Characterization of Chemically Modified Wood Fibers Using FTIR Spectroscopy for Biocomposites

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ABSTRACT: Chemical modifications of wood fibers (Lignocel® C120) were performed for biocomposite applications, and chemically modified wood fibers were analyzed by FTIR spectroscopy. NaOH treatment showed band shifts from Cell-I to Cell-II in FTIR spectra from 2902 cm^{-1}, 1425 cm^{-1}, 1163 cm^{-1}, 983 cm^{-1}, and 897 cm^{-1} to 2894 cm^{-1}, 1420 cm^{-1}, 1161 cm^{-1}, 993 cm^{-1}, and 895 cm^{-1} and the change in peak height at 1111 cm^{-1} and 1059 cm^{-1} assigned for Cell-I structure. Silane treatment showed peak changes at 1200 cm^{-1} assigned as Si—O—C band, at 765 cm^{-1} assigned as Si—C symmetric stretching bond, at 700 cm^{-1} assigned as Si—O—Si symmetric stretching, and at 465 cm^{-1} assigned as Si—O—C asymmetric bending. Benzoyl treatment resulted in an increase in the carbonyl stretching absorption at 1723 cm^{-1} and in band characteristics of aromatic rings (1604 cm^{-1} and 710 cm^{-1}) and a strong absorption at 1272 cm^{-1} for C—O band in aromatic ring. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3212–3219, 2010

Key words: crystalline structure; hydrophilic polymer; FTIR; coupling agent; NaOH

INTRODUCTION

Studies on the development of biocomposites using natural wood fibers as reinforcing fillers have attracted great attention in various applications, mainly because of their low cost, low density, and high physical properties.[1,2] Wood fiber reinforced plastic composites usually show drastic increase in their mechanical properties compared with those of the base polymer. Glass fiber or carbon fiber reinforced thermoplastic materials possess good mechanical properties, but they have environmental concerns and they are relatively expensive. Wood fibers have long been considered as a future candidate to replace glass fiber or carbon fiber in thermoplastic composites, and thus it can help resolving environmental issues and taking economic advantage over those artificial fibers.

Wood fiber reinforced plastic composites have been used in automotive, construction, furniture, and biomedical industries. However, the incompatibility of the natural fibers and the polymer matrix sometimes reduces the possibility of wood fibers to act as fillers and thus limits their usages. In general, cellulose is a major composition of all constituents in biofiber. Each of the cellulose repeating unit has three hydroxyl groups and they are able to interact with one another forming intramolecular and intermolecular hydrogen bonds. Hydrogen bond gives high bending strength between the units, but it has hydrophilic characteristics on the fiber surface. Therefore, wood fibers require extra compatibilizers or additional chemical modifications for final uses in plastic composite manufacturings.

Polyolefins grafted with maleic anhydride (MA), such as polyethylene-MA,[3] polypropylene-MA,[4] styrene-ethylene-butylene-styrene-MA,[5] and ethylene-propylene-diene-monomer-MA,[6] were used to enhance the mechanical properties of the polymer/wood fiber composites. The MA functional group increases adhesion between wood fibers and the base polymer chain with increased compatibility in polymer phase. Lysine-based diisocyanate was also used as a coupling agent in poly lactic acid biocomposite for compatibilization.[7]

In addition to the use of an extra compatibilizer, many types of chemically modified wood fibers were examined to improve physical properties of wood composites. Generally, coupling agents are molecules possessing ambiphilic functions. The first function is to react with —OH groups of cellulose fibers and the second is to mix with the polymer matrix. Various surface chemical modifications of wood fibers such as alkali treatment, isocyanate treatment, acrylation, silane treatment, and peroxide

Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)
41.0	27.5	28.1	3.4

treatment have achieved in various levels of success in improving fiber strengths and fiber-matrix adhesion in wood fiber composites. Silane modifications,[8,9] benzoyl treatment,[10,11] and benzyl treatment[12,13] to wood fibers have been reported to improve physical properties of wood fiber composites. These chemical modifications improve overall properties of the composites compared with the cases of no chemical treatment, and it is believed that the adhesion between polymer matrix and the chemically modified wood fiber is significantly increased.

We performed a sequential approach to modify wood fiber (Lignocel® C120): first, alkali (NaOH) treatment, and then coupling (silane or benzoyl) agent treatment. As can be seen in Table I, wood fiber mainly consists of cellulose, hemicellulose, lignin, and extractives (pectins and waxes) differing from the cotton having 100% cellulose. One of the roles of alkali (NaOH) treatment in natural fiber is to change the crystal structure of cellulose from Cell-I to Cell-II. The original Cell-I crystal structure is transformed into different Cell-II type, typically with NaOH concentration higher than 10 wt %[14–17]. This new lattice structure (Cell-II) was reported as thermodynamically more stable than the original structure (Cell-I),[18] and sodium hydroxide has been recognized as the most efficient in lattice transformation. In addition, an important role of coupling agent in wood fiber treatment is to change the surface nature (hydrophilic → hydrophobic). The FTIR spectroscopy technique usually gives very useful information for the change of chemical bonding of the molecules during crystal transformation of cellulose,[14] and it is also a useful technique for confirmation of the functional group in coupling agents after reaction. In this study, we carried out a systematic investigation of the FTIR peak changes because of the cellulose crystal structure transformation in wood fiber (Lignocel® C120) by NaOH treatment and the change of absorption intensity because of the functionalization on the wood fiber surface by coupling agent (silanes and benzoyl) treatments.

EXPERIMENTAL

Materials

Lignocel® C120 (Natural wood fiber from JRS, Germany) was used for chemical treatments. Its grain size and bulk density are 70–150 μm and 100–135g/L, respectively. For alkali treatment, a reagent grade of NaOH (Ducsan pure chemicals Co., Korea) bottle was purchased and used without further purification. In silane modification, two types of silanes (3-aminopropyltriethoxysilane (APTES), 99% and triethoxyvinylsilane (TEVS), 97%, both from Aldrich®) were used as received. In addition to silanes, benzoyl chloride (BC, ReagentPlus®, 99% from Aldrich) was also used for benzoyl modification. For all NaOH solution preparation, deionized water (resistivity > 18MΩ) was used for various weight percent concentrations. In silane reaction with the wood fibers after treated with NaOH solution, pure ethanol (Ducsan pure chemicals Co., Korea) was used.

NaOH treatment

The wood fibers were immersed in NaOH solutions up to 15.3 wt % of NaOH at 25°C for 30 min with vigorous stirring. Solution to wood fiber ratio was 20 : 1 (weight percent). The treated wood fibers then washed out thoroughly with the deionized water until the rinsed solution became neutral. The rinsed fibers were then dried at 80°C in a convection oven for 24 h.

Generally, alkali treatment affects the swelling of a cellulose fibers and the degree of swelling depends on the alkali concentration. Na^+ ion plays a crucial role in widening the smallest pores in between the lattice planes and diffuses into those planes, and thus NaOH leads a high swelling. After removal of excess NaOH, the new form of Na-Cell-I lattice (which has relatively large distance between the cellulose molecules filled with water molecules) is formed. The OH groups in the cellulose fiber are changed into ONa-groups expanding the molecular dimension. Next, rinsing step with water removes the linked Na^+ ions and converts the cellulose structure to a new crystalline structure of Cell-II. Figure 1 shows schematic representation of crystalline transformation by the NaOH treatment.

Silane treatment

Wood fibers treated with various NaOH concentrations were used for 3-aminopropyltriethoxysilane (APTES) and triethoxyvinylsilane (TEVS) reactions. For the APTES reaction, first the 5% APTES was hydrolyzed for 1 h in the ethanol solution at a pH value of 4.5–5, and then the wood fibers were immersed for 2 h at room temperature for silane coupling with the wood fibers. After the coupling reaction, the fibers were filtered with filter papers and dried at 80°C in the convection oven for 24 h. For the TEVS, ethanol solution with 40% water
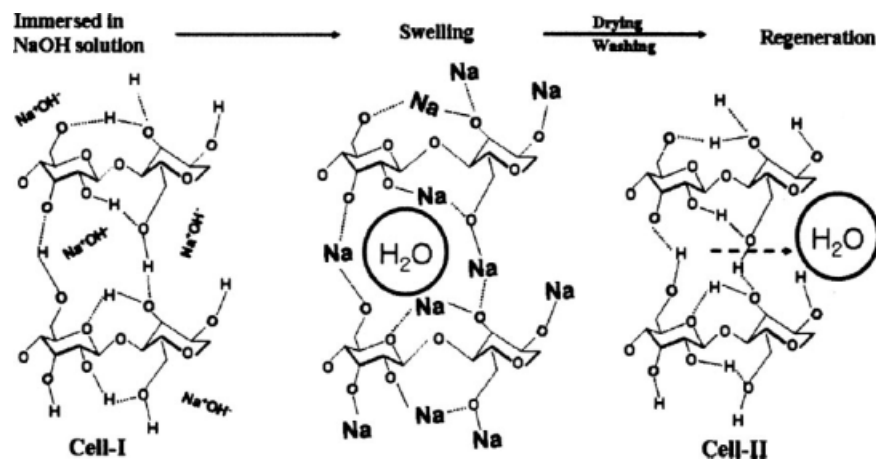
Figure 1 Schematic of the crystalline structure transformation by NaOH treatment.

content was used for reaction because it was very difficult to confirm the vinyl silane reaction by FTIR at 95% ethanol solution. The TEVS treated fibers were also filtered and dried with the same method described above.

In this step, hydrophilic surface of the wood fibers is transformed to hydrophobic surface by coupling reaction. In Figure 2, the schematics of the coupling reactions with wood fibers are shown. Through silanization as shown in Figure 2(a), hydrolysis of silane (silanol formation), condensation between silanols, and bond formation between siloxane and wood fibers were consecutively achieved.

Benzoyl treatment

Five grams of wood fibers pretreated with NaOH solution were suspended in 10 wt % NaOH solution and mixed well with 5% benzoyl chloride for 30 min. Excess amount of water was used to wash out NaOH solution, and the benzoylated fibers were immersed in ethanol solution for 1 h to remove unreacted benzoyl chloride. Finally, the fibers were washed out with deionized water and dried at 80°C in a convection oven for 24 h.

For benzoylation reaction in Figure 2(b), Na ions attached to wood fiber by NaOH treatment is further reacted with Cl atoms and NaCl is extracted.

FTIR analysis

Fourier transformed infrared spectroscopy spectra were obtained with the spectrum RXI (Perkin–Elmer). Samples of the wood fiber (2 mg) were grounded and dispersed in a KBr (28 mg) matrix. A pellet was then formed by compression at the pressure of about 200 MPa. Spectra with samples were obtained from 16 scans and a resolution of 4 cm^{-1}. During scanning, nitrogen gas was purged for stable operations.

Chemical composition analysis of Lignocel® C120

Holocellulose is the total polysaccharide (cellulose and hemicelluloses) content of wood. Holocellulose determination by removing all of the lignin from wood fiber without disturbing the carbohydrates was performed according to ASTM Standard D 1104. The lignin in the wood fibers is a residue remaining after solubilizing the carbohydrates with 72% H_2SO_4. The lignin content was measured according to ASTM Standard D 1106. The alcohol-benzene soluble content of wood is a measure of the waxes, fats, gums, resins, water soluble, and ether-insoluble components. The extractives content of wood fiber was measured according to ASTM D 1107. Every value of the chemical analyses represents the mean of three replicates.

RESULTS AND DISCUSSION

Transformation of crystal structure

Chemical modification of wood fibers leads to changes in molecular interactions, which in turn shows wavenumber shifts in the FTIR spectra. First, we show the effect of amount of NaOH on the changes of cellulose crystalline structures. Next, the NaOH treated wood fibers were further used for reactions with two silanes (APTES and TEVS) and one benzoyl chloride.

Figure 3 shows wavenumber shifts in FTIR for the spectrum range from 1500 cm^{-1} to 400 cm^{-1} with NaOH treatment. As reported by other investigators,[14,18,19] NaOH treatment changed the cellulose crystalline structures. Major wavenumber shifts occur around 1420 cm^{-1}, 1227 cm^{-1}, 1160 cm^{-1}, 1110 cm^{-1}, 1059 cm^{-1}, and 990 cm^{-1} for the amount of NaOH higher than 9.1 wt %. The band at 1227 cm^{-1} assigned as C—OH bending in plane at C_6[14,20,21] starts to appear as long as wood fibers are treated with NaOH solution, and it shows a clear peak
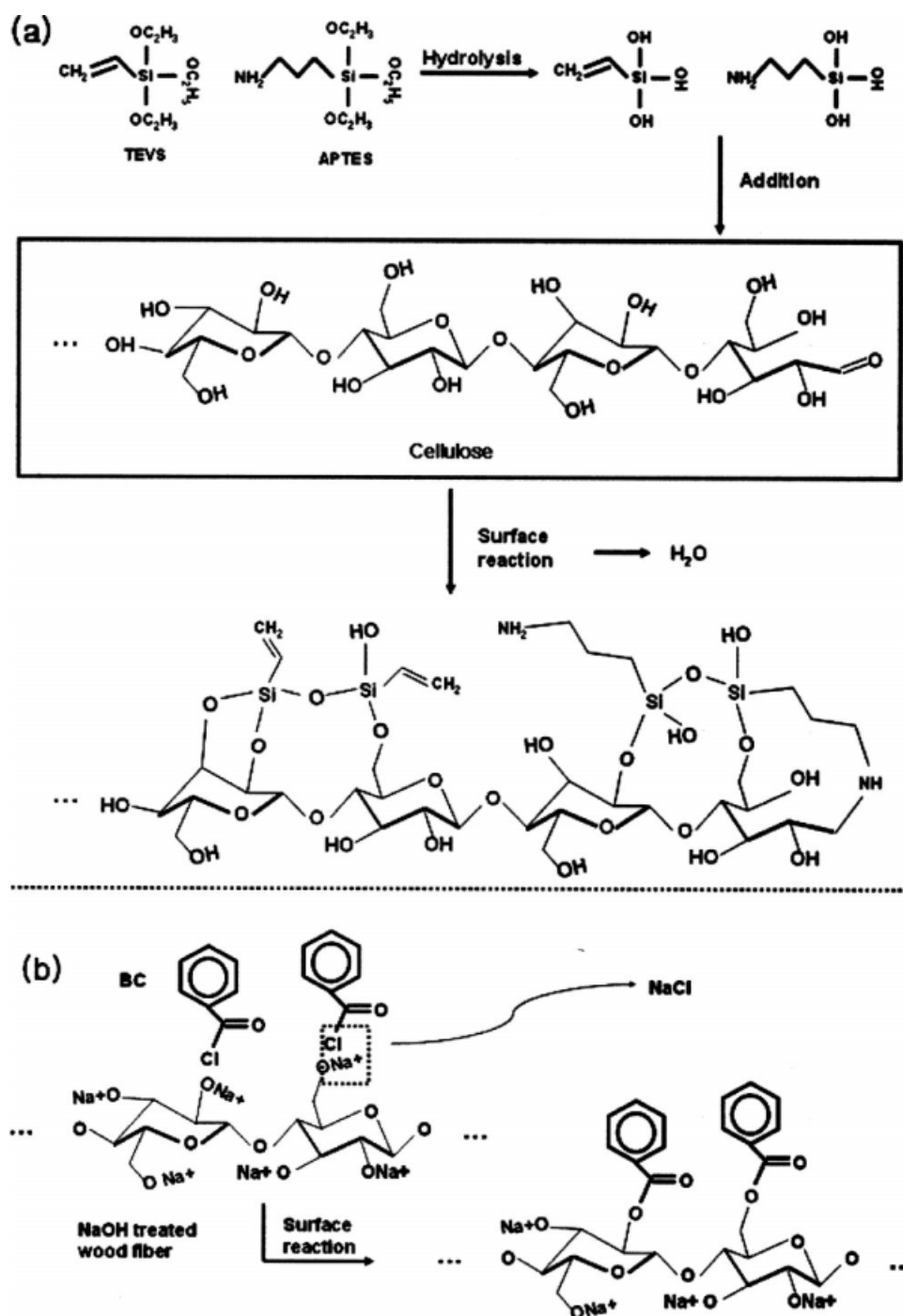
Figure 2 Schematics of coupling reactions between wood fibers and silane chemicals (a) and benzoyl chloride (b).

increase at NaOH concentration higher than 10.7 wt %. Other details of peak changes of cellulose crystalline structure by NaOH treatment for various NaOH concentrations are demonstrated in following Figures (Fig. 4 through Fig. 7).

For the wavenumber between 1180 cm^{-1} and 970 cm^{-1}, Figure 4 shows gradual shifts of cellulose structures from Cell-I to Cell-II by observing the wavenumber changes: from 1163 cm^{-1} to 1161 cm^{-1}, disappearing discrete bands at 1111 cm^{-1} and 1059
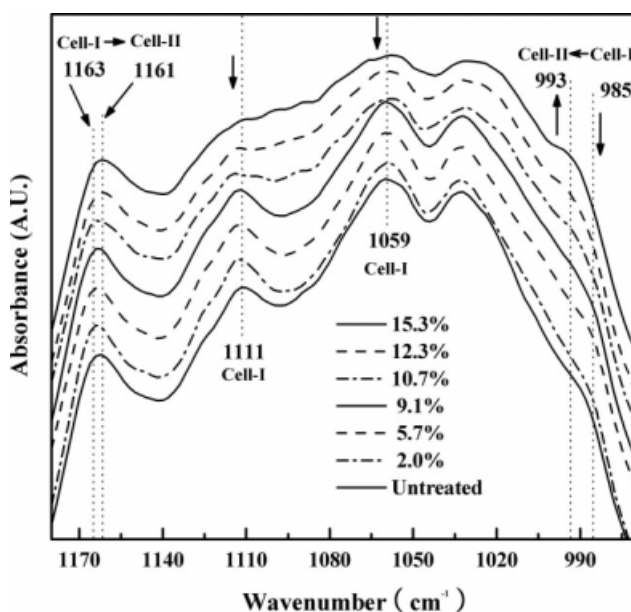
cm^{-1}, and from 983 cm^{-1} to 993 cm^{-1}. The band at 1163 cm^{-1} assigned as C—O—C asymmetric stretching[14,19,22] is shifted to 1161 cm^{-1} at NaOH concentration above 10.7 wt %, and it is a clear evidence of the change of Cell-I crystal structure to Cell-II crystal structure as previously demonstrated by others.[14,21] Similarly, the bands at 1111 cm^{-1} assigned as ring stretching in plane[21–23] and 1059 cm^{-1} assigned as C—O stretching at C$_6$[19,22] start to disappear at the NaOH concentrations higher than 10.7 wt %, and it
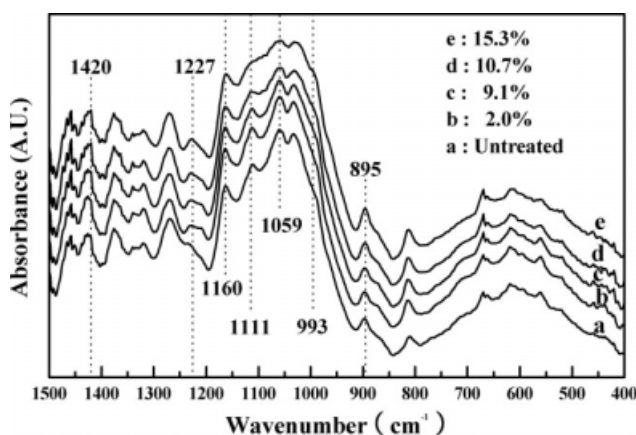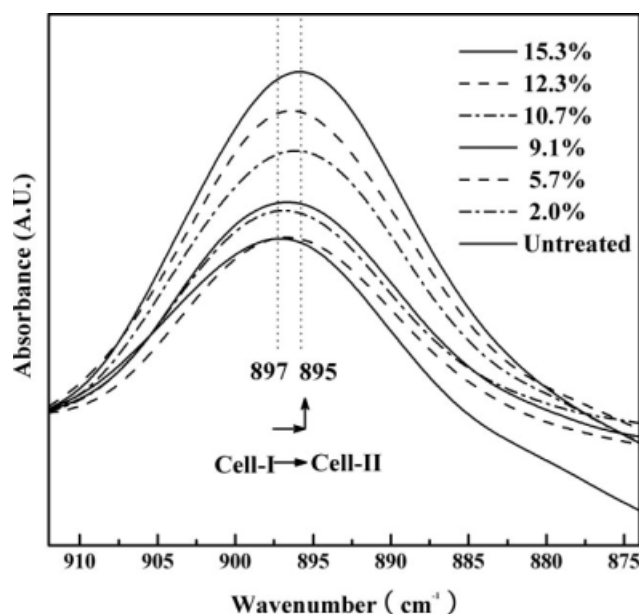
Figure 3 FTIR spectra of the wood fibers treated with various NaOH solution concentrations. Wavenumber ranges from 1500 cm^{-1} to 400 cm^{-1}.

is also because of the transformation of crystalline structure from Cell-I to Cell-II, which is also reported previously.[14,21] The band at 983 cm^{-1} assigned as also C—O stretching at C$_6$[19,23] is shifted to 993 cm^{-1} at the NaOH concentrations higher than 10.7 wt %, which is also because of the change of cellulose crystal structure.

The band at 897 cm^{-1} assigned as C—O—C asymmetric stretching[14,19,21,22] for the Cell-I structure is shifted to 894 cm^{-1} for the Cell-II structure at the NaOH concentration higher than 10.7 wt %, and it is shown in Figure 5. Absorbance increase of the band at 897 cm^{-1} (or 895 cm^{-1}) was also observed after the NaOH concentration of 10.7 wt % by structure
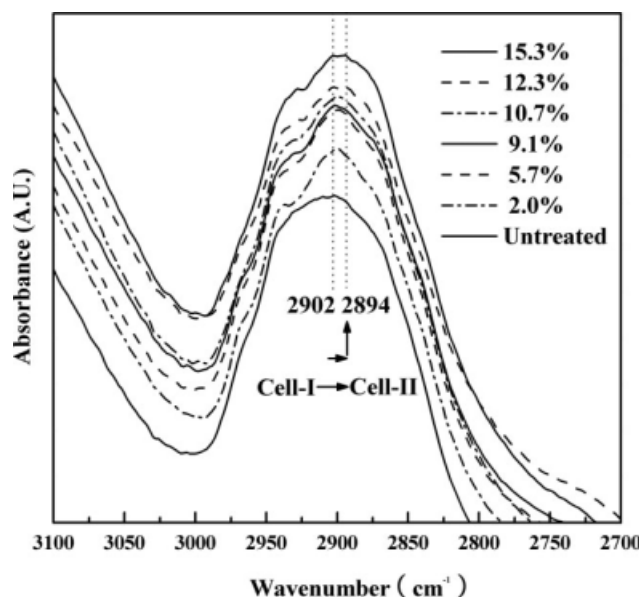

Figure 5 FTIR spectra of the wood fibers treated with various NaOH solution concentrations. Specific range of the spectra from 913 cm^{-1} to 870 cm^{-1} is shown for detail variations.

transformation. In addition, Figure 6 demonstrates the band shift from 2902 cm^{-1} to 2894 cm^{-1}. The band at 2902 cm^{-1} for the Cell-I is shifted to 2894 cm^{-1} for the Cell-II, assigned as CH stretching in methyl and methylene[22] at NaOH concentration of 15.3 wt %. The absorbance peaks at 2902 cm^{-1} (or 2894 cm^{-1}) become sharp as long as NaOH treatment was performed compared with the untreated

Figure 4 FTIR spectra of the wood fibers treated with various NaOH solution concentrations. Specific range of the spectra from 1180 cm^{-1} to 970 cm^{-1} is shown for detail variations.

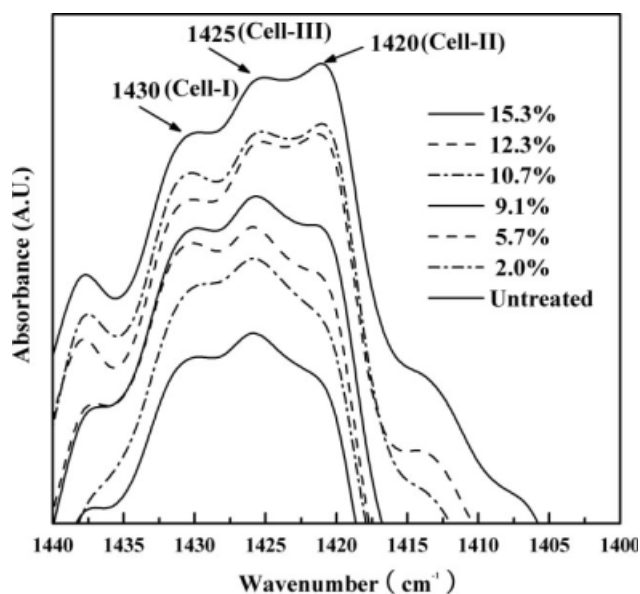
Figure 6 FTIR spectra of the wood fibers treated with various NaOH solution concentrations. Specific range of the spectra from 3100 cm^{-1} to 2700 cm^{-1} is shown for detail variations.
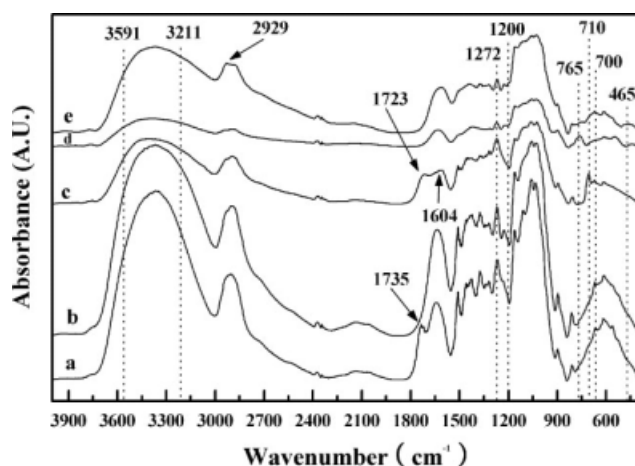
Figure 7 FTIR spectra of the wood fibers treated with various NaOH solution concentrations. Specific range of the spectra from 1440 cm^{-1} to 1400 cm^{-1} is shown for detail variations.

sample. It is mostly believed that cellulose crystal structure likely becomes the Cell-II.

Figure 7 shows gradual increase of band at 1420 cm^{-1} (Cell-II) assigned as CH$_2$ symmetric bending.[21] The Cell-II crystalline structure is clearly observed at NaOH concentration higher than 10.7 wt %. The band at 1420 cm^{-1} in Cell-II was assigned by Liang and Marchessault[23] to the CH$_2$ scissoring motion, and it implies that changes in the peak intensity are related to alterations in the environment of the C$_6$ group. However, the Cell-I band at 1430 cm^{-1} and the Cell-III band at 1425 cm^{-1} show moderate inten-

sity and remains regardless of NaOH concentrations within our experimental ranges.

As a result, FTIR measurements of the NaOH treatment of wood fibers showed clear evidences in change of cellulose crystalline structures. Most likely, the NaOH treatment of wood fibers leads to the Cell-II structure, which can provide high thermal stability in producing wood plastic composites (WPC).[24] For final WPC applications, another chemical treatment step is required to increase adhesion between wood fibers and plastic materials. In following, two types of silanes and one benzoyl are further used for modification of fiber surfaces.

Modification of wood fiber surface

Figure 8 demonstrates the changes of characteristic peaks representing the chemical reactions including coupling agents. Various peak changes by NaOH treatment were already explained in Figure 3 for the wavenumber ranging from 1500 cm^{-1} to 400 cm^{-1}, and it is also necessary to show a band change at 1735 cm^{-1} with NaOH treatment. It represents carbonyl groups in hemicellulose[25] and this observation demonstrates disappearing of the carbonyl groups even at low concentration of NaOH. In addition, three more curves show peak changes for APTES, TEVS, and BC treatments. The introduction of benzoyl groups resulted in an increase in the carbonyl stretching absorption at 1723 cm^{-1} and in bands characteristics of aromatic rings (1604 cm^{-1} and 710 cm^{-1}) and a strong absorption at 1272 cm^{-1} for C—O band in aromatic ring. It demonstrates the clear evidence of benzoyl group attachment to wood fibers. Treatments of wood fibers with amino- and vinyl-silanes also showed peak changes at 1200
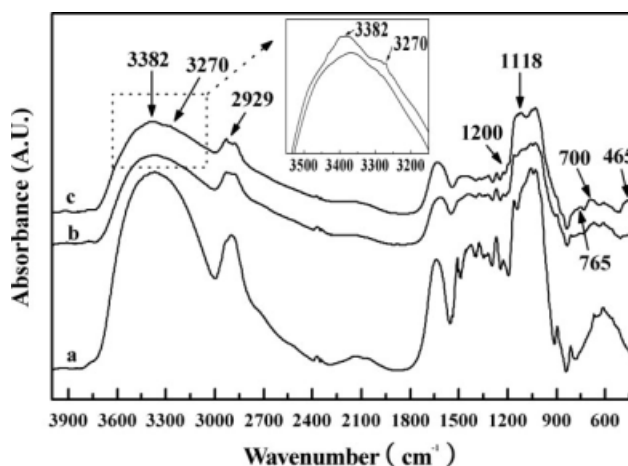

Figure 8 FTIR spectra of the wood fibers treated with coupling agents. Wood fibers were treated with: (a) untreated, (b) 15.3 wt % NaOH, (c) 15.3 wt % NaOH + 5 wt % benzoyl chloride, (d) 15.3 wt % NaOH + 5 wt % TEVS, and (e) 15.3 wt % NaOH + 5 wt % APTES.

Figure 9 FTIR spectra of the wood fibers treated with APTES coupling agents. Wood fibers were treated with: (a) 15.3 wt % NaOH, (b) 15.3 wt % NaOH + 5 wt % APTES, and (c) 15.3 wt % NaOH + 10 wt % APTES. The inset shows detail variations of the absorbance spectra.

TABLE II
Locations of the FTIR Band Spectra and Their Assignments for Silane Compounds

Peak (cm^{-1})	Assingment	Reference
3591-3200	NH$_2$ stretch vibration	28
2955-2837	Aliphatic CH$_2$-stretching vibration	28,29
2972	C—NH$_2$ stretching vibration	30
1673	Vinyl silane end group	31
1605	NH bending vibration	29
1518 broad band	NH$_2$ deformation	29
1200	Si—O—C bond	26
1150-950 broad band	Si—O—Si asymmetric stretching and/or Si—O—C band	26
1150-1043	NH bending vibration	28
1050 broad band	Si—O—Si bond	29
949	Si—O—Si stretching vibration	28
812	Si—O symmetric stretching vibration	28
765	Si—C asymmetric stretching	26
700	Si—O—Si asymmetric stretching	26
465	Si—O—C asymmetric bending	27

cm^{-1} assigned as Si—O—C band, at 765 cm^{-1} assigned as Si—C symmetric stretching bond, at 700 cm^{-1} assigned as Si—O—Si symmetric stretching,[26] and at 465 cm^{-1} assigned as Si—O—C asymmetric bending.[27]

In FTIR analysis, the peak height often represents the relative amount of the functional groups. For those coupling reactions, all cases showed increased peak height with the use of increased amount of coupling agents. Of all those reactions, for example, Figure 9 shows the gradual increase in peak height for the wavenumber at 3382 cm^{-1} and 3270 cm^{-1} assigned as NH$_2$ stretching vibration,[28] at 2929 cm^{-1} assigned as CH$_2$ stretching vibration,[29] at 1200 cm^{-1} assigned as Si—O—C band, and 1118 cm^{-1} assigned as NH bending vibration[28] with the APTES coupling reaction. More detail FTIR peak locations and their assignments for silane coupling agents are listed in Table II. It likely implies that the coupling reaction between wood fiber and coupling agent is linearly proportional to the concentration of the coupling agents. Therefore, the amount of coupling agent required in modification of wood fiber can be optimized by measuring the physical properties of WPC materials for final applications.

CONCLUSIONS

Chemically treated natural wood fiber (Lignocel® C120) was analyzed by FTIR spectroscopy and it provides clear evidences of transformation of crystalline structure in observing wavenumber shift from Cell-I to Cell-II. The NaOH treatment of the wood fiber influenced inter- or intra-molecular hydrogen bonds during crystal transformation, and it shifted the bands locations or it changes the peak height. From the FTIR spectra, the bands were shifted from 2902 cm^{-1}, 1425 cm^{-1}, 1163 cm^{-1}, 983 cm^{-1}, and 897 cm^{-1} to 2894 cm^{-1}, 1420 cm^{-1}, 1161 cm^{-1}, 993 cm^{-1},

and 895 cm^{-1}, respectively, and those bands demonstrated the change of the crystalline structure from Cell-I to Cell-II. Meanwhile, the absorbance of the bands at 1111 cm^{-1} and 1059 cm^{-1} assigned for Cell-I structure decreased or disappeared. Treatments of wood fibers with amino- and vinyl-silanes showed peak changes at 1200 cm^{-1} assigned as Si—O—C band, at 765 cm^{-1} assigned as Si—C symmetric stretching bond, at 700 cm^{-1} assigned as Si—O—Si symmetric stretching, and at 465 cm^{-1} assigned as Si—O—C asymmetric bending. The use of benzoyl groups resulted in an increase in the carbonyl stretching absorption at 1723 cm^{-1} and in bands characteristics of aromatic rings (1604 cm^{-1} and 710 cm^{-1}) and a strong absorption at 1272 cm^{-1} for C—O band in aromatic ring.

We confirmed the transformation of crystalline cellulose structure in wood fiber through NaOH treatment and attachments of silane or benzoyl coupling agents by FTIR spectra. These chemical modifications of wood fibers would be expected to enhance adhesion between wood fibers and base polymer for final wood-composite applications with increasing compatibility.

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