# ORIGINAL ARTICLE

Nobuhisa Okuda · Keko Hori · Masatoshi Sato

# Chemical changes of kenaf core binderless boards during hot pressing (I): influence of the pressing temperature condition

**Abstract** Self-bonding is the main factor of the performance expression of binderless boards, and therefore its clarification is considered to be an important issue. For this purpose, a series of chemical analyses were conducted on kenaf core binderless boards and their chemical changes during the hot-pressing process are discussed in this article. First of all, binderless boards were prepared from kenaf core powder at different pressing temperatures (without steam-explosion process) and were used for chemical analyses after they were reduced into powders and extracted with methanol. To investigate their chemical changes, lignin, holocellulose, and neutral sugar contents were determined, Fourier transform infrared (FTIR) spectra were recorded, and the nitrobenzene oxidation procedure was applied. As a result, it was found that parts of lignin and hemicellulose were decomposed during the hot-pressing process; however, the contribution of the resulting fractions to self-bonding was not observed. In addition, progress of condensation reactions in lignin and the formation of chemical bonds by low molecular weight conjugated carbonyl compounds in methanol extractives were observed. Thermal softening of lignin is also suggested to play an important role in the expression of board performance.

**Key words** Chemical change · Self-bonding mechanism · Binderless board · Thermal softening of lignin · Condensation reaction

N. Okuda (✉) · K. Hori · M. Sato
Department of Global Agricultural Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan
Tel. +81-3-5841-7507; Fax +81-3-5841-7507
e-mail: aa47125@mail.ecc.u-tokyo.ac.jp

## Introduction

Although synthetic resins play an important role in the effective utilization of wood resources, from the viewpoint of recycling or even abolishment of synthetic resins, binderless boards are considered to be of growing importance. So far, we have developed binderless boards from finely ground powder of kenaf core in our previous studies.[1] However, the water resistance of the binderless boards was low and required further improvement. In the study, the basic principle at issue is self-bonding, which is the main factor of the board performance expression. Clarification of the self-bonding mechanism is considered to be important for designing better manufacturing conditions to improve the binderless board performances, and for expanding the possibility of application of the self-bonding mechanism to other lignocellulosic materials. It has been proposed in some studies on this subject that furfural generated from hemicellulose during hot pressing contributed to the self-bonding,[2,3] but the details have not been clarified. In addition, binderless boards in our study are different from those in other studies[4–9] in that we omitted the steam treatments such as steam explosion or steam-injection pressing, and thus their self-bonding mechanism should be examined separately. Furthermore, in other studies, analyses were conducted not on the binderless boards but on the pretreated raw materials of binderless boards.[2,5,10] To discuss the self-bonding factors, analyses on the binderless boards were required.

Therefore, in this study, to provide basic information for further discussion on self-bonding, a series of chemical analyses were conducted on binderless boards manufactured under different pressing temperature conditions to investigate their chemical changes, which may affect the binderless board properties.

## Materials and methods

### Sample preparation

Finely ground powder of kenaf core (ORI) (average powder size 53 $\mu$m and moisture content 8%–9%) was made into three types of binderless boards (B14, B16, and B18) by changing the pressing temperature conditions: 140°, 160°, and 180°C, respectively. The other manufacturing conditions for the board preparations were identical to each other: pressing pressure 5.3 MPa, pressing time 10 min, target density 1.0 g/cm³, and board thickness 5 mm. The mechanical properties were found to be greatly improved with increasing pressing temperature.[1] After the properties were tested, the binderless boards were ground to pass through a 1-mm sieve in a Wiley mill. These ground binderless boards and the original kenaf core powder (ORI) were extracted with methanol using a Soxhlet extractor for more than 8 h and their extracts were evaporated to dryness to obtain the methanol extractives (eB14, eB16, eB18, and eORI). The residues (rB14, rB16, rB18, and rORI) and the methanol extractives were analyzed to investigate the effect of the pressing temperature conditions on the chemical changes of binderless boards. In this study, we considered that the contribution factors of self-bonding may remain in the residues rather than in the extractives; thus, the residues were the main target for the chemical analyses.

### Lignin, holocellulose, and monosaccharide contents

To examine the changes in the chemical compositions of cell wall during the hot-pressing process, lignin and holocellulose content of the residue samples were determined. Klason lignin and acid-soluble lignin were measured by the Klason method.[11] In this procedure, a dry sample of 1.0 g was used; the secondary hydrolysis with 3% sulfuric acid was carried out at 121°C for 30 min. Holocellulose content was determined as the NaClO₂-delignified residue: samples (2.5 g) were repeatedly (four times) treated with 2 g of NaClO₂ in dilute acetic acid aqueous solution (150 ml) at 75°C for 1 h.[12]

To examine the neutral sugar composition of the polysaccharide, the alditol acetate procedure modified by Blakeney et al.[13] was applied to the residue samples and to the extractives, by using a Shimadzu gas chromatograph GC-1700 with a TC-17 capillary column. The conditions that were different from the original procedure are as follows: hydrolysis condition (H₂SO₄ concentration 4%, temperature 121°C for 60 min using an autoclave),[3] quantity of ammonia water (0.2 ml), and the reduction time (90 min).

For the extractives, the concentration of the organic matter having ultraviolet absorption was examined in the following procedure:[14] dried samples (5 mg) were dissolved in a solution of 25% (w/w) acetyl bromide in acetic acid (2.5 ml) containing perchloric acid (70%, 0.1 ml) at 70°C for 30 min with occasional shaking; the solution was transferred to a 50 ml volumetric flask containing 2 M sodium hydroxide (10 ml) and acetic acid (12 ml), made up to 50 ml with acetic acid, and was analyzed by measuring the ultraviolet absorbances at 280 nm. Generally, this method is known as an acetyl bromide procedure to examine the lignin content in wood and is not designed for the analysis of extractives. However, we considered the application of this procedure to the extractives would provide significant information regarding the organic matter with ultraviolet absorption, including the components derived from lignin.

### General information regarding changes in chemical structure

Fourier transform infrared (FTIR) spectra of the residues and methanol extractives were recorded using a FT/IR-615 (Jasco, Japan) as KBr tablets to investigate any changes in chemical bonds during the hot-pressing process.

### Structural characteristics of lignin

To focus on changes in the lignin structure, the aromatic composition of lignin was examined by the alkaline nitrobenzene oxidation procedure.[15] The benzaldehyde derivatives were analyzed as trimethylsilyl derivatives using a Shimadzu gas chromatograph GC-1700 with a Neutrabond-1 capillary column. The (syringaldehyde and syringic acid)/(vanillin and vanillic acid) mole ratio was defined as S/V ratio and was used to investigate the structure of lignin.

## Results and discussion

### Chemical compositions

Table 1 shows the yields of methanol extractives (eORI, eB14, eB16, and eB18). The yield increased with increasing pressing temperature. It was suggested that some fragments that could be extracted with methanol were generated from cell wall components of kenaf core as a result of its decomposition and depolymerization during hot pressing. This is discussed further below.

Table 2 shows the chemical compositions of the residues (rORI, rB14, rB16, and rB18) and the extractives. First, we note that the holocellulose content was higher than the published value,[16] which was due to the extent of delignification after four treatments with NaClO₂. Second, the value determined by the acetyl bromide procedure is

**Table 1.** The yield of methanol extractives of the original kenaf core powder and the binderless boards

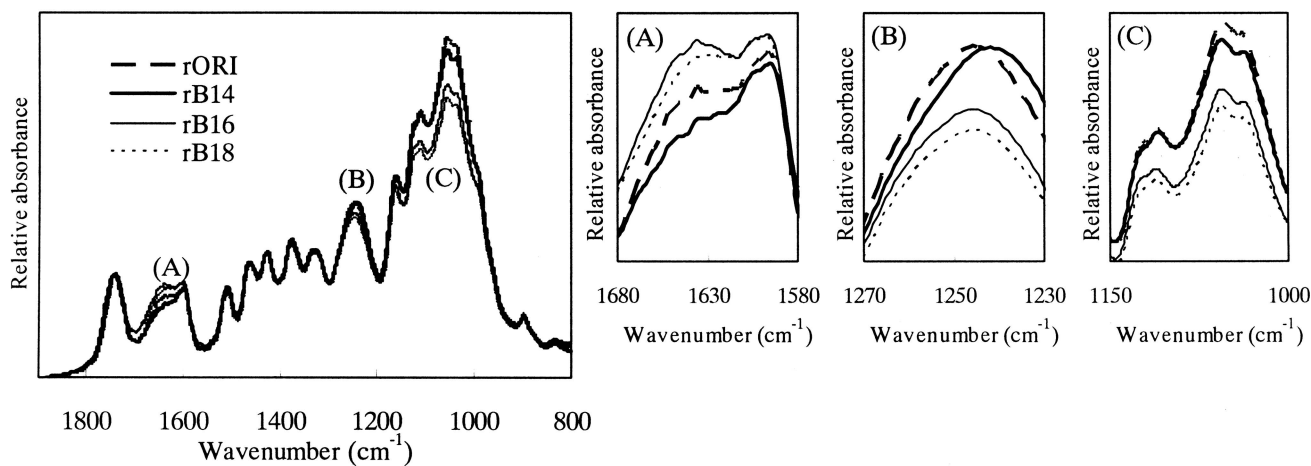| Sample | Extract yield (%) |
| --- | --- |
| ORI | 4.6 |
| B14 | 4.6 |
| B16 | 5.7 |
| B18 | 8.0 |

ORI, kenaf core powder; B14, binderless board 140°C pressing temperature; B16, binderless board 160°C; B18, binderless board 180°C

**Table 2.** The chemical compositions of the residues and extractives

| Sample | Lignin[a] (wt%) | Holocellulose (wt%) | Neutral sugar (wt%) | | | | | | | Components derived from lignin (wt%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Rha | Ara | Xyl | Man | Glc | Gal | Total | |
| rORI | 25.3 | 84.7 | 4.4 | 0.0 | 22.8 | 1.6 | 42.1 | 0.2 | 71.1 | – |
| rB14 | 25.2 | 85.0 | 4.8 | 0.0 | 24.0 | 1.4 | 40.5 | 0.0 | 70.7 | – |
| rB16 | 25.1 | 83.4 | 4.9 | 0.0 | 24.2 | 1.4 | 41.9 | 0.1 | 72.5 | – |
| rB18 | 25.7 | 78.4 | 4.5 | 0.0 | 23.3 | 1.5 | 41.2 | 0.1 | 70.6 | – |
| eORI | – | – | 0.0 | 0.0 | 0.0 | 0.1 | 2.9 | 0.0 | 3.0 | 65.3 |
| eB14 | – | – | 0.0 | 0.0 | 0.0 | 0.0 | 0.5 | 0.0 | 0.5 | 65.8 |
| eB16 | – | – | 0.0 | 0.0 | 0.0 | 0.0 | 0.2 | 0.0 | 0.2 | 67.8 |
| eB18 | – | – | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 78.3 |

Rha, rhamnose; Ara, arabinose; Xyl, xylose; Man, mannose; Glc, glucose; Gal, galactose
[a] Sum of Klason lignin and acid-soluble lignin



**Fig. 1.** Fourier transform infrared (FTIR) spectra of the residue samples; the magnifications at different wavenumbers: **A** around $1635\,cm^{-1}$, **B** around $1250\,cm^{-1}$, **C** $1000-1150\,cm^{-1}$. *ORI*, kenaf core powder; *B14*, binderless board 140°C pressing temperature; *B16*, binderless board 160°C; *B18*, binderless board 180°C; prefix *r* indicates residue

shown as the components derived from lignin in Table 2. Although it actually indicates the presence of organic matter having ultraviolet absorption at 280 nm, we regard it as a convenient indicator of the content of the components derived from lignin.

Little difference was observed in the lignin content, but the holocellulose content of rB18 was lower than that of the others. However, the total neutral sugar content of the residue samples was almost identical to each other, indicating that the decrease in holocellulose was caused by $NaClO_2$ attack during the holocellulose preparation. It can therefore be presumed that the polysaccharides in rB18 were depolymerized, allowing them to be more easily attacked by $NaClO_2$.

Other studies have suggested the possibility of the contribution of furfural derived from hemicellulose to self-bonding.[2,3] However, in this study, no obvious change was observed in the amount of rhamnose and xylose even if the extract yields were taken into consideration. Therefore, it is reasonable to suppose that little furfural was generated from hemicellulose, indicating little contribution of furfural to the self-bonding. This is probably because we did not apply the steam-explosion pretreatment, which has been reported to generate furfural.[3]

In the extractives, little neutral sugar was observed and the content of the components derived from lignin increased with increasing pressing temperature. The methanol extractives were found to be mainly composed of the components from lignin with aromatic units showing ultraviolet absorption at 280 nm. Part of the lignin seemed to be decomposed during the hot-pressing process and the resulting fragments were extracted. In addition, the pattern of FTIR spectra of the extractive samples (shown and discussed below) was quite similar to that of milled wood lignin (MWL) samples of wood,[17,18] indicating that the principal components of the methanol extractives were derived from lignin.

Chemical structure

Figures 1 and 2 show the FTIR spectra of the residue and methanol extractive samples, respectively, and parts of which are illustrated under magnification (Fig. 1A–C and Fig. 2A–B). The lignin content of the residue samples was almost identical as shown in Table 2 and thus it is reasonable to suppose that it would give almost the same peak intensity at $1507\,cm^{-1}$ derived from the aromatic units in

4

**Fig. 2.** FTIR spectra of the methanol extractive samples; the magnifications at different wavenumbers: **A** around 635 cm$^{-1}$, **B** around 1250 cm$^{-1}$. Prefix *e* indicates extractives
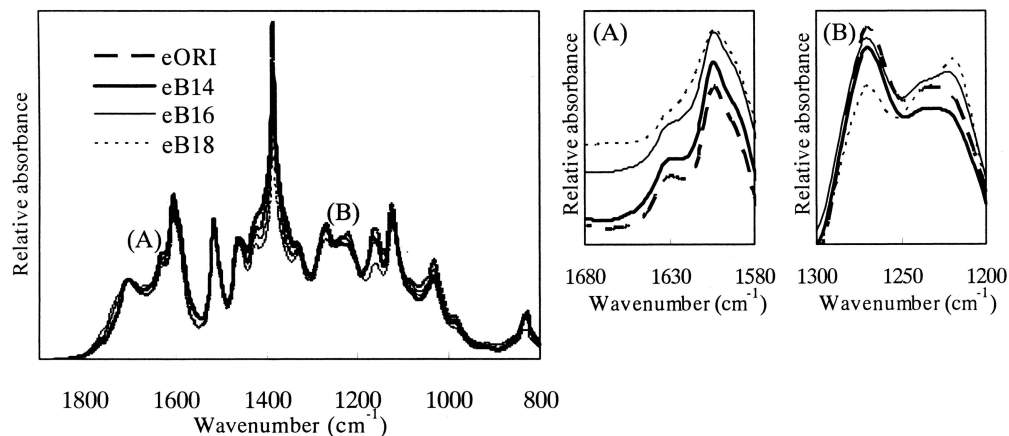


lignin. Therefore, the peak at 1507 cm$^{-1}$ was used as a constant standard to derive the relative absorbance of all residue and extractive samples at different wavenumbers.

Although other studies have investigated the chemical changes that occur during the steam-explosion process and their contribution to the self-bonding mechanism,[2,3] recent investigations have demonstrated that the characteristics of lignin as a plastic material could improve the mechanical properties of binderless boards.[5–7,10] On the whole, we see from Fig. 1 that the differences among the FTIR spectra of the residues pretreated at different pressing temperatures were small. This suggests either of two possibilities: the chemical changes that occurred during the hot-pressing process were actually small or infrared inactive. As a possible candidate for this, it can be presumed that thermal softening of lignin[19,20] might play an important role in the board performance expression. The thermal softening changes might involve the glass transition, because $T - T$g ($T$, local temperature of board during hot pressing; $T$g, local glass transition temperature) value was reported to be correlated to mechanical properties of boards.[20]

However, three small differences were observed in Figs. 1 and 2. First, the peak around 1635 cm$^{-1}$, correspondingly shown as Fig. 1A and Fig. 2A, is derived from C=O stretching vibration of conjugated carbonyl compounds. A small peak was observed at around 1635 cm$^{-1}$ for ORI and B14 samples (Figs. 1A and 2A), indicating the carbonyl compounds were free or present in low molecular weight compounds at first and were easily extracted with methanol. In contrast, for the B16 and B18 samples, the peak occurred only in the residues (Fig. 1A). This suggests that low molecular weight carbonyl compounds experienced some chemical changes during the hot pressing to form new chemical structures and remained in the residues, a process which might contribute to the self-bonding and to the improvement of the board properties.

Second, we see from Fig. 1B that the peak intensity around 1250 cm$^{-1}$ (derived from aryl ether structure)[18,21–23] decreased with increasing pressing temperature, indicating the cleavage of intermonomer linkages in lignin during the hot-pressing process. However, no new peaks occurred from the constituents released by this cleavage (Fig. 1) and the content of the lignin degradation products in extractive samples increased with increasing pressing temperature

(Table 2). Therefore, it is reasonable to suppose that part of the lignin experienced decomposition during hot pressing and the resulting fraction was extracted with methanol. Here, the extracted lignin fraction was observed as two corresponding peaks (Fig. 2B): around 1270 cm$^{-1}$ (assigned to guaiacyl unit) and around 1220 cm$^{-1}$ (assigned to syringyl unit).[22,23] In addition, considering the fact that the decomposed lignin fraction was able to be easily extracted with methanol instead of forming new chemical bonds, the decomposition of lignin did not seem to have any significance from the viewpoint of self-bonding. However, the fact that the S/V values could be defined for the methanol extractives samples (as is discussed below) indicated the presence of vanillin generated from lignin as a result of its decomposition during hot pressing. The vanillin generated from lignin decomposition might play a role as a lignin plasticizer.[20]

Last, the FTIR absorption band in the region shown in Fig. 1C was mainly derived from hydroxyl groups in polysaccharides. However, their quantities were found to be almost identical in the residue samples (Table 2). Thus, even though the quantities of sugars appear to decrease with increasing pressing temperature, further interpretations are difficult here because the influence of the data processing error (due to the scaling to derive the constant standard at 1507 cm$^{-1}$) is dominant in the wavenumber region of Fig. 1C.

### Changes in lignin structure

Figure 3 shows the S/V ratio (for all samples) and the yield of benzaldehyde derivatives based on the lignin content (for residues). The S/V values increased with increasing pressing temperature for all samples and the yields decreased. This clearly indicated the progress of condensation reactions of the guaiacyl unit of lignin, which was considered to be playing an important role in the self-bonding mechanism.

As Kawamura et al.[22,23] pointed out, in lignin samples, the ratio of the IR peak intensity at 1270 cm$^{-1}$ ($D_{1270}$) to 1220 cm$^{-1}$ ($D_{1220}$) has strong correlation with S/V values. We should point out that, in the extractive samples, the increasing S/V value with increasing pressing temperature was related to the decreasing $D_{1270}/D_{1220}$ value (obvious from Fig. 2B).
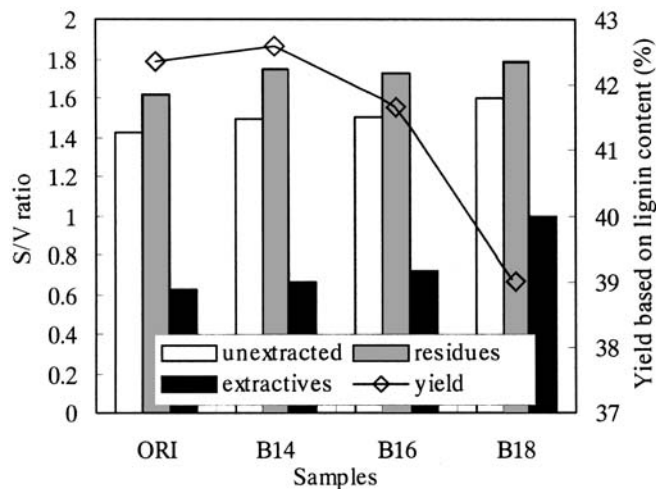
**Fig. 3.** The S/V (syringyl/vanillyl) ratio of all samples and the yield of benzaldehyde derivatives based on the lignin content of the residues

## Conclusions

A series of chemical analyses were conducted to investigate the chemical changes of kenaf core binderless boards during the hot-pressing process. The influence of pressing temperature on the chemical changes was discussed from the viewpoint of self-bonding. The conclusions are summarized as follows:

1. Part of the lignin and hemicellulose experienced decomposition during the hot-pressing process. However, a contribution of the resulting fractions to self-bonding was not observed. The results of other studies were different from those of present studies in that they suggested the contribution of furfural derived from hemicellulose to the self-bonding mechanism. This difference might be because we did not apply steam-explosion pretreatment or steam-injection pressing in this study.
2. Condensation reaction in lignin was observed. Additionally, the thermal softening of lignin was suggested to play an important role for the board performance expression.
3. It was found that low molecular weight conjugated carbonyl compounds in the methanol extractives experienced some chemical changes during hot pressing to form new chemical structures.

## References

1. Okuda N, Sato M (2004) Manufacture and mechanical properties of binderless boards from kenaf core. J Wood Sci 50:53–61
2. Mobarak F, Fahmy Y, Augustin H (1982) Binderless lignocellulose composite from bagasse and mechanism of self-bonding. Holzforschung 36:131–135
3. Suzuki S, Shintani H, Park SY, Saito K, Laemsak N, Okuma M, Iiyama K (1998) Preparation of binderless boards from steam exploded pulps of oil palm (*Elaeis guneensis* Jaxq.) fronds and structural characteristics of lignin and wall polysaccharides in steam exploded pulps to be discussed for self-bonding. Holzforschung 52:417–426
4. Angles MN, Reguant J, Montane D, Ferrando F, Farriol X, Salvado J (1999) Binderless composites from pretreated residual softwood. J Appl Polym Sci 73:2485–2491
5. Angles MN, Ferrando F, Farriol X, Salvado J (2001) Suitability of steam exploded residual softwood for the production of binderless panels. Effect of the pre-treatment severity and lignin addition. Biomass Bioenerg 21:211–224
6. Velasquez JA, Ferrando F, Salvado J (2002) Binderless fiberboard from steam exploded *Miscanthus sinensis*: the effect of a grinding process. Holz Roh Werkst 60:297–302
7. Velasquez JA, Ferrando F, Salvado J (2003) Effects of kraft lignin addition in the production of binderless fiberboard from steam exploded *Miscanthus sinensis*. Ind Crop Prod 18:17–23
8. Laemsak N, Okuma M (2000) Development of boards made from oil palm frond II: properties of binderless boards from steam-exploded fibers of oil palm frond. J Wood Sci 46:322–326
9. Xu J, Han G, Wong ED (2003) Development of binderless particleboard from kenaf core using steam-injection pressing. J Wood Sci 49:327–332
10. van Dam JEG, van den Oever MJA, Teunissen W, Keijsers ERP, Peralta AG (2004) Process for production of high density/high performance binderless boards from whole coconut husk. Part 1: lignin as intrinsic thermosetting binder resin. Ind Crop Prod 19:207–216
11. Iiyama K, Stone BA, Macauley BJ (1994) Compositional changes in compost during composting and growth of *Agaricus bisporus*. Appl Environ Microbiol 60:1538–1546
12. Takuya A, Sugimoto T, Matsumoto Y, Meshitsuka G (2002) *Erythro/threo* ratio of β-O-4 structures as an important structural characteristics of lignin. I: Improvement of ozonation method for the quantitative analysis of lignin side-chain structure. J Wood Sci 48:210–215
13. Blakeney AB, Harris PJ, Henry RJ, Stone BA (1983) A simple and rapid preparation of alditol acetates for monosaccharide analysis. Carbohydr Res 113:291–299
14. Iiyama K, Wallis AFA (1988) An improved acetyl bromide procedure for determining lignin in woods and wood pulps. Wood Sci Technol 22:271–280
15. Sugimoto T, Akiyama T, Matsumoto Y, Meshitsuka G (2002) The *erythro/threo* ratio of β-O-4 structures as an important structural characteristic of lignin. Part 2. Changes in *erythro/threo* (E/T) ratio of β-O-4 structures during delignification reactions. Holzforschung 56:416–421
16. Neto CP, Seca A, Fradinho D, Coimbra MA, Domingues F, Evtuguin D, Silvestre A, Cavaleiro JAS (1996) Chemical composition and structural features of the macromolecular components of *Hibiscus cannabinus* grown in Portugal. Ind Crop Prod 5:189–196
17. Faix O, Janezic TS, Lundquist K (1994) The lignin of the diffuse porous angiosperm tree *Triplochyton scleroxylon* K. Schum with low syringyl content. J Wood Chem Technol 14:263–278
18. Faix O (1991) Classification of lignins from different botanical origins by FT-IR spectroscopy. Holzforschung 45 Suppl:21–27
19. Goring DAI (1963) Thermal softening of lignin, hemicellulose and cellulose. Pulp Paper Mag Can T517–T527
20. Bouajila J, Limare A, Joly C, Dole P (2005) Lignin plasticization to improve binderless fiberboard mechanical properties. Polym Eng Sci 45:809–816
21. Colom X, Carrillo F (2005) Comparative study of wood samples of the northern area of Catalonia by FTIR. J Wood Chem Technol 25:1–11
22. Kawamura I, Shinoda Y, Nonomura S (1974) The comparison of relative intensities of IR absorption bands of MWL of various woods from tropical and temperate zones. Mokuzai Gakkaishi 20:15–20
23. Kawamura I, Shinoda Y, Ai TV, Tanada T (1977) Chemical properties of lignin of *Erythrina* wood. Mokuzai Gakkaishi 23:400–404