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Biochemical Group Characteristics of Self-Bonded Boards During Acidic Oxidation for Public Health

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It has been proved that the more than 80% leukemia were caused by indoor formaldehyde pollution. To improve the self-bonding reactivity and prepare self-bonded board with formaldehyde-free, *Eucalyptus* wood fibers were pretreated, processed and analyzed by ^{13}C-NMR and FT-IR. The results showed that the IB of SBBs reached the maximum of 1.53MPa with the pretreatment time of 3h. FT-IR and ^{13}C-NMR spectra showed that the group and reactivity of wood fibers had different changes by acidic oxidation pretreatment. It suggested that cellulose, hemicellulose and lignin produced the bonding reaction, helped the pretreated fiber to be self-bonded, improved the water resistance and the high IB.

Key words: Biochemical groups; Acidic oxidation; Public health; NMR; FT-IR; Self-bonded board.

Leukemia, which was a group of blood cancers that began in the bone marrow, resulted in high numbers of abnormal white blood cells which was viewed as a family of diseases as opposed to a single disease in 1900. Boston pathologist Sidney Farber believed that aminopterin and a folic acid mimic could potentially cure children's leukemia in 1947. Subsequently, more and more researches on leukemia treatment were carried out. Wu et al found that the hENT1 mRNA level was significantly higher in response compared with non-response patients (P = 0.004), and the DCK level was significantly reduced for relapse (P = 0.012) compared with those with continued marrow CR (P = 0.222), indicating that the decitabine metabolic pathway affects its therapeutic effects, lower hENT1 expression could induce primary resistance and down-regulated DCK expression could be related to secondary resistance[1]. Raphael et al reported the multivariate analysis which high risk cytogenetics (P = 0.022) and peripheral blasts >10% (P < 0.0001) at onset of azacitidine were independently predictive of poor prognosis, and identified a subgroup of 48% of patients with intermediate risk cytogenetics and peripheral blasts d"10% and a median OS of 11.3 months. These results warrant further investigation of azacitidine-based regimens in this subgroup of patients[2]. Jones et al evaluated four genetic screening methods for their ability to detect a series of different CALRmutations; Sanger sequencing, fragment analysis PCR, high resolution melt (HRM) and

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targeted next generation sequencing (NGS), resulting that HRM and fragment analysis PCR were better at detecting low mutation levels compared to Sanger sequencing but targeted NGS had the lowest LoD at a 1% mutation burden[3]. However, bone marrow failure syndromes, which were characterized by a failure of the hematopoietic stem cells to produce adequate blood cells, often went together with leukemia treatment for cytopenia (defect in one or more blood cell lineages) or pancytopenia (defect in all blood cell lineages)[4]. Thus, leukemia patients were still growing. About 245,000 people in the United States were affected by leukemia, and approximately 44,270 new cases of leukemia were diagnosed only in 2008 in the US. As well as about 5,000,000 patients with leukemia were in China. Leukemia developed in 352,000 people globally and caused 265,000 deaths in 2012. Especially, leukemia was the most common type of cancer in children, with three quarters of leukemia cases in children being ALL. Further, It was proved that 80% leukemia were caused by indoor formaldehyde pollution which came from wooden-based panels productions.

Since wood-based panels were production-manufactured, the people's demand of self-bonding boards (SBB) has been grown eagerly with no formaldehyde emission[5-8]. SBBs were one kind of wood-based panels with wood fiber bonded together without resin under pressure and heat. And the BBS was improved by activating the components of wood fibers during hot press[9]. With the eager market demand of SBB, it was the scientific research task to find out the self-bonding mode of fiber, especially the groups of the fibers during hot press. Therefore, To improve the self-bonding reactivity, *Eucalyptus* wood fibers were pretreated by acidic oxidation, processed by hot press, and analyzed by FT-IR and . ^{13}C-NMR.

MATERIALS AND METHODS

The 4.5-years-old *Eucalyptus urophydis* was gathered from Yangjiang Forestry Bureau owned forest farm. Eucalyptus urophydis wood was processed into wood chips, dried to oven dry, and mechanically disintegrated to 40-60 mu short fiber. $H_2C_2O_4$ and H_2O_2 (30%), which were prepared for the subsequent experiments, were analytical reagent.

Experiment methods

Acidic oxidation. The above short fiber was pretreated by acidic oxidation for 1h, 3h, 5h, 7h, and 9h, respectively. The acidic oxidation solution was mixed 100 ml water, 2g $H_2C_2O_4$ and 5ml H_2O_2 (30%). After pretreatment, the short fiber was filtered, dried at room temperature, done to oven dry at 103ºC. The pretreated fiber was named CG11, CG12, CG13, CG14, CG15, respectively.

Self-bonding process

The pretreated fiber was hotly pressed to self-bond under the conditions of 20 min, 160ºC and gauge pressure 15MPa. The obtained self-bonding boards, which thickness were all 4mm, were named CG21, CG22, CG23, CG4 and CG25, respectively. Then the internal bond strength (IB) of the self-bonding boards (SBB) was determinated according to GB/T 11718-2009.

Goup Characterization

FT-IR spectra of the above samples were obtained using a Thermo Scientific Nicolet iN10 FT-IR microscope as previously[8,9]. CP-MAS ^{13}C-NMR spectra of the above samples were determinated on solid state and obtained using a Bruker AVIII 400.M spectrometer (Germany) as previously[9,10].

Experiment Results

Analysis on internal bond strength

The internal bond strength of self-bonding boards was tested and done by statistical analysis. Effect acid oxidation pretreatment on IB of SBBs. With the prolongation of time, the IB of SBBs firstly increased and then decreased. While the pretreatment time was 3h, the IB of SBBs reached the maximum of 1.53MPa. The intrinsic reasons would be analyzed as follows.

FT-IR Spectra

FT-IR spectra could be used to investigate the structural goups of the SBBs. For comparison, the spectra of the SBBs were plotted in supporting information Figure 1. The spectra of all samples showed the 3347cm^{-1} (O-H stretch), 2904cm^{-1} (-CH_2 stretch), 1736cm^{-1}(unconjugated C=O stretch), 1458cm^{-1} (C-H deformation vibration), 1369cm^{-1} (C-H bending vibration), 1229cm^{-1} (C-C, C-O plus C=O stretch), 1158cm^{-1} (C-O-C stretch), 1109cm^{-1} (C-O or C-C stretch), 1034cm^{-1} (C-O-C stretch), 897cm^{-1} (cellulose beta glycosidic bond stretching vibration). Particularly, the conjugated units in lignin were probably related to oxidation at ±-position of side-chain of lignin during hot press. The similar spectra patterns of aromatic skeletal vibrations in the lignin samples (1593cm^{-1}, 1503cm^{-1}, and 1422cm^{-1}) suggested that the basic aromatic structures of lignin were not changed during these processes. The syringyl lignin stretching vibration was at 1322cm^{-1}.

Based on Fig.1, after the fiber was pretreated in acidic oxidation, -OH stretching vibration at 3347cm^{-1} strengthene. And –OH increased to urge the fiber self-bonding. The absorption intensity of the group at 1737cm^{-1} also strengthene. The characteristic absorption peaks at 1593cm^{-1}, 1503cm^{-1}, and 1422cm^{-1} increased, and it shown that Ar of lignin openly react and enhanced the reaction activity. The peaks at 1460 cm^{-1} and 1030cm^{-1} reduced.

After hot press, -OH stretching vibration reduced, resulting that hydroxyl was formed by hydrogen bond association. The characteristic absorption peaks at 1593cm^{-1}, 1503cm^{-1}, and 1423cm^{-1} reduced, and it shown lignin participated in the self-bonding reaction. The characteristic absorption peaks at 2904cm^{-1}, 1735cm^{-1}, 1458cm^{-1}, 1322cm^{-1}, 1229cm^{-1}, 1158cm^{-1}, 1369cm^{-1}, and 1109cm^{-1} all reduced, and it shown cellulose, hemicellulose and lignin also participated in the self-bonding reaction.

The characteristic groups of $-CH_3$, $-CH_2$, –OH, C=O and Ar had all the obvious changes after the hot press, suggesting that lignin, cellulose and hemicellulose produced the united chemical reaction and helped the pretreated fiber to be self-bonded. The number of hydroxyl group decreasd, it showed that the interaction of -OH formed hydroxyl, and reduced the number of free hydroxyl hydrophilic so as to make the board with a fine water resistance and the higher IB.

Analysis on ^{13}C-NMR **goups**

^{13}C-NMR spectroscopy is a reliable method for investigating the structural features of samples and it also provided a more comprehensive view of the entire lignin macromolecule. The ^{13}C-NMR spectra of the three samples are shown in Fig. 2. As can be seen from the Fig.2, C=O of ester

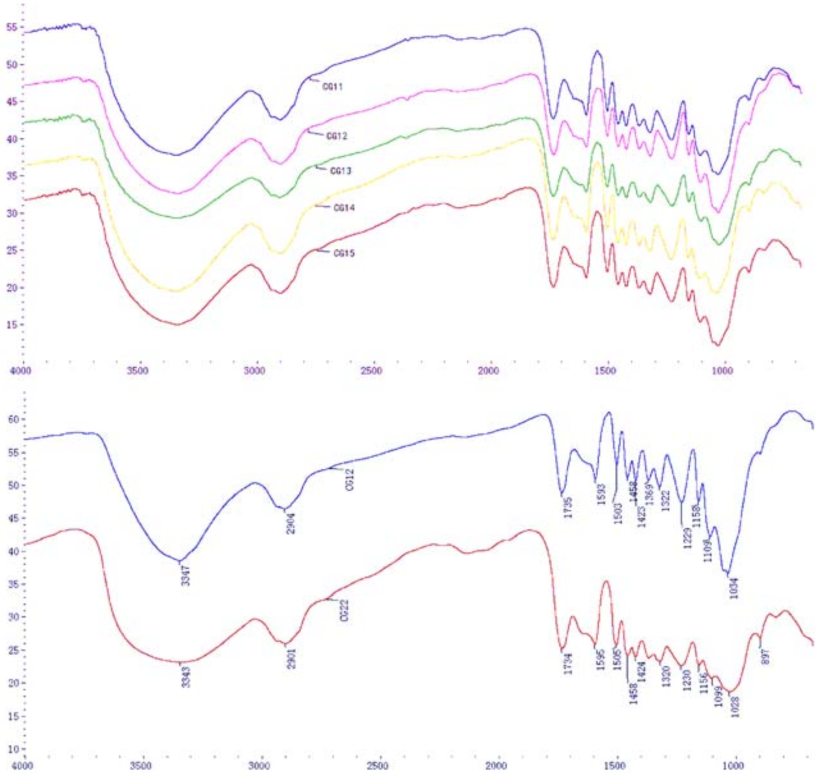

Fig.1. FTIR spectra of some samples

bond presented 172 ppm. The groups of lignin appeared 110-160 ppm, C3/C5 of etherification S-lignin at 151.7/152.5ppm, C-1 of unetherification S-lignin and G-lignin at 133.1 ppm, Ar of lignin at 121.5 ppm. Cellulose peak decreased such as C-1 of cellulose at 104.5 ppm, C-4 (crystalline region) of cellulose at 88.5 ppm, C-4 (amorphous regions) of cellulose at 83.6 ppm, C-3/C-2/C-5 of cellulose at 74.4 ppm, C-6 of cellulose at 64.3 ppm, showing that alkalescent salt and cellulose reacted and its crystalline structure destructed. C-^{3}of lignin side chain at 61.7 ppm, -OCH_3 of ligin at 55.4 ppm, and -CH_2 of lignin Side chain at 20.6 ppm.

After acidic oxidation, the peaks at 171.4 ppm, 133.1 ppm, and 121.5 ppm attenuated, resulting that Ar of lignin opened. The peaks of C-^{3}in lignin side chain at 61.7 ppm became weaker, resulting that lignin side chain was broken. The –OCH_3 at 55.4 ppm disappeared, resulting that –OCH_3 sheded.

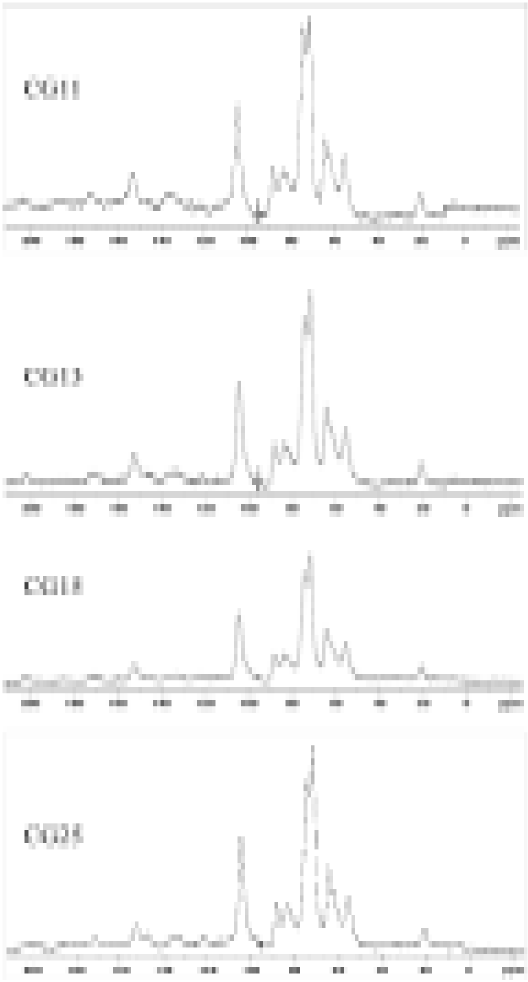

Fig. 2. ^{13}C-NMR spectra of some samples

After hot press, the peaks weakened such as the groups of lignin at 110-160 ppm, C3/C5 of etherification S-lignin at 153.0 ppm and 152.3 ppm, Ar of lignin at 122.0 ppm. Cellulose peak decreased such as C-1 of cellulose at 104 ppm, C-4 (crystalline region) of cellulose at 88.6 ppm, C-4 (amorphous regions) of cellulose at 82.9 ppm, C-3/C-2/C-5 of cellulose at 74.7 ppm, C-6 of cellulose at 64.6 ppm, C-^{3}of lignin side chain at 71.9 ppm, -OCH_3 of ligin at 55.6 ppm, and -CH_2 of fatty hydrocarbon at 32.1 ppm.

C=O of ester bond at 172ppm, C3/C5 of S-lignin at 153.0/152.6 ppm, C-4 of S-lignin or C-1 of G-lignin at 133.5/132.8 ppm, C-1 of paraben at 121.8/121.4/121.1 ppm, C-3/C-5 of ester S-lignin or C-4 of unester G-lignin at 147.6ppm, C-1 of cellulose at 104.6 ppm, C-4 (crystalline region) of cellulose at 88.4 ppm, C-4 (amorphous regions) of cellulose at 83.6 ppm, C-3/C-2/C-5 of cellulose at 74.4 ppm, C-6 of cellulose at 64.3 ppm, C-^{3} of lignin side chain at 62.0 ppm, -OCH_3 of ligin side chain at 55.4 ppm, and -CH_2 of lignin Side chain at 20.6 ppm. It resulted that cellulose, hemicellulose and lignin also participated in the self-bonding reaction during the hot press. It was the same as FT-IR analysis.

CONCLUSION

FT-IR and ^{13}C-NMR spectra showed that the chemical structure and reactivity of *Eucalyptus* wood fibers had different changes after pretreated by acidic oxidation, aromatic ring structure was destroyed, part of methoxy sheded, aromaticring hydroxylate.

The characteristic groups of -CH_3, -CH_2, –OH, C=O and Ar had all the obvious changes during the hot press, reducting that lignin, hemicellulose and cellulose produced the bonding reaction. and help the pretreated fiber to be self-bonded. The –OH number decreasd, it shown that the interaction of -OH formed hydroxyl, and reduced the number of free hydroxyl hydrophilic so as to make the board with a good water resistance and the higher self-bonding strength.

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