

## Structure Characteristics of Acidic Pretreated Fiber and Self-bind Bio-boards for Public Health

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(Received: 20 February 2015; accepted: 15 April 2015)

Abortion, which has been induced by indoor formaldehyde pollution, is more and more severely threatening public health. To fundamentally eliminate indoor formaldehyde pollution, wood fiber was done by acid pretreatment and self-bind process, and analyzed by FT-IR and SEM. The results shown that the bond strength firstly increased and then decreased with the increase of pretreatment time, reached the maximum value 0.52 MPa (HOOC-COOH) for 10h and 0.82 MPa (1%CH<sub>3</sub>COOH) for 15h. lignin did not change during the acid pretreatment,  $\alpha$ - glycosidic bond of cellulose decreased, other groups all increased during acid pretreat. And the active groups, lignin and cellulose all took part in the chain reaction during self-bind process. Wood fiber was better done by 1% CH<sub>3</sub>COOH pretreatment than by 1% H<sub>2</sub>COOH pretreatment in favor of self-bind bio-boards.

**Key words:** FT-IR, SEM, Self-bind bio-boards, Formaldehyde pollution, Abortion.

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Pregnant woman was one or more offspring develops inside a woman<sup>1</sup>. Although the woman need go through a painful period, her family was full of love and happiness<sup>2</sup>. However, pregnant woman had abortion which was a criminal offense a few decades ago, and birth was the number born deceased. It was so bad that the family would be full of pain and sad<sup>1-4</sup>. Abortions were the termination of an embryo or fetus, either naturally or via medical methods. For example, if pregnant woman took the wrong medicine or food, failed or intense impacted, pregnant woman would have abortion. Moreover, women reduced immunity during pregnancy<sup>3-6</sup>. If

formaldehyde air was absorbed into the body and went into the blood, immune cells would be killed, and it could initiated that women reduced less and less immunity and cause abortion<sup>3-7</sup>. Now, more than 20 million pregnant woman aborted around the world year after year<sup>8</sup>. It was reported that abortion had be about 13 million cases per year in China<sup>9</sup>. Where they lived in indoor formaldehyde pollution which came from wood-based panels productions, more and more pregnant women aborted. So the elimination of indoor formaldehyde pollution was in urgent and key need of public health security.

Since the birth of wood-based panels, the people's demand of self-bind bio-boards had been grown more and more eagerly with no high formaldehyde emission<sup>10-13</sup>. Self-bind bio-boards were one class of wood-based panels with wood fiber binded together without urea formaldehyde resin and others under heat and

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pressure. And the self-bind bio-boards was improved by activating the wood fibers before hot press<sup>14</sup>. With the eager market demand of bio-boards, it was the critical task to find out the self binded mode of fiber. Especially, the groups of the fibers were crossed during hot press. Therefore, to improve the self binded reactivity, *Eucalyptus urophydis* wood fibers were pretreated in acid, processed by hot press, and then analyzed by FT-IR and SEM.

## MATERIALS AND METHODS

*Eucalyptus urophydis* wood, which collected from Yangjiang forest zone in Guangdong Province China, was 4.5-years-old. The fresh wood was processed into wood chips, dried to oven dry, and powdered to 40-60 mu short fiber<sup>15</sup>. HOOC-COOH and CH<sub>3</sub>COOH, which were prepared for the subsequent experiments, were analytical reagent.

### Acid pretreatment

The above fresh short fiber was weighed, and each was 100 g (accuracy 1.0mg), and was pretreated in acidic solution for 5h, 10h, 15h and 20h at room temperature, respectively. The mass percentage concentration of HOOC-COOH and CH<sub>3</sub>COOH solutions were 1%, respectively. After pretreatment, the fresh short fiber was filtered, dried at room temperature, done to oven dry at 103°C. The pretreated fiber was named Y11, Y12, Y13, Y14, C11, C12, C13, and C14, respectively.

### Self-bind process

The 90g above pretreated fiber was self-binded at 160°C under the pressure of 15MPa for 20min, respectively. The self-bind boards were obtained and named Y21, Y22, Y23, Y24, C21, C22, C23, C24, respectively. Their bond strength was detected according to the China national standards GB/T11718-2009.

### FT-IR spectra

Fourier transform infrared spectrum (FT-IR) spectra of the above samples were obtained by using a Thermo Scientific Nicolet iN10 FT-IR microscope as previously<sup>13, 14</sup>.

### SEM observations

The sample surfaces were coated in a vacuum evaporator with a thin film of Au (JFC-1600) and observed by using an SM6490LV microscope<sup>13</sup>.

## RESULTS AND DISCUSSION

### Bond strength of self-bind bio-boards

The bond strength was the main mechanical strength of self-bind bio-boards. The detected results showed that the bond strength of self-bind bio-boards were 0.09 MPa, 0.52 MPa, 0.15 MPa, 0.13 MPa after the fiber was pretreated in 1%HOOC-COOH solution for 5h, 10h, 15h and 20h, respectively; their bond strength were 0.27 MPa, 0.32 MPa, 0.82 MPa, 0.16 MPa after the fiber was pretreated in 1%CH<sub>3</sub>COOH solution for 5h, 10h, 15h and 20h, respectively. The effect of acid pretreatment time on bond strength was significant. With the increase of pretreatment time, the bond strength firstly increased and then decreased, reached the maximum value 0.52 MPa (HOOC-COOH) for 10h and 0.82 MPa (1%CH<sub>3</sub>COOH) for 15h. The reason was that hemicellulose of *Eucalyptus* wood fiber were degraded and produced active groups when acid pretreat was initial. However, the components of *Eucalyptus* wood fiber were overly degraded so as to decrease the bond strength of self-bind bio-boards. The further results yet need further analysis.

### Group characteristics of wood fiber during acid pretreatment

FT-IR spectra could be used to investigate the groups of the wood fiber samples during acid pretreatment. For comparison, the spectra of the pretreated wood fiber were described in Fig.1 and Fig.2.

The FT-IR spectra of all samples displayed the O-H stretch at 3345cm<sup>-1</sup>, -CH<sub>2</sub> stretch at 2916cm<sup>-1</sup>, unconjugated C=O stretch at 1735cm<sup>-1</sup>, C-H deformation vibration at 1459cm<sup>-1</sup>, C-H bending vibration at 1372cm<sup>-1</sup>, C-O, C-C plus C=O stretch at 1235cm<sup>-1</sup>, C-O-C stretch at 1160cm<sup>-1</sup>, C-C or C-O stretch at 1113cm<sup>-1</sup>, C-O-C stretch at 1032cm<sup>-1</sup>, cellulose beta glycosidic bind stretching vibration at 898cm<sup>-1</sup>[13]. Fig.1 showed that the spectra of 1% HOOC-COOH pretreated wood fiber were plotted in supporting information. During the 1% HOOC-COOH pretreatment, the absorbance of O-H stretch peak increase, resulting that the number of O-H increased. The absorbance of -CH<sub>2</sub> stretch peak increase, resulting that the number of -CH<sub>2</sub> increased. The absorbance of unconjugated C=O stretch peak increased because cellulose and hemicellulose had the occurrence of hydrolysis

reaction in 1% HOOC-COOH solution. The characteristic absorption peaks of lignin ( $1593\text{cm}^{-1}$ ,  $1503\text{cm}^{-1}$  and  $1422\text{cm}^{-1}$ ) were largely unchanged, resulting that lignin did not change during the 1% HOOC-COOH pretreatment. The absorption peaks at  $1458\text{cm}^{-1}$ ,  $1369\text{cm}^{-1}$ , and  $1154\text{cm}^{-1}$  all increased, but the absorption peak at  $897\text{cm}^{-1}$  decreased.

Fig.2 showed that there were different changes in the FT-IR spectra of 1%  $\text{CH}_3\text{COOH}$  pretreated wood fiber. During the 1%  $\text{CH}_3\text{COOH}$  pretreatment, the absorbance of O-H stretch peak increase, resulting that the number of O-H increased. The absorbance of  $-\text{CH}_2$  stretch peak increase, resulting that the number of  $-\text{CH}_2$  increased. The absorbance of unconjugated C=O stretch peak increased because cellulose and hemicellulose had the occurrence of hydrolysis reaction in 1%  $\text{CH}_3\text{COOH}$  solution. The characteristic absorption peaks of lignin ( $1593\text{cm}^{-1}$ ,  $1503\text{cm}^{-1}$  and  $1422\text{cm}^{-1}$ ) were largely unchanged, resulting that lignin did not

change during the 1%  $\text{CH}_3\text{COOH}$  pretreatment. And the absorption peak at  $897\text{cm}^{-1}$  decreased. Comprehensive results of Fig.1 and Fig.2, lignin did not change during the acid pretreatment,  $\beta$ -glycosidic bond of cellulose decreased, other groups all increased.

#### Group characteristics of self-bind bio-boards

FT-IR spectra could be used to investigate the structural groups of self-bind bio-boards. For comparison, the FT-IR spectra of self-bind bio-boards were displayed in Fig.3 and Fig.4.

As could be seen from Fig.3, after the self-bind bio-boards made by the 1% HOOC-COOH pretreated wood fiber, the absorbance of O-H stretch peak became lower, resulting that some O-H might produce hydrogen bond. The absorbance of unconjugated C=O stretch peak decreased, resulting that some C=O and  $-\text{COOH}$  might produced link polymerization. The skeletal vibrations of lignin ( $1591\text{cm}^{-1}$ ,  $1504\text{cm}^{-1}$ , and

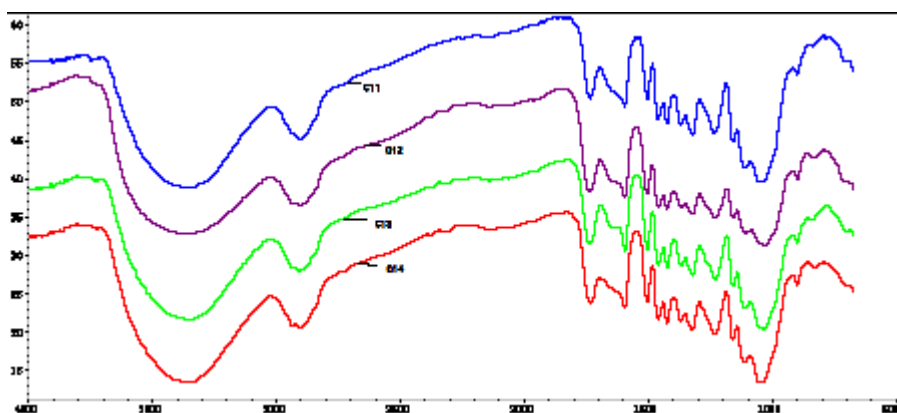


Fig.1. FT-IR spectra of 1% HOOC-COOH pretreated Euralytus wood fiber

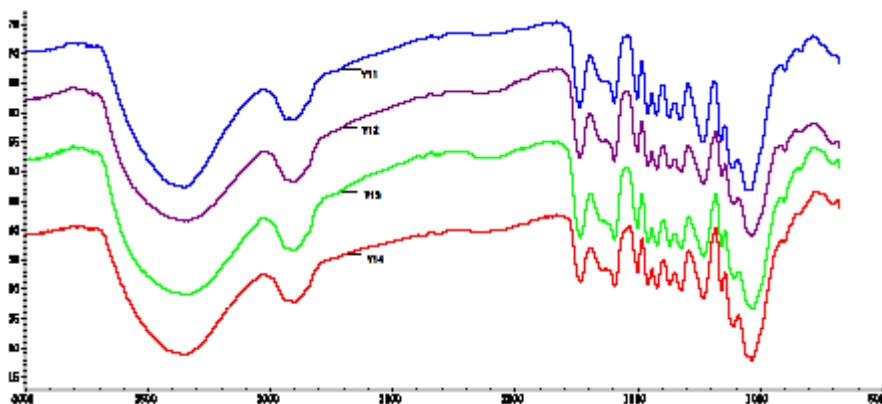


Fig. 2. FT-IR spectra of 1%  $\text{CH}_3\text{COOH}$  pretreated Euralytus wood fiber

1423 $\text{cm}^{-1}$ ) decreased, resulting that some lignin might produced the chemical bonding reaction. The 1157 $\text{cm}^{-1}$  and 1369 $\text{cm}^{-1}$  peaks became lower, suggesting that cellulose reacted. Moreover, the absorbance of C-C or C-OC-H (1107 $\text{cm}^{-1}$ ), C-H (2904 $\text{cm}^{-1}$ ) and C-O-C (1031 $\text{cm}^{-1}$ ) peaks both decreased.

As could be seen from Fig.4, after the self-bind bio-boards made by the 1%  $\text{CH}_3\text{COOH}$  pretreated wood fiber, the absorbance of O-H stretch peak became lower, resulting that some O-H might produce hydrogen bond. The skeletal vibrations of lignin (1594 $\text{cm}^{-1}$ , 1504 $\text{cm}^{-1}$ , and 1424 $\text{cm}^{-1}$ ) decreased, resulting that some lignin might produced the chemical bonding reaction. The 1159 $\text{cm}^{-1}$  and 1372 $\text{cm}^{-1}$  peaks became lower, suggesting that cellulose reacted. Moreover, the absorbance of C-C or C-O (1109 $\text{cm}^{-1}$ ), C-H (2917 $\text{cm}^{-1}$ ) and C-O-C (1036 $\text{cm}^{-1}$ ) peaks both decreased.

According to the above analysis results, after the pretreated wood fiber was self-bound, groups had the approximate variation characteristics (seen in Fig.3 and Fig.4). The characteristic absorption peaks of lignin and cellulose both decreased. It suggested that the active groups, lignin and cellulose all took part in the chain reaction during self-bind process.

#### Morphology characteristics of self-bind bio-boards

Scanning electron microscope (SEM) could observe the small changes of self-bind bio-boards. Fig.5, Fig.6, Fig.7, and Fig.8 showed SEM photo of C23 sample with the maximum bond strength, C24 sample with the minimum bond strength, Y22 sample with the maximum bond strength, Y21 sample with the minimum bond strength. As could be seen from Fig. 5 and Fig.7, when the self-bind bio-boards C23 of wood fiber by 1%  $\text{HOOC-COOH}$  pretreat broke, the fiber was

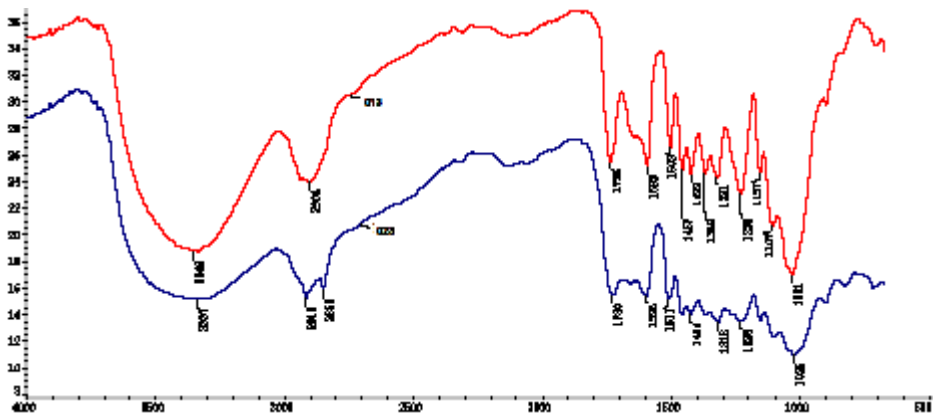


Fig. 3. FT-IR spectra of self-bind bio-boards made by 1%  $\text{HOOC-COOH}$  pretreated wood fiber

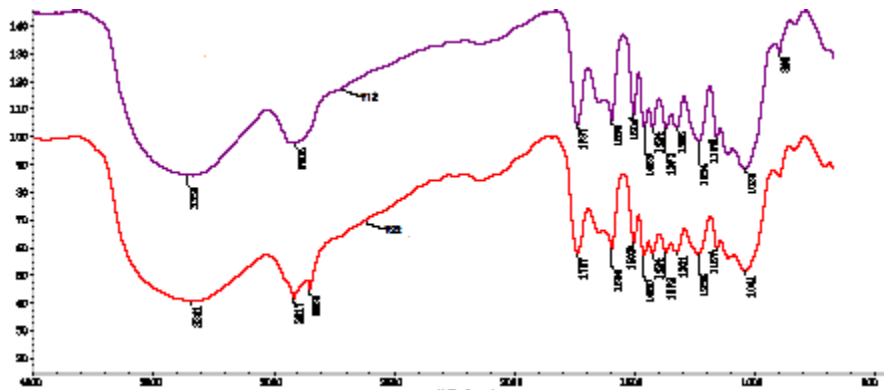
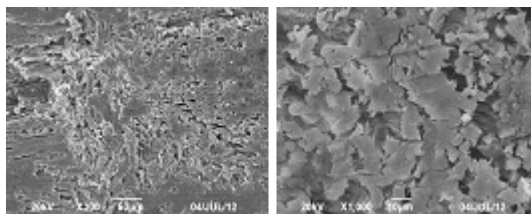
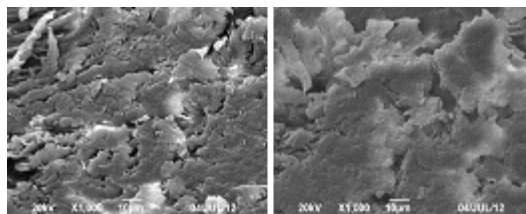


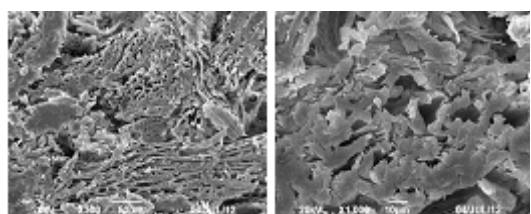
Fig. 4. FT-IR spectra of self-bind bio-boards made by 1%  $\text{CH}_3\text{COOH}$  pretreated wood fiber



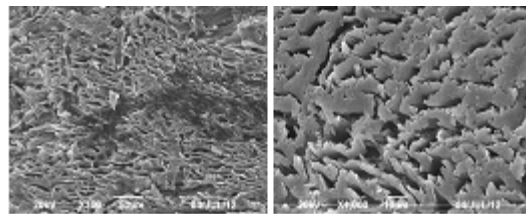
**Fig. 5.** SEM of C23 sample made by 1% HOOC-COOH pretreated wood fiber



**Fig. 6.** SEM of C24 sample made by 1% HOOC-COOH pretreated wood fiber



**Fig. 7.** SEM of Y22 sample made by 1% CH<sub>3</sub>COOH pretreated wood fiber



**Fig. 8.** SEM of Y21 sample made by 1% CH<sub>3</sub>COOH pretreated wood fiber

complete, there was a gap between the fibers, but the interface was inseparable, resulting that fibers were self-binded and changed into fiber bundles so as to have the high bond strength. However, when the self-bind bio-boards Y22 of wood fiber by 1% CH<sub>3</sub>COOH pretreat broke, fiber bundles was little, there was a gap between the fibers, cavitationis was many, but the interface was clear so as to have the low bond strength. As could be seen from Fig.7 and Fig.8, there were rough fiber morphology, more empty, obvious pull-off phenomenon on the interface of Y21 sample, but there were little empty, broken phenomenon on the interface of Y22 sample. The above results showed that wood fiber was better done by 1% CH<sub>3</sub>COOH pretreatment than by 1% HOOC-COOH pretreatment in favor of self-bind bio-boards.

### CONCLUSION

The effect of acid pretreatment time on bond strength was significant. With the increase of pretreatment time, the bond strength firstly increased and then decreased, reached the maximum value 0.52 MPa (HOOC-COOH) for 10h and 0.82 MPa (1% CH<sub>3</sub>COOH) for 15h.

FT-IR spectra showed that lignin did not change, 2- glycosidic bond of cellulose decreased, other groups all increased during the acid pretreatment. And the characteristic absorption

peaks of lignin and cellulose both decreased, suggesting that the active groups, lignin and cellulose all took part in the chain reaction during self-bind process.

SEM photo of self-bind bio-boards showed there were complete fibers, inseparable interface, fiber bundles so as to have the high bond strength. There were rough fiber morphology, more empty, obvious pull-off phenomenon on the interface of Y21 sample, but there were little empty, broken phenomenon on the interface of Y22 sample. It was resulted that wood fiber was better done by 1% CH<sub>3</sub>COOH pretreatment than by 1% HOOC-COOH pretreatment in favor of self-bind bio-boards.

### ACKNOWLEDGMENT

This work was financially supported by the National Natural Science Foundation of China (31170532), Special Fund for Forest Scientific Research in the Public Welfare (201504507), and Invitation Fellowship Programs for Research in Japan of Japan Society for the Promotion of Science (ID No. S14748).

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