Effects of modifications of bamboo cellulose fibers on the improved mechanical properties of cellulose reinforced poly(lactic acid) composites

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Abstract
Three kinds of modifications, alkali soaking or silane coupling cellulose and maleic anhydride grafting poly(l-lactic acid), were applied in the preparation of cellulose/poly(l-lactic acid) composites. The effects of treatments of the cellulosic fibers on the mechanical properties of cellulose/poly(l-lactic acid) composites were comparatively investigated. The results demonstrated that the alkali soaking provided the composites with highest strength and Young's modulus, increased by 28.6% and 34.6%, respectively, than untreated samples. The highest impact toughness and elongation were achieved by silane agent pretreatment, which were 115% and 62% higher than those of poly(l-lactic acid) reinforced with virgin bamboo cellulosic fibers. Maleic anhydride grafting had moderate effects on both the stiffness and ductility, exhibiting best over-all properties. From the scanning electron microscopy observations and Fourier transform infrared spectrum analysis, it was found that the interfacial interactions between the filler and matrix were improved after all the modifications mentioned.

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1. Introduction

The growing environmental concerns and increasing scarcity of fossil resources have provoked an intensive demand for biomasses with controllable properties, with the desire to reduce petroleum consumption and mitigate pollution [1,2]. Poly (lactic acid) (PLA), made from renewable agricultural raw materials which are fermented to lactic acid, has been considered to be a type of commercially available and fully biodegradable polymers [3–5]. Combined with its high mechanical properties and good processability, PLA is now one of the most promising biodegradable polymers for industrial plastic applications, as an alternative to conventional synthetic polymers [6]. However, there is a need of overcoming the deficiencies of PLA such as brittle, low impact strength, and low ability in resisting thermal deformation [7]. In order to make them appropriate in many technical applications, the mechanical properties of PLA can be improved by using reinforcements.

Fibers, including synthetic fibers (e.g. carbon, glass and aramid) and natural fibers, have long been considered as good reinforcements for polymeric matrix [8–11]. Natural fibers exhibit many advantages over the synthetic counterparts such as low density, low cost, high strength-to-weight ratio, easy processing, excellent specific strength and high specific modulus, and especially their recyclability [12,13]. The reinforcement of PLA with natural fibers seems to be a logical alternative in order to increase their mechanical performance as well as keeping the final material environmentally friendly. Natural fibers such as kenaf [14,15], hemp [16], jute [17], bamboo [18], and flax [19,20] have served as reinforcements of PLA due to their good mechanical properties.

Cellulosic fibers, as one of the most abundant natural material on earth, have been used as reinforcing material in lignocellulosic/thermoplastic composites, and the advantages in cellulosic fiber reinforced PLA composites have been reported by many researchers [21,22]. The cellulose/PLA composites have better mechanical properties than cellulose reinforced PE or PP composites, but the interfacial adhesion needs to be optimized to improve their mechanical properties [21]. Oksman et al. presented that the tensile strength of cellulose reinforced PLA was 50% better than
cellulose/PP composites, while poor interfaces were observed from SEM images [21]. Different kinds of cellulose fillers were reported to make different contributions to enhancing mechanical and thermal properties of PLA, but bad dispersion of cellulose fibers would nullify the good performance of reinforcing fillers [23,24]. It is suggested that the mechanical properties of biocomposites depended greatly upon feature of the filler, the properties of matrix, and their interfaces. The main disadvantages of biocomposites are the low compatibility and poor interfacial adhesion between the hydrophilic natural filler and the hydrophobic matrix polymer. The natural fillers with polar hydroxyl groups on the surface form poor bonded interfaces with nonpolar matrix, leading to an inefficient stress transfer under load and low mechanical strength and stiffness [25].

Therefore, a study on improvement of the interface adhesion between natural fillers and bio-degradable polymers is of essential importance [26]. Various studies have been carried out to enhance the interfacial properties of the cellulose/PLA composites through physical, chemical treatments of cellulose fiber and grafting reactions of PLA matrix [27,28]. However, there exist few systematically study on how different modifications affect the mechanical thermal properties of cellulose/PLA composites. It was reported that nanosized cellulose can increase the interfacial adhesion considerably, but both of the preparation of nanosized cellulose and decentralization of it in the polymer matrix are time and energy consuming [29]. If simple but efficient surface treatments were discovered and yield PLA composites with high mechanical and thermal properties, it would broaden the use of PLA in industrial applications.

Three easy operating and time saving modifications, say alkali immersing or silane coupling agent pretreating of the cellulosic fibers, and maleic anhydride (MA) grafting poly (lactic acid) (PLA) were comparatively investigated. The effects of the different pretreatments on the mechanical properties of cellulose/PLA composites were studied by mechanical tests. Scanning electron microscopy (SEM), wide angle X-ray diffraction (WXRD) and Fourier transform infrared spectroscopy (FTIR) were applied to investigate the morphology, the chemical structures of the cellulose fibers, and the interfacial behaviors in the composites, respectively. The results showed that the NaOH solution treatment provided the composites with highest stiffness, KH560 treated samples achieved best toughness, MA grafting had moderate effects on both strength and toughness.

2. Experimental section

2.1. Materials

PLLA (2003D, D-isomer content = 4.3%, Mw = 2.53 × 10⁵ g/mol, melt flow rate (MFR) = 4–8 g/10 min (190 °C/2.16 kg), and a density of 1.24 g/cm³) was purchased from Nature Works, USA. The raw material of bamboo cellulose fiber (BCF), from bamboo fiber pulp with cellulose content of 96% and less than 2% lignin, was provided by Sichuan Anxian Paper Co., Ltd. The bamboo fiber pulp was crushed with a high-speed universal grinder (FW-400A, 26,000 r/min) to be cellulose powder with average width and length of 8 and 500 μm respectively. The silane coupling agent (commercial code: KH560), NaOH, ethanol, dicumyl peroxide (DCP), and maleic anhydride (MA), as analytical grade and used as received, were provided by Chengdu Kelong Chemical Reagent Factory.

2.2. Pretreatment of the bamboo cellulose fiber

The alkali treatment of BCF was to soak the crushed cellulose powder into 5 wt% NaOH aqueous solution, the mixture was heated to 60 °C and kept for 4 h under stirring with a magnetic stirrer. Finally, the NaOH treated bamboo cellulose fiber (NBCF) was filtered and washed with deionized water for several times to neutral before dried at 80 °C. As for silane coupling agent KH560 pretreatment, the crushed cellulose powders were immersed in 3 wt% of KH560 solution for 3 h at room temperature and were then washed and dried at 80 °C in an electric oven.

2.3. Preparation of test samples of cellulose/PLA composites

PLLA reinforced with 2 wt% BCFs, NBCFs and KH560 modified cellulose fibers (KBCFs) were processed, respectively, in a mini-extruder and a mini-injection molding machine (DSM Research, Netherlands). The mini-extruder had three consecutive heating zones and the processing temperatures in these three heating zones (top, center and bottom) were 180, 175 and 170 °C, respectively. The screw rotation speed of the extruder was fixed at 100 rpm. PLLA and cellulose fibers were mechanically mixed and fed to the mini-extruder through the feeding zone (top). After the fixed processing time in the mini-extruder, the molten mix was transferred to a preheated mini-injection molding machine for specimen fabrication. Finally, the specimen was removed from the mold for characterization. The BCF reinforced MA-grafted PLLA (MA–PLLA–BCF2) was prepared by the similar process, the only difference was before fed into mini-extruder, the PLLA was mixed by the BCF coupled with 2 wt% MA and 0.2 wt% DCP. The reason for that the MA–PLLA–BCF2 was prepared by one step instead of the traditional two step process and the amount of DCP was set to be very low was to avoid the side reaction and the degradation of the PLLA. The grafting ratio of MA was determined by titration analysis according to the literature [30], samples of 1.15 ± 0.01 g were completely dissolved in 100 mL of a mixed solution of chloroform:methanol (3:2 v/v), and 8–10 drops of 1% phenolphthalein in ethanol were added, the titration was carried out with 0.03 N of potassium hydroxide (KOH) in methanol, and the pH of the samples at end point was determined. The percentage of MA grafting was calculated according to Eqs. (1)–(3) [30], and the ultimate grafting ratio was about 0.9% in three tests.

\[
\text{Normality of KOH} = \frac{g \text{ KHP} \times \text{ purity of KHP (\% fraction)}}{\text{I KOH} \times 204.22}
\]

(1)

\[
\text{Acid number (mg KOH/g)} = \frac{\text{ml KOH} \times N \text{ KOH} \times 56.1}{\text{g polymer}}
\]

(2)

\[
\% \text{MA grafting} = \frac{\text{Acid number} \times 98.06}{2 \times 561}
\]

(3)

2.4. Mechanical tests

Tensile properties were measured using Instron Universal Tester Model 3365 (AGS-J, Suzhou, China) with a solid fixture at a tensile speed of 2 mm/min. The tensile gauge length was fixed at 25 mm. Each sample with dumbbell-shape and dimensions of 50 mm length, 3 mm width, and 3 mm thickness was analyzed. A pendulum impact tester (XC, Chengde, China) was employed to test the impact toughness of the composites. The samples for impact test were 65 × 10 × 4 mm³, and a 2 mm deep standard V-notch was carved on each sample. The maximum impact energy was set to be 1 J. All tests were carried out at 25 °C. Values of the mechanical properties of each group were decided by the means of five tests. The percentage of errors as determined by percentage (Standard Deviation/ Mean) × 100 was less than 10%.
2.5. Scanning electron microscopy (SEM)

Tensile fractures of the composites were observed by SEM (QUANPA200, Netherlands) operating in the high vacuum mode at accelerating voltage of 20 kV. The morphologies of those three kinds of BCFs were also characterized by SEM observations. Prior to examination, the samples were sputtered with gold using JEOL Fine Coater JFC-1200 for 50 s at argon pressure of 8 Pa and current of 30 mA.

2.6. Fourier transform infrared (FTIR) spectroscopy

The transformations in the chemical structures of virgin BCF, NBCF and KBCF were analyzed by FTIR (Nicolet 5700, America). The samples were completely dried in an oven before prepared as KBr pellet and being tested by FTIR on the sample holder. All spectra were record in the wave number range from 400 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). The FTIR spectroscopy of PLLA and its composites were also recorded to detect the chemical changes after modifications.

2.7. Wide angle X-ray diffraction (WXRD)

The crystalline structures of different BCFs samples were investigated by a wide angle X-ray diffraction (WAXD, DX-1000). The crystallinity of the PLLA in different samples was also detected by this characterization. The continuous scanning angle range used in this study was 5–40°, and the machine was operated at 35 kV and 25 mA. The degree of crystallinity of the cellulose was obtained from crystallinity index (CrI) which could be calculated according to the following equation [31]:

\[
CrI_{XRD} = \frac{I_{200} - I_{am}}{I_{200}} \times 100\%
\]

where \(I_{200}\) is the intensity of peak corresponding to (200), \(I_{am}\) is the intensity of amorphis, usually taking the lowest peak between 18° and 20°.

2.8. Differential scanning calorimetry (DSC)

The pure PLLA and cellulose/PLLA composites were analyzed by differential scanning calorimetry (DSC) using a TA Instruments Q2000 analyzer to learn about the glass transition temperatures \(T_g\) of the different samples. Under nitrogen purge, the samples (8 ± 1 mg) contained in aluminum pans were heated from 30 to 200 °C, kept at 200 °C for 5 min and cooled to 30 °C quickly, to release any heat history of the samples. Then the samples were heated again to 80 °C at the rate of 10 °C/min, during which the DSC curves were recorded.

3. Results and discussion

3.1. Characterizations of pre-treated samples

In this part, the properties of the pre-treated cellulosic fibers were characterized before they were applied in the preparation of the composites. The SEM observations of the cellulosic fiber samples, named as bamboo cellulosic fiber (BCF), NaOH treated cellulosic fiber (NBCF) and KH560 treated cellulosic fiber (KBCF), enable one to obtain the size and surface features of these fibers. As shown in Fig. 1a–c, the virgin cellulose displayed a fibriform shape, having an average diameter of 8 μm, and the modifications had led to obvious differences in morphology. From Fig. 1a, the surface of the untreated cellulose was found to be considerably covered with amorphous cellulose and/or impurities. After being treated with NaOH aqueous solution, the cellulosic microfibers displayed a neat and ordered surface (Fig. 1b), demonstrating dislodging of the impurities. The wrinkled surface of the treated fibers increased the surface area, which would provide more efficient contact with the matrix polymer. Judging from Fig. 1c, a tiny thin film appeared on the surface of KH560 modified cellulosic fibers, which was constructed by the silane coupling agent molecules.

The FTIR were applied to investigate the chemical structures of the virgin cellulose and the changes after pretreatments, and the results were shown in Fig. 2. The FTIR spectrum of the BCF (curve-a) was substantially identical with the typical absorptions of cellulose. There was no new functional groups introduced to the cellulose structure after NaOH treatment, but some absorption peaks in NBCF had been shifted from the corresponding peaks in the virgin BCF as marked in carve-b. For instance, the
O—H stretching vibration peak at 3421 cm\(^{-1}\) was shifted to 3415 cm\(^{-1}\), which was ascribed to the disturbing of the hydrogen-bond interaction that connected the cellulose and the impurities. Combined with the SEM observations in Fig. 1, it appeared that the structure of the BCF was changed because of the removal of impurities after NaOH pretreating. Two new peaks appeared at 1117 cm\(^{-1}\) and 802 cm\(^{-1}\) in curve-c after KH560 modification, of which 1117 cm\(^{-1}\) corresponded with the stretching vibration of Si—O—C, and 802 cm\(^{-1}\) related to Si—C stretching. This demonstrated that new chemical bonds had been formed after the cellulose being modified by coupling agent of KH560. The reaction between BCF and KH560 was presented in our previous study [32]. The hydroxyl groups on silanol hydrolyzed from KH560 condensed with the hydroxyl groups on cellulose, thus CH\(_2\)CH(O)CH\(_2\)O(CH\(_2\))\(_3\)SiO-group had been grafted onto the cellulosic molecules.

The crystalline structure of the virgin BCF, NBCF, and KBCF were characterized by WXRD, and the results were shown in Fig. 3. It could be seen that the virgin BCF exhibited diffraction peaks at 2\(\theta\) = 15.8\(^{\circ}\), 22.5\(^{\circ}\), 34.5\(^{\circ}\), corresponding to the cellulose I polymorph structure, among which the peak at 22.5\(^{\circ}\) was attributed to the characteristic (200) crystal planes of cellulose I. Neither the NaOH treatment nor the KH560 modification changed the positions of diffraction peaks of BCF, but the intensity of this peak of (200) varied obviously. The values of CrI were 0.629, 0.735 and 0.622 for BCF, NBCF and KBCF, respectively. Thus, NaOH treatment increased the crystallinity while KH560 modification changed the positions of diffraction peaks of BCF, but the intensity of this peak of (200) varied obviously. The values of CrI were 0.629, 0.735 and 0.622 for BCF, NBCF and KBCF, respectively. Thus, NaOH treatment increased the crystallinity while KH560 modification slightly decreased it. The higher crystallinity of NBCF was ascribed to the selective dissolution by NaOH, because the lower crystallinity of impurities could be dissolved by NaOH solution and was removed from the fibers, and this led to the increase of the mechanical properties of the fiber itself.

### Table 1
Mechanical properties of PLLA and its composites.

<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus (GPa)</th>
<th>Ultimate tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Impact toughness (kJ/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLLA</td>
<td>1.7 ± 0.1</td>
<td>61 ± 3.2</td>
<td>15 ± 1.3</td>
<td>4.3 ± 0.3</td>
</tr>
<tr>
<td>PLLA–BCF2</td>
<td>1.9 ± 0.2</td>
<td>56 ± 2.1</td>
<td>6 ± 1.1</td>
<td>4.2 ± 0.2</td>
</tr>
<tr>
<td>MA-PLLA–BCF2</td>
<td>2.3 ± 0.2</td>
<td>69 ± 3.3</td>
<td>12 ± 2.1</td>
<td>6.1 ± 0.3</td>
</tr>
<tr>
<td>PLLA–KBCF2</td>
<td>2.4 ± 0.2</td>
<td>67 ± 2.2</td>
<td>13 ± 2.3</td>
<td>6.8 ± 0.4</td>
</tr>
<tr>
<td>PLLA–NBCF2</td>
<td>2.6 ± 0.2</td>
<td>72 ± 3.4</td>
<td>11 ± 2.4</td>
<td>4.9 ± 0.2</td>
</tr>
</tbody>
</table>

Fig. 3. WXRD of different cellulose fibers.

Fig. 4. SEM of tensile fractures surfaces of (a) PLLA–BCF2, (b) PLLA–NBCF2, (c) PLLA–KBCF2, and (d) MA-PLLA–BCF2.
3.2. Effects of modifications on mechanical properties of cellulose/PLLA

The mechanical properties of the PLLA and its composites were shown in Table 1. With the addition of virgin BCFs, the Young’s modulus was increased slightly because of the high stiffness of the BCF itself. While the ultimate tensile strength, the elongation at break as well as the impact toughness were decreased obviously, this was mainly attributed to the bad dispersion of BCF and poor interfacial interaction between the filler and matrix (as illustrated in Fig. 4a). From the SEM photograph of the tensile-fracture of PLLA reinforced with untreated BCFs in Fig. 4a, one could found that the surfaces of the BCFs were very smooth and without any coverage. The interfaces between the BCFs and the matrix were very clear, and interfacial debonding was observed, which indicated that the interfacial adhesion between the untreated BCFs and matrix was poor. Furthermore, obvious aggregation of BCFs could be found from the morphologies of the tensile fracture which would become defects under the load and induce the failure of the material. That aggregation was caused by bad incompatibility of the BCFs and matrix, as mentioned in introduction section. The interactions among BCFs themselves were stronger than those between BCFs and matrix, displaying the tendency of cellulose to be aggregated. Since the mechanical properties of the composites decreased with the filling of the virgin BCFs, the necessity of the surface modifications of BCF was realized.

All the three kinds of pretreatments in this work caused significant improvements in the mechanical properties of the composites compared with PLLA reinforced by untreated BCFs. The increases in Young’s modulus, tensile strength, elongation at break and impact toughness were found after each of the modifications. Among all the composites, the PLLA−NBCF2 possessed highest Young’s Modulus and tensile strength, increased by 36.8% and 28.6%, respectively, than PLLA filled with untreated BCFs. While the PLLA−KBCF2 had the optimal elongation at break and impact toughness, which were increased by 116% and 62%, respectively, as compared with PLLA−BCF2.

From the above analysis, it could be seen that the cellulose pretreated with 5 wt% NaOH provided the PLLA composites with higher strength, and KH560 coupling achieved best toughness. Particularly, MA grafting PLLA displayed moderate effects on improving both strength and toughness. Compared with other reports [33,34], the mechanical properties of the composites prepared in this work after the modifications were positive. The composites filled with 2 wt% NBCF had higher tensile strength than 5 wt% nanocellulose reinforced PLLA composites reported by Jonoobi et al. [34]. When compared with pure PLLA, despite of a very slight decrease in elongation at break, significant increases in Young’s modulus, tensile strength and impact toughness were obtained after the three easy operating modifications, which inferred that application of PLLA composites after appropriate treatments was promising.

3.3. Further analysis of the composites

As mentioned that the mechanical properties of biocomposites depended greatly upon the filler, the properties of the matrix, and their interface characteristic. To manifest the mechanism for the improvements in mechanical properties of BCF/PLLA composites after the modifications, it is important to have knowledge of whether there was obviously change of the matrix after these treatments and how the change affected their properties. The crystalline morphology and glass transition of PLLA and its composites were investigated by WXRD and DSC, and the results were shown in Fig. 5. From Fig. 5a, the diffraction patterns of PLLA and its composites, only one broad pick at around 10–20° could be found in all the samples, which demonstrated that the pure PLLA, PLLA reinforced with BCFs and modified BCF/PLLA composites were hardly crystallized in the processing conditions. The temperatures of glass transition (Tg) of all the composites were slight higher than that of pure PLLA, as shown in DSC curves (Fig. 5b). Tg is the temperature at which the segments of the polymer start to move, and the higher the Tg, the more hindered the segments by its surrounding are. There must be some interactions between the cellulosic fibers and its matrix PLLA because of the higher Tg of the composites than pure PLLA. It was also indicated from the DSC curves that the degradation of PLLA had not occurred during the MA grafting modification, because Tg could be decreased if some of the PLLA molecules degrade into smaller ones which could act as plasticizer.

Because the PLLA was amorphous in all the samples, the difference between the matrix was not the dominate reason for the enhancement in mechanical properties, it was interest to learn about the interfacial interactions between the filler and matrix before and after the modifications. The tensile fractures of PLLA composites reinforced with virgin and modified BCFs were observed by SEM, and the results were shown in Fig. 4. The interfacial adhesion was poor for PLLA−BCF2, as shown in Fig. 4a, and which was described before. By contrast, from the tensile fractures shown in Fig. 4b, it was found that a good link between the filled fiber and the matrix PLLA had been formed in PLLA−NBCF2. The NBCFs were wrapped and well trapped by the matrix, and the interfaces between the NBCFs and PLLA were not obvious. In addition, from
the large magnification of the SEM images (Fig. 6a) of the composites, it seemed that after being soaked in NaOH solution, some BCFs had exposed its micro-fibrillation structures, with some fibrillations broken by tensile loading, showing the load well transported through those cellulosic fibers. These results suggested that the interfacial adhesion between the filler and PLLA matrix became much more favorable and stronger upon the pretreatment of the cellulose with NaOH solution. The links between the KBCF and the matrix PLLA could be seen from Fig. 4c. Compared with PLLA–BCF2 (Fig. 4a), one could see that better wetting of the BCF through the matrix was achieved after KH560 modification, few KBCFs appeared on the tensile fractures in the composites. The deformation of the PLLA near the filled KBCFs, as shown in Fig. 6b, could be observed, demonstrating that the stress could be transformed from the fiber to the matrix without debonding the interface. The tensile fracture surfaces of MA-PLLA–BCF2 were quite similar to that of PLLA–KBCF2, but the interfacial adhesion between fibers and matrix in MA-PLLA–BCF2 (shown in Figs. 4d and 6c) was a little better than that in PLLA–KBCF2. The improved interfacial interaction between the cellulosic fibers and PLLA after the modifications could also be confirmed by FTIR of the composites, as shown in Fig. 7. For the pure PLLA, the absorption peaks at 3657 and 3502 cm\(^{-1}\) corresponded to the \(\text{O-H} \) stretching vibration. The \(\text{C-H} \) stretching vibration could be observed at 2994, 2944 and 2880 cm\(^{-1}\). The strong spectra band at about 1735 cm\(^{-1}\) was attributed to \(\text{C=O} \) stretching vibration. After filled with untreated BCFs, these absorption peaks were almost the same as that of pure PLLA, this could be ascribed to the poor interaction between the fiber and the matrix. While after the three modifications, the \(\text{O-H} \) stretching vibration at 3657 cm\(^{-1}\) shifted to about 3650 cm\(^{-1}\), which indicated the interactions between the BCFs and PLLA were improved after the modifications.

From the above analysis, the reason for improvement of the mechanical properties of the composites after KH560 pretreating...
cellulose and MA grafting PLLA was mainly ascribed to the better interfacial adhesion between matrix and filler. While NaOH solution soaking cellulose not only improved interfaces, but also enhanced the cellulosic fibers itself (as illustrated in Section 3.1). The mechanisms for the improvements in interfacial adhesion after these modifications could be reflected by the schematic diagrams in Fig. 8. The BCF was constructed by the well ordered micro-fibrillar covered by impurities and amorphous cellulose. Poor compatibility, due to their differences in polarity and hydrophilicity, between the fiber and the matrix made the interfaces of the composites poor. The removal of the impurities on the surface BCF by NaOH led to smaller sized and higher crystallinity of the cellulosic fibers, as well as to increasing the surface area that was available for contact with the matrix. After the removal of the cementing materials, originally, a whole fiber became cellulosic fibrillations, partly into nanoscaled sizes (as shown Fig. 6a). The structural changes in cellulosic fibers resulted in more effectively interfacial adhesion. For KH560 modifications, the KH560 molecules on the surface of cellulosic fiber link the PLLA and cellulose together. The epoxy end-groups on KH560 which had grafted onto the cellulose molecules resulted in more effectively interfacial adhesion. For KH560 modifications, the KH560 molecules on the surface of cellulosic fiber link the PLLA and cellulose together. The epoxy end-groups on KH560 which had grafted onto the cellulose molecules could react with the matrix and formed chemical bonds, which significantly improved the adhesive force between the interfaces of the components. Similarly, the MA grafted onto the molecules of PLLA could link the matrix and the filler together and resulted in better interfaces. As reported in the literature, MA was highly reactive with PLLA based on free radicals which induced by the initiator, DCP. The anhydride group grafted on the molecular chain of PLLA could react with hydroxyls from cellulose, forming ester linkages. The carboxylic groups, arising from the hydrolyzed anhydride, could also form hydrogen bonding with the hydroxyl groups of cellulose [1]. These chemical reactions and hydrogen bonding at the interfaces provide the composites with better mechanical properties than PLLA filled with untreated BCFs.

4. Conclusions

From the above experimental results and analysis, it could be realized that the modified modifications improved the mechanical properties of the cellulose/PLLA composites by improving the interfacial adhesion of the cellulose fiber and the matrix. NaOH solution pretreatment of cellulose provided the composites with highest stiffness, KH560 modification resulted in best ductility. MA grafting onto PLLA balance the improvements of stiffness and ductility, exhibiting best over-all properties. These results suggested that appropriate modifications can be selected according to actual requirements, and the application of PLA composites with some modifications was promising.

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