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ORIGINAL ARTICLE

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Chemical changes of kenaf core binderless boards during hot pressing (II): effects on the binderless board properties

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Abstract To provide basic information on self-bonding in kenaf core binderless boards, a series of chemical analyses was conducted on binderless boards and their chemical changes during hot pressing were examined in our previous study. In this study, binderless boards were manufactured under conditions that may accelerate the supposed chemical changes to investigate their effect on the board properties. First, to investigate the influence of the chemical bonds formed by carbonyl compounds on self-bonding, the influence of acetic acid addition prior to board manufacturing was studied and the effect of methanol extractives (containing the carbonyl compounds) was also examined. Second, the influence of the condensation reaction in lignin was discussed from the viewpoint of board density. Last, to examine the influence of thermal softening of lignin, the influences of temperature condition and moisture content, as well as those of microwave pretreatment, were investigated. As a result, the estimated chemical changes were suggested to influence the binderless board properties.

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

Introduction

Clarification of the self-bonding mechanism is considered to be an important issue for the further improvement of binderless board performance, and for the possibility of expanding its application to other lignocellulosic materials. So far, however, little information has emerged on the detail of the self-bonding mechanism. To provide some basic information for the further discussion on self-bonding, in our previous studies,[1,2] a series of chemical analyses was conducted and the chemical changes of binderless boards during the hot-pressing process were discussed. As a result, several chemical changes were observed: decomposition of part of the lignin and hemicellulose, the progress of condensation reaction in lignin, and the formation of chemical bonds by low molecular weight carbonyl compounds in methanol extractives. Thermal softening of lignin, although it may involve slight chemical changes, was also considered to be an important factor for the expression of binderless board performance. In this study, therefore, binderless boards were manufactured to investigate the influences of these chemical changes on the binderless board properties.

First, the influence of methanol extractives was investigated. It was suggested that low molecular weight carbonyl compounds in the extractives formed chemical bonds during hot pressing.[2] The compounds may contain aromatic carbonyl groups, however, in this study, acetic acid was used as a first approximation and was added to kenaf core powder to manufacture binderless boards. It was reported that fatty acids were contained in light petroleum extract of kenaf core and acetic acid was considered to be one of the components contained in the methanol extractives.[3] Then, according to the previous study,[1,2] it was suggested that the methanol extractives contained compounds derived from lignin as well as the carbonyl compounds of interest, and hence the effect of methanol extractives was investigated by removing or adding the extractives prior to board manufacture.

Next, the contribution of lignin was studied. First, the influence of lignin was reviewed by manufacturing binderless boards from delignified or lignin-added raw materials. Second, to study the influence of the progress of condensation reactions of lignin, binderless boards with different board densities were manufactured to change the degree of contact among the powder elements, and the influence was discussed. Last, the influence of lignin softening was examined. Although it was considered that lignin softening involved little chemical change, it was suggested that the phenomenon played an important role in board

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performance, and, thus, it is worth further investigation. It was reported that thermal softening of lignin is associated with the temperature and the water uptake.[4] From the viewpoint of board manufacturing, this means that the pressing temperature and the moisture content (MC) of the raw materials are considered to be the most important conditions. We also considered that the softening could be accelerated by the application of microwaves to heat the material inside the board by activating water molecules. Therefore, combinations of the pressing temperature and the MC of the raw material were studied, and the application of microwaves as a pretreatment was investigated.

Materials and methods

Influence of methanol extractives

Influence of acetic acid addition

Kenaf core was crushed into powder (average powder size 53 μm and MC 8%–9%) using a flourmill (Model ACM-10, Hosokawa Micron, Japan). Acetic acid, as one of the typical carbonyl compounds, was added to the kenaf core powder in concentrations of 0%, 2.1%, and 4.7% to manufacture binderless boards (A0, A2.1, and A4.7, respectively) by the same technique used in our previous study.[5] The board manufacturing conditions were as follows: pressing temperature 180°C, pressing pressure 5.3 MPa, pressing time 10 min, board thickness 5 mm, board size 300 × 300 mm, and target density 0.8 g/cm^3. To evaluate the physical effect of acetic acid addition, modulus of rupture (MOR) and its retention, modulus of elasticity (MOE), internal bonding strength (IB) and its retention, thickness swelling (TS), and water absorption (WA) were determined according to JIS A 5905–1994 (fiberboard). MOR retention ratio was determined by measuring the retained MOR after soaking in hot water (70°C) for 2 h, followed by soaking in water at 20°C water for 1 h. IB retention was determined after soaking in water at 20°C for 24 h and drying at 20°C.

After testing their mechanical properties, binderless boards were ground in a Wiley mill (WT-150, MIKI Seisakusho, Japan) to pass through a 1-mm sieve. The powder was subsequently extracted with methanol using a Soxhlet extractor for more than 8 h. Fourier transfer infrared (FTIR) spectra of the resulting residues were recorded on a Jasco FT/IR-615 FTIR spectrometer as KBr tablets, and the effect of acetic acid addition was discussed from a chemical viewpoint.

Influence of extractives addition

To investigate the influence of methanol extractives, first, the kenaf core powder (estimated average grain size 0.6 mm and MC 8%–9%) was extracted with methanol and the resulting residue powder (free from methanol extractives) and methanol extractives were obtained after methanol evaporation. Then, binderless boards were prepared from three types of raw materials: the residue powder (free from methanol extractives) (R-type), the original powder mixed with an additional 5% of methanol extractives based on the oven-dry weight (E-type), and the original kenaf core powder (original). The manufacturing conditions were the same as above except for the board size of 200 × 200 mm. After that, to evaluate the bonding properties, IB and its retention (by the same method as above), TS, and WA were determined.

Influence of lignin

To study the influence of lignin, first, holocellulose and periodate lignin were prepared under the following procedures.

Holocellulose preparation

Holocellulose was prepared from kenaf core powder (estimated average grain size 0.6 mm and MC 8%–9%) in the same procedure used in our previous study[2] except for the sample quantity (around 100 g per treatment), the quantity of the diluted acetic acid aqueous solution (around 4 l), the quantity of $NaClO_2$ (20 g), and the treatment repetition times (six times). The yield of holocellulose was 82%.

Periodate lignin preparation

Kenaf core powder (as described above) (around 100 g per procedure) was pretreated with 1% sodium hydroxide solution (NaOH) (3.5 l) for 12 h, neutralized, and subsequently oxidized with sodium periodate ($NaIO_4$) (125 g) by adding acetic acid (16.7 ml) for 1 week in the dark. After centrifuging, the resulting residue was reduced with sodium borohydride (50 g) in 0.1 N NaOH (2 l) for 24 h. After centrifuging, the resulting residue was hydrolyzed with 0.5 N hydrochloric acid (HCl) (2 l) for 24 h. After centrifuging, the resulting residue was determined as periodate lignin (yield 22%). In this procedure, all the treatments were conducted at room temperature.

Boards were prepared from three types of raw materials: the kenaf core powder substituted by 20% periodate lignin based on oven-dry weight (L-type), holocellulose (C-type), and the original kenaf core powder (original) (kenaf core binderless board). The board manufacturing conditions were the same as those described in the previous section. Finally, IB and its retention (by the same method as above), TS, and WA were determined to investigate the influence of the lignin content.

Influence of lignin: progress of condensation reaction

Influence of board density

To examine the effect of the progress of condensation reaction in the chemical structure of lignin, the influence of the contact degree among the powder elements was studied by manufacturing binderless boards from kenaf core powder (average powder size 53 μm and MC 8%–9%) with different

board densities: 0.5 and 1.0 g/cm^3 (D-0.5, and D-1.0, respectively). The board manufacturing conditions were the same as those described in the previous section. After testing the mechanical properties, the binderless boards were reduced to powder in a Wiley mill, subsequently extracted with methanol, and then the resulting residues were characterized by the alkaline nitrobenzene oxidation procedure.[2] The syringyl/vanillyl (S/V) ratio was used to discuss the changes in the lignin structure.[2]

Influence of lignin: thermal softening of lignin

Influence of pressing temperature and moisture content

Binderless boards were prepared from kenaf core powder (estimated average grain size 0.6 mm and initial MC 8%–9%) by changing the pressing temperature and the MC of the raw material. The pressing temperature and the MC investigated in this study were as follows: MC of 0%, 5%, 10%, and 20% for a pressing temperature of 120°C, MC of 0%, 5%, 10%, and 15% for 150°C, and MC of 0%, 2%, 4%, 5.3%, 8%, 10%, 12%, and 14% for 180°C. The other manufacturing conditions were the same as those described in the previous section except for the pressing schedule: 5 MPa for 4 min, followed by 3 MPa for 3 min, and 1 MPa for 3 min (three-step-down). The target MCs higher than the initial value were obtained by spraying water directly and those lower than the initial value were obtained by spraying water after drying which was carried out in a vacuum oven at 70°C for 48 h. The spraying was performed in a sealed plastic bag and sufficiently mixed before the board preparation. After board preparation, MOR, MOE, IB, TS, and WA were determined and the effect of the pressing temperature and the MC was examined.

Influence of preheating

Kenaf core chips (average grain size 6 mm and MC 8%) were preheated in a microwave oven (600 W) for 0, 1, and 2 min (in a glass container sealed by plastic film) and immediately made into binderless board under the same manufacturing conditions mentioned above except for the pressing temperature of 170°C. After that, the mechanical properties of these binderless boards were investigated and the influence of preheating examined.

Results and discussion

Effect of methanol extractives

Effect of acetic acid addition

Figure 1 shows the relationships between the acetic acid addition ratio and the mechanical properties of the binderless boards prepared. MOR and its retention ratio, IB and its retention ratio, TS and WA, and MOE improved with increasing acetic acid addition ratio, indicating that the bonding property was improved by the acetic acid addition. Figure 2 shows the FTIR spectra of the methanol-extracted residues of binderless boards manufactured with the addition of acetic acid (A0, A2.1, and A4.7). The peak around 1500 cm^{-1} (derived from aromatic moieties) was used as a constant standard to derive relative absorbance of all the samples at different wavenumbers.[2] According to Fig. 2, the peak intensity at 1635 cm^{-1} (derived from C=O stretching vibration of aromatic carbonyl compounds), considered to be associated with self-bonding,[1,2] increased with increasing acetic acid addition ratio. It seems reasonable to suppose

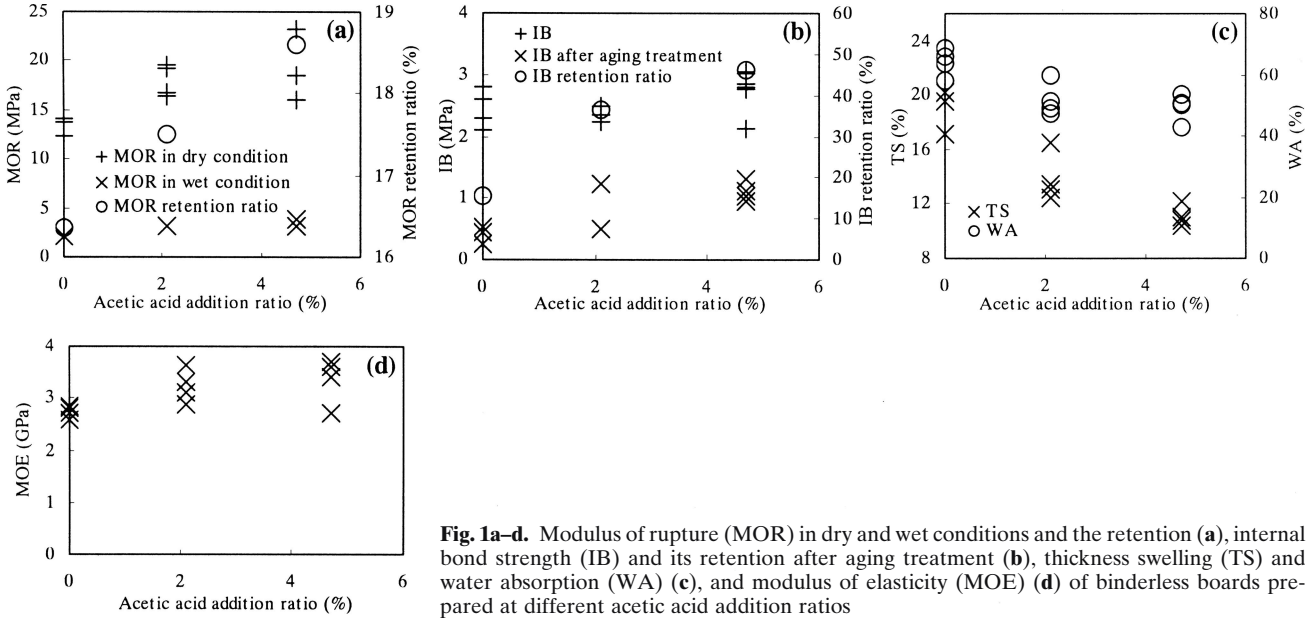

Fig. 1a–d. Modulus of rupture (MOR) in dry and wet conditions and the retention (**a**), internal bond strength (IB) and its retention after aging treatment (**b**), thickness swelling (TS) and water absorption (WA) (**c**), and modulus of elasticity (MOE) (**d**) of binderless boards prepared at different acetic acid addition ratios

that the acetic acid, as a low molecular weight carbonyl compound, experienced chemical change during the hot-pressing process and remained in the residues after the methanol extraction, indicating the contribution to self-bonding. It was suggested that acetic acid addition could be an effective way to accelerate the chemical changes and to improve the board properties.

Effect of extractives addition

Figure 3 shows the IB and its retention, and the TS and WA for different board types. As shown in Fig. 3a, the IB values were almost identical to each other, whereas the effectiveness of the methanol extractives was recognized in the IB after the aging treatment and the IB retention ratio. The IB retention after aging treatment increased with the methanol extractive addition (E-type) and decreased with the removal of methanol extractives (R-type) when compared with the original state (original). The same tendency was observed for TS and WA (Fig. 3b), suggesting that the methanol extractives containing the compounds derived from lignin and the carbonyl compounds[2] contributed to some improvement of the bonding properties.

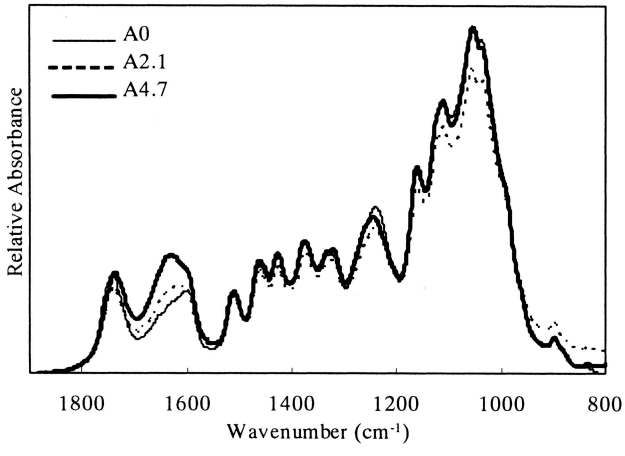

Fig. 2. Fourier transform infrared spectra of the extracted residues of binderless boards manufactured with the addition of different amounts of acetic acid. *A0*, 0% acetic acid; *A2.1*, 2.1% acetic acid; *A4.7*, 4.7% acetic acid

Effect of lignin

Figure 4 shows the IB and its retention, and TS and WA for different binderless board types. As shown in Fig. 4, the mechanical properties of the L-type board were superior to those of the original, whereas the properties of the original were found to be decreased to some extent by lignin removal (C-type). This clearly showed that lignin played an important role in the self-bonding mechanism and contributed to improvements in the board properties, as has been suggested.[6,7] From our previous study,[2] the effects of lignin were considered to occur through condensation reactions and themal softening, and these are discussed below.

Effect of lignin: progress of condensation reaction

Effect of board density

Table 1 shows the influence of the board density on the progress of condensation reaction in the chemical structure of lignin. If we compare the initial state (kenaf core powder) and D-0.5 or D-1.0, the S/V value increased and the yield of the benzaldehyde derivatives decreased by the hot-pressing process, indicating that the condensation reaction progressed affected the chemical structure of lignin during board manufacturing. It is not appropriate to conclude that the reaction contributed to self-bonding because of the possibility of the reaction being progressed only within each particle. In Table 1, small differences are observed between D-0.5 and D-1.0: the D-0.5 sample showed a lower S/V ratio and a higher yield than the D-1.0 sample. This means that the extent of the progress of the condensation reaction was dependent on the board density, or, in other words, the degree of the contact among powder elements. It was suggested that the condensation reaction occurred not only inside the particles, but also between particles to some extent. Thus, the progress of the condensation reaction in lignin might play an important role in the self-bonding mechanism and the acceleration of the reaction is thought to be effective for the improvement of the board properties.

Fig. 3a,b. IB and its retention after the aging treatment (**a**) and TS and WA (**b**) of three types of binderless boards. R-type, the residue powder (free from methanol extractives); E-type, the original powder mixed with 5% additional methanol extractives based on the oven-dry weight; original, the original kenaf core powder

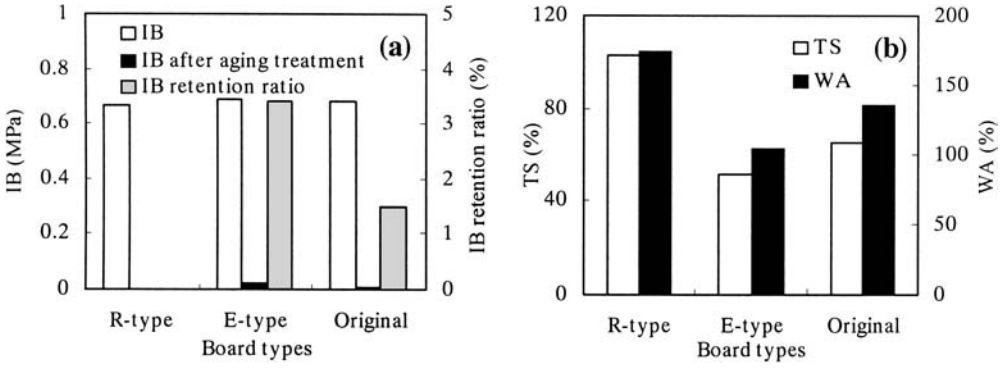

Table 1. The effect of target board density on the progress of the condensation reaction in lignin

Samples	Target board density (g/cm^3)	Lignin content[a] (wt%)	S/V ratio	Yield[b] (%)
Kenaf core powder	–	25.3	1.6	41.7 ± 0.2
D-0.5	0.5	25.4	1.7	40.9 ± 0.1
D-1.0	1	25.7	1.8	38.9 ± 0.1

S/V ratio, syringyl/vanillyl ratio
[a]The sum of Klason lignin and acid-soluble lignin
[b]Yield of total benzaldehyde derivatives based on lignin content, determined as the average value of three samples

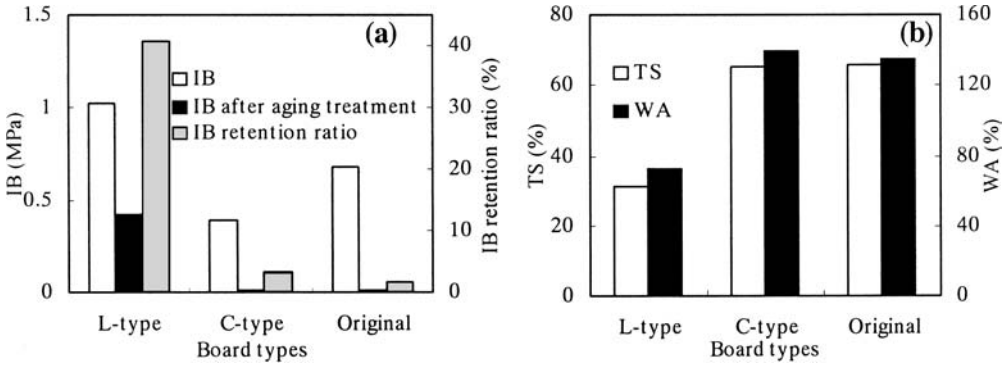

Fig. 4a,b. IB and its retention after the aging treatment (**a**), and TS and WA (**b**) of three types of binderless boards. L-type, the kenaf core powder substituted with 20% periodate lignin based on oven-dry weight; C-type, holocellulose (including a small amount of lignin); original, the original kenaf core powder

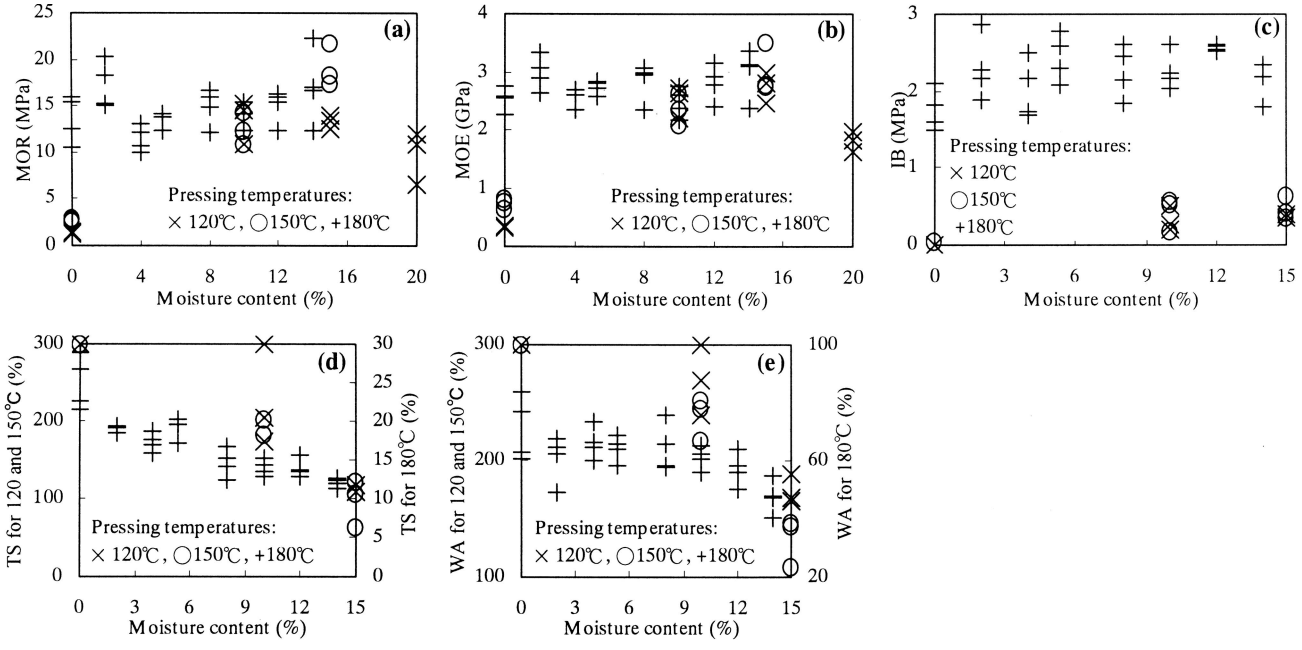

Fig. 5a–e. MOR (**a**), MOE (**b**), IB (**c**), TS (**d**), and WA (**e**) of the binderless boards manufactured under different combinations of moisture content and pressing temperature conditions

Effect of lignin: thermal softening of lignin

Effect of pressing temperature and moisture content

Figure 5 shows the mechanical properties of binderless boards at different MC and pressing temperature. The binderless boards manufactured at 120°C at the MC of 20% were delaminated because of steam explosion, which lowered the MOR and MOE (Fig. 5a,b). For the 120°C and 150°C samples, MOR, MOE, and IB increased and TS and WA decreased with increasing MC. However, in the 180°C samples, no obvious tendencies were observed in MOR, MOE, and IB, which suggests the thermal softening of lignin.[4] Goring[4] examined the softening temperature of ten types of lignin and reported that it was dependent on the kinds of the lignin and was substantially decreased by water uptake. According to the results,[4] even though kenaf lignin was not investigated, it can be presumed that softening of the kenaf core lignin did not occur at the pressing temperatures of 120° or 150°C with MC of 0%, which made

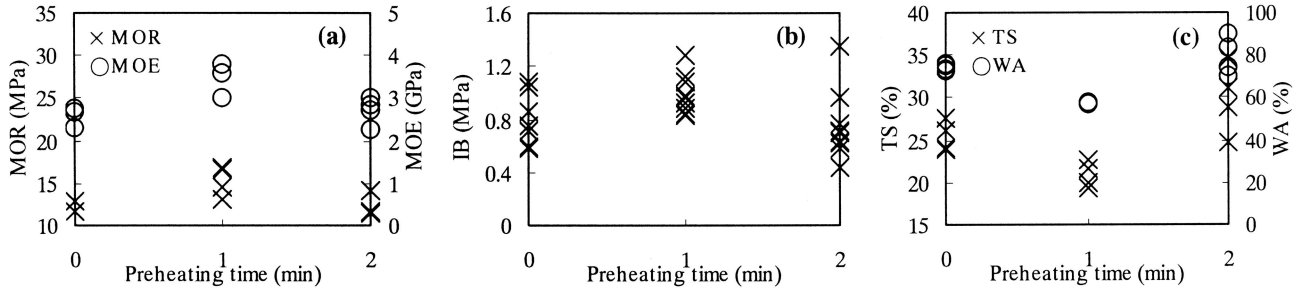

Fig. 6a–c. MOR and MOE (**a**), IB (**b**), and TS and WA (**c**) of the binderless boards manufactured by changing the microwave preheating time

the IB values almost zero (Fig. 5c). The increase in MC enhanced lignin softening, and in connection with this, the mechanical properties showed MC dependence (Fig. 5a–e). On the contrary, for the 180°C samples, it could be interpreted that the lignin softened at 180°C even though the MC was 0%, and, therefore, the mechanical properties were independent of the MC condition. Consequently, it is reasonable to suppose that lignin softening plays an important role in the expression of binderless board properties.

Effect of preheating

Figure 6 shows the effects of preheating on the MOR, MOE, IB, TS, and WA values. The IB values (Fig. 6b) and the other board properties (Fig. 6a,c) improved slightly with a preheating time of 1 min, whereas no obvious effect was observed with a preheating time of 2 min. The results could be explained on the basis of lignin softening. The improvements with a preheating time of 1 min were due to the microwave preheating, which could accelerate the thermal softening of lignin. On the other hand, with a preheating time of 2 min, the effect of the preheating treatment may partly be compensated by the influence of excessive drying during preheating, considering the fact that part of the raw material was burned black and the resulting MC was less than 3% after 2 min of preheating. This interpretation is consistent with the idea that the thermal softening of lignin is to some extent responsible for board performance. Here, we should point out that the microwave preheating could be used as a simple pretreatment to improve binderless board properties, although further study of the preheating conditions would be required.

Conclusions

Binderless boards were manufactured under conditions that may accelerate the changes observed in our previous study[2] and the influence of the chemical changes on the binderless board properties was investigated. The experimental results are summarized as follows:

1. The addition of acetic acid was considered to accelerate the chemical changes during hot pressing and was found to be effective for the improvement of board properties. It was considered that the acetic acid formed new chemical structures during hot pressing and became insoluble to methanol, although further studies are required for the clarification of the detailed mechanism. This effect of the carbonyl compounds was found to be influenced by the amount of methanol extractives.
2. The progress of the condensation reaction in lignin was found to be dependent on the degree of the contact among particles affected by the board density, indicating that the reaction partly occurred among powders. The acceleration of the reaction was supposed to be effective for the improvement of the board properties.
3. The thermal softening of lignin, although it may involve little chemical change, was indicated by the fact that the mechanical properties of binderless boards were associated with the temperature condition and the moisture content.

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