respectively.

Natural fiber will get various morphologies through different pretreatments, so integrate different pretreatments will be an advisable way to obtain good properties. Further investigations have to be carried out to determine the biodegradability of these composites.

NOMENCLATURE

UNT	untreated
DSAP	dilute sulfuric acid pretreatment
MAOP	mild alkaline/oxidative pretreatment
SEP	steam explosion pretreatment
SSF	sweet sorghum fiber
F-DSAP	fiber with DSAP

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