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ORIGINAL ARTICLE

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Preparation of board-like moldings from composites of isolated lignins and waste paper II: effect of inorganic salt addition on board performance and evaluation of practical use of MDF

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Abstract Board-shaped composites with medium density (MDF) were prepared from isolated lignins and waste newspaper, in addition to preparation of the composites with high density (HB). The board properties of both composites concerning bending strength and water resistance were improved by the addition of hardwood acetic acid lignin (HAL). The internal bond strength and water resistance of MDF, in particular the degree of thickness swelling (TS), were also improved by prolonged molding time. Adding inorganic salts contributed to the improvement of TS. The effect depended on the charge of the cation. Considering practical utilization of lignin-based MDF as a structural material, its performance was evaluated by combination of the single-shear test of nailed joints and the modulus of rigidity. As a result, this MDF had sufficient strength to be utilized as an internal shear wall material. Therefore, lignin can be considered as an alternative to conventional adhesives for the production of boards such as HB and MDF.

Key words Acetic acid lignin · Waste papers · Lignin adhesive · Hardboard · MDF

Introduction

Much emphasis has been placed on the effective utilization of biomass, in particular woody biomass that is the most abundant in nature, as an alternative to fossil resources in order to establish a sustainable recycling society with a low load on the environment. In woody biomass utilization, it is essential to make effective use of lignin, because it has not been utilized efficiently as an organic feedstock except for recovering the energy in paper mills, even though lignin is the second most abundant component of wood. However, lignin has high potential as a source for chemicals, synthetic polymers, and so on.[1] From this viewpoint, extensive research on lignin utilization, mainly as an adhesive or a resin, have been reported.[2,3] However, only a few industrial products have emerged from this basic research. High production costs per unit of performance in comparison with those of synthetic polymers from petroleum, which are the most serious obstacle to technological transfer, mainly come from the multistep chemical treatments required for production of lignin-based chemicals. This indicates that lignin should be utilized with little or no modification. As an example of lignin utilization without modification, board production using lignin has been reported.[4] When using softwood kraft lignin (KL), thickness swelling was significantly large. This result suggested that KL had low water-repellent ability, and was consistent with previous findings.[5]

Acetic acid lignin (AL) obtained from spent liquor of atmospheric acetic acid pulping has a unique thermal property, that is, fusibility.[6] Technical lignins, such as kraft lignin and lignosulfonate, do not have such a property. On the basis of this property, AL could be converted to moldings with various shapes.[7,8] However, the mechanical strengths of the moldings were very weak because of the relatively low molecular mass of AL.[6] The poor mechanical strengths of the moldings were improved by the addition of cellulosic materials, such as viscose rayon and pulps.[9] This cellulosic fiber–lignin matrix composite is an example of direct lignin utilization without any chemical modification.

In the development of this strategy for lignin utilization, we attempted to prepare board-like moldings with a density of 1.4 g/cm^3 from a mixture of AL and waste papers by dry-forming and wet-forming methods used in previous work.[5] The properties of the moldings were examined according to the standards of fiberboards (FB) from the analogy in constituents. The prepared moldings were categorized as hardboard (HB) (density >0.8 g/cm^3). Both forming types of lignin-based HB fulfilled the Japanese industrial standard (JIS) regulation for HB of the highest mechanical grade, although the wet-formed boards had relatively superior

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properties, mechanical strength and water resistance, to the dry-formed ones. These results suggested that lignin acted more effectively as a hydrophobic adhesive than did KL. The FB from the mixture of lignin and waste papers would bring about an environmentally friendly application of them.

The density (1.4 g/cm^3) of the lignin-based HB required to obtain satisfactory performance,[5] however, was too high for handling in construction sites. In this study, we attempt to improve the strength per density of lignin-based HB by adding inorganic salts. This attempt was conducted to produce medium density fiberboards (MDF, $0.35 <$ density $<$ 0.8 g/cm^3) with satisfactory mechanical properties. An expected use of the MDF prepared from the mixture of lignin and waste papers may be a sheet material of wooden shear walls of residential timber constructions. The principal advantage of using this MDF is that they are harmless to the human body even when they are used as interior surfaces, because of no formaldehyde-based adhesive. We attempt to conduct a numerical simulation to estimate the practical potential of the shear walls with this MDF.

Materials and methods

Materials

Hardwood acetic acid lignin (HAL) was isolated from the spent liquor of atmospheric acetic acid pulping of birch.[10] Indulin AT was used as commercially available kraft lignin (KL). Waste newspaper (WN) was used as a fiber component.

Dry-formed HB preparation

Waste newspaper was suspended in water, and then disintegrated by a domestic mixer. After filtration and drying in an oven at 105°C, the WN was mixed with a given amount of lignin by the mixer. The mixture (30 g) was placed in a cylindrical mold (diameter 10 cm), and then molded to a board for 15 min by thermal pressing at 3 and 24 MPa at 130°C. The densities of the resulting moldings were 1.0 and 1.4 g/cm^3, respectively.

Dry-formed MDF preparation

Waste newspaper and lignin were suspended together in water, and mixed well by the mixer. After filtration, the mixture was dried at 75°C overnight. The moisture content was about 2%. The mixture (HAL 20%) was molded to a board with the cylindrical mold or a rectangular one (5 × 20 cm) for 30 min at less than 3 MPa at 180°C. The volume of the mold or thickness was maintained by controlling the stroke of the press head.

$Al_2(SO_4)_3$, $CaCl_2$, and NaCl were added to the aqueous suspension of the WN–HAL mixture. The inorganic salt concentration was 0.3% (W/V %) on solution. After drying, MDF and HB with 20% HAL were prepared by the same procedure as above.

Commercial MDF (type-M: 9 mm thick for structural use) was used as a reference. Three specimens of each board were prepared and subjected to the following tests. However, only one specimen for both the KL-based MDF and the MDF prepared from WN alone was prepared because of a limited supply of lignin and easy destruction of MDF, respectively.

Mechanical properties and water resistance

The bending modulus of rupture (MOR) and bending modulus of elasticity (MOE) of the prepared rectangular boards were evaluated by the Japanese standard testing method for FB, JIS A 5905. For the circular boards, on the other hand, another testing standard, JIS K 6911, provided for plastics material was adopted because of the restriction of small size of the prepared boards. Internal bond strength (IB) was measured in accordance with JIS A 5905. Water absorption (WA) and the degree of thickness swelling (TS) were calculated from the difference in weight and thickness of specimens before and after soaking in water for 24 h.

Estimation of lateral resistance of wooden shear walls with prepared MDF

To estimate the practical potential of the dry-formed MDF of HAL20%–WN, a numerical simulation was conducted on the lateral resistance of wooden shear walls sheathed with the prepared MDF. Shear walls assembled by nailing sheet materials onto wooden frames are principal structural elements of light timber frame constructions to resist wind or earthquake forces. The lateral resistance of nailed shear walls results from load-slip properties of nailed joints between sheet materials and wooden frames, and in-plane shear rigidity of sheet materials.

The load–slip properties of the nailed joints were evaluated as follows. Two prepared MDF pieces, 7.5 mm in thickness, were nailed onto softwood lumber with two CN50 common nails, as shown in Fig. 1, and the relative slip between them was measured throughout the loading. Nailed joints with commercial MDF (type-M: for structural use; nominal thickness 9 mm, density 0.56 g/cm^3) were also tested as the reference. Lumber main members combined with side members of prepared and commercial MDF were end matched to each other. The average air-dry density of them was 0.48 g/cm^3. Three specimens, consisting of six MDF side members and nails, were tested for each kind of MDF. Moduli of rigidity (G) of both MDF were evaluated by torsional tests.

Lateral load–deformation curves of the nailed shear walls with the prepared or commercial MDF were simulated by incremental analyses,[11,12] in which we assumed a typical wall with a 3″ by 8″ (910 × 2440 mm) MDF panel nailed on one side with spacing of less than 100 mm.[13] As illustrated in Fig. 2, the allowable shear wall resistance was

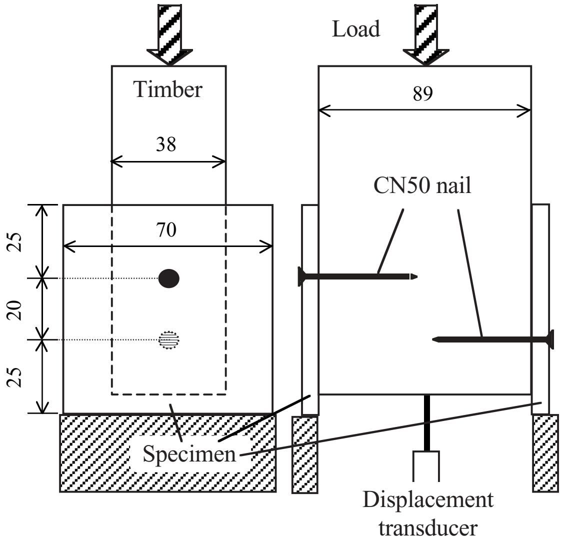

Fig. 1. An experimental single-shear test of nailed joint

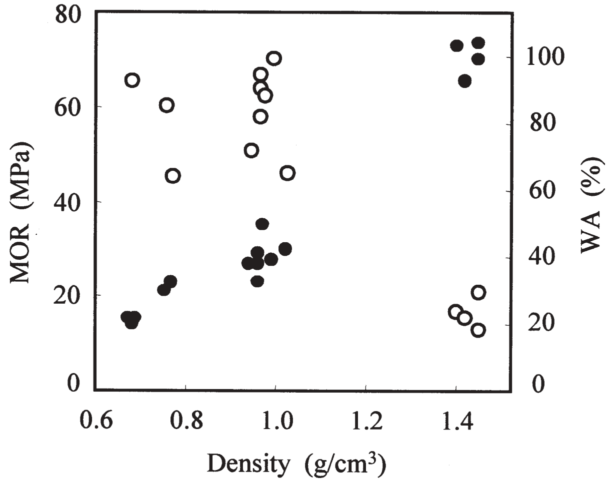

Fig. 3. Modulus of rupture (MOR, *filled circles*) and water absorption (WA, *open circles*) of the boards as a function of their density. The molding temperature and time were 180°C and 15 min, respectively

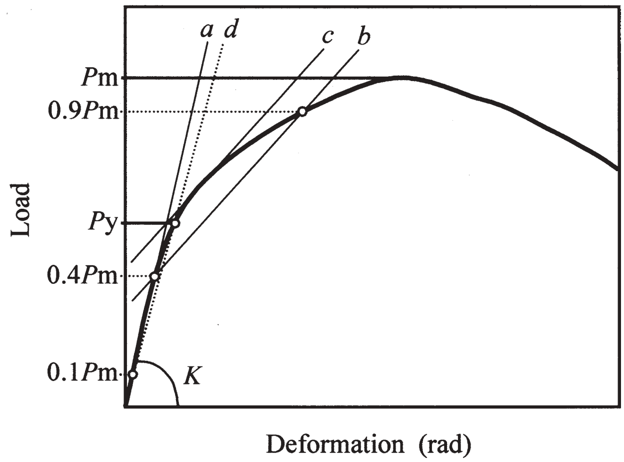

Fig. 2. A typical load–deformation curve for determination of allowable resistance. P_m, maximum lateral load; P_y, yield load defined at the intersection of *lines a* and *c*; *K*, initial modulus defined at slope of *line d*. Note that *line a* links $0.1P_m$ and $0.4P_m$ on the curve. *Line b* links $0.4P_m$ and $0.9P_m$ on the curve. *Line c* is the tangent parallel to *line b*. *Line d* links the origin and the yield point on the curve that is transferred parallel to the horizontal axis from the intersection of *lines a* and *c*

calculated from the simulated load–deformation curve as the minimum value among the following four lateral loads according to the standard evaluation method.[12] The loads are (1) the yield load (P_y), (2) 2/3 of the maximum load (P_m), (3) the load at the allowable shear strain 1/150 rad, and (4) $0.2/D_s$ of the maximum load P_m where D_s is the structural characteristic factor.[12] The calculated value was modified to the standardized allowable shear wall resistance per unit wall width of 1 m.

Results and discussions

Properties of HB

We have already revealed that HB with a density of 1.4 g/cm^3 prepared from the composites of HAL and WN by dry forming fulfilled the JIS regulation with the highest mechanical grade.[5] When using 15% HAL, the HB showed a maximum strength that was about threefold of that of HB from WN alone. The water resistance was also improved by the addition of HAL. These results suggest that HAL acted as a hydrophobic and hot-melt type of adhesive. However, the board density was higher than that of conventional HB (<1.0 g/cm^3), and, for practical use, the density should be decreased. By controlling the molding pressure, a decrease of the density was achieved. The properties of MOR and water resistance of the resulting board (HAL 20%, diameter 10 cm) deteriorated with decreasing board density (Fig. 3).

Improvement of the properties of the dry-formed HB was attempted by the addition of inorganic salts as retention-aid agents, which were used for enforcement of bonding between cellulosic fibers in the paper making.[14] The MOR of HB with a density of 1.0 g/cm^3 was significantly increased by the addition of NaCl, while the other salts, $CaCl_2$ and $Al_2(SO_4)_3$, showed slight effects (Fig. 4). However, WA and TS, which are parameters indicative of water resistance were remarkably improved by salt addition, and the effect was dependent on the charge of the cations. The effect of cation on board performance was interpreted as follows. Cation-containing pulp swelled well in the water because of osmotic pressure of free cations.[14] In particular, the monovalent sodium ion has a strong effect. When the swollen pulp was subjected to dryness, much more extensive hydrogen bonding occurred. Therefore, the bonding strength between fibers was improved. In addition, multivalent cations would have contributed to crosslinking between

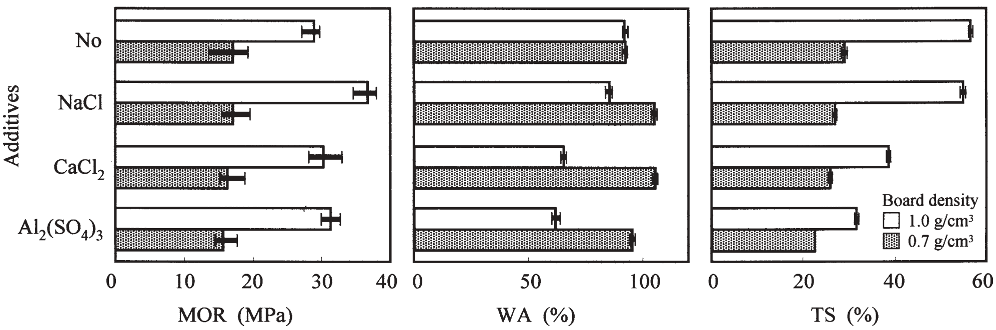

Fig. 4. Effect of inorganic salts on MOR, WA, and thickness swelling (TS) of boards with densities of 1.0 and 0.7 g/cm^3. The molding temperature and time were 180°C and 15 min, respectively. The *bars* show the range between maximum and minimum values in the three specimens tested

pulp with a negative zeta potential and relatively anionic lignin by electrostatic interaction to prevent swelling in water. However, the pulp-swelling ability of multivalent cations is too weak to enhance mechanical strength drastically.

Dry-formed MDF

Recently, the production and consumption of MDF has markedly increased. Therefore, commercially available MDF should also be produced from the mixture of lignin and waste paper. Lowering the molding pressure can produce low-density boards. However, the press machine that was used in this study could not be regulated in a range of low pressure. We prepared MDF with a density of 0.6–0.8 g/cm^3 and a thickness of about 4 mm (diameter 10 cm) and 7.5 mm (5 × 20 cm) by controlling molding volume, which was carried out by maintaining the stroke of the press machine at a certain distance. As shown in Fig. 3, the MOR in the density range of MDF was very low, and WA was significantly high. The bending strength fulfilled the minimum criterion of JIS for MDF, but WA should be improved.

In order to improve the board property, molding time was prolonged so that the molten lignin dispersed well into the space between fibers and covered the fibers to give water resistance, because HAL acted as a hot-melt adhesive. The internal bond strength was significantly improved by extending the molding time, although it had no clear effect on MOR, as shown in Fig. 5. These results revealed that it took a long molding time to transmit the heat required to melt and disperse HAL throughout the thickness of a board. This means that the molding time significantly affected the internal bond strength, in which the strength of the weakest layer of a board was critical. The MOR, on the other hand, was mainly determined by the strength of the outer layers, which could be easily heated. Water resistance, TS in particular, which was reflected throughout the thickness, was also improved. The resultant MOR and TS were a little less than the JIS regulations, MOR > 15 MPa and TS < 12% for MDF with thickness of 7–15 mm.

As well as HB, the effect of inorganic salts on the board property of MDF (density 0.7 g/cm^3) was investigated (Fig. 4). The addition of inorganic salts did not influence the mechanical strength. However, the TS was unambiguously improved by $Al_2(SO_4)_3$. In the MDF regulation of JIS, TS is regarded as a more important parameter than WA. Hence, salt addition impacted positively on the MDF properties.

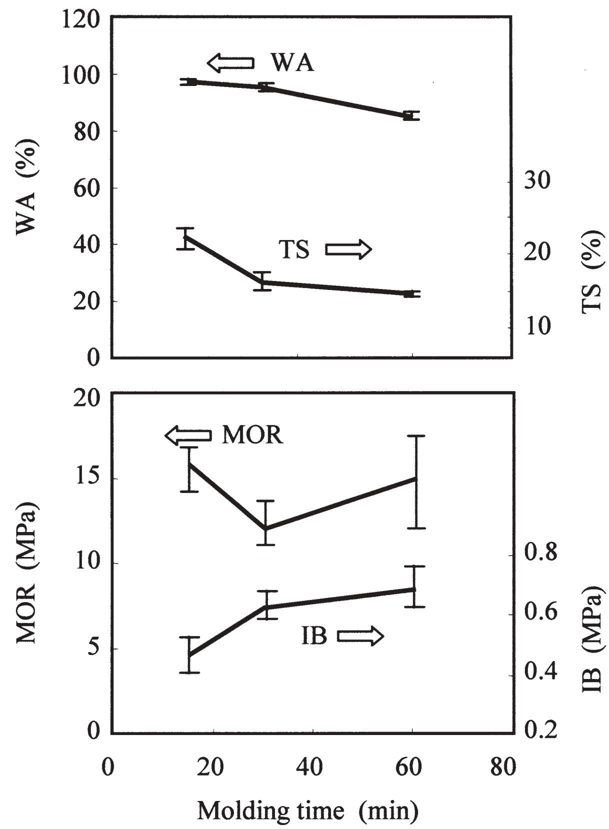

Fig. 5. Effect of molding time on MOR, IB, WA, and TS of the boards. The molding temperature was 180°C and the board density was 0.7 g/cm^3

The characteristics of the salt-treated MDF were compared with that of commercially available MDF, as shown in Table 1. Larger specimens (width 5 cm; length 20 cm; density 7.5–9.0 g/cm^3) were used in accordance with fiberboard regulations. To investigate the influence of lignin type, the properties of $Al_2(SO_4)_3$-containing MDF prepared from KL–WN mixture and WN alone were also listed. The MDF prepared from WN alone had a very weak strength and poor water resistance. By the addition of KL, the performance was slightly improved, but was much less than the commercial MDF. The HAL-based MDF showed a slightly

Table 1. Properties of medium density fiberboard (MDF)

MDF type	Thickness (mm)	Density $(g/cm)^3$	MOR (MPa)	MOE (GPa)	IB (MPa)	WA (%)	TS (%)
WN alone[a]	7.7	0.60	1.2	0.38	0.01	710	321
20% KL–WN[a]	7.5	0.69	3.6	0.69	0.09	214	107
20% HAL–WN[a]	7.5	0.68	11.6 (10.4–12.8)	1.80 (1.72–1.87)	0.74 (0.71–0.79)	100 (96.5–103.5)	22 (21.1–22.3)
Commercial	9.0	0.60	22.6 (22.1–25.6)	1.92 (1.85–1.96)	0.65 (0.60–0.69)	46 (44.1–48.6)	10 (8.9–11.0)

The values in parentheses show the maximum and minimum values for the three specimens tested
MOR, modulus of rupture; MOE, modulus of elasticity; IB, internal bond strength; WA, water absorption; TS, thickness swelling; WN, waste newspaper; KL, kraft lignin; HAL, hardwood acetic acid lignin
[a]The boards were fabricated by the addition of $Al_2(SO_4)_3$

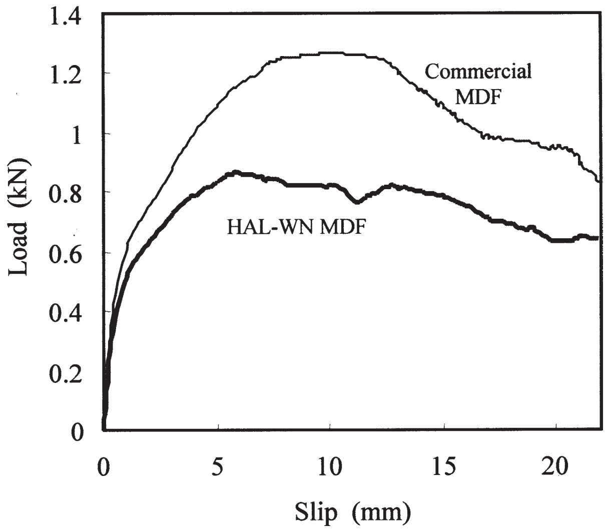

Fig. 6. Averaged load–slip curves of the nailed joints in single-shear tests for commercial medium-density fiberboard (MDF) and hardwood acetic acid–waste newspaper (HAL–WN) MDF

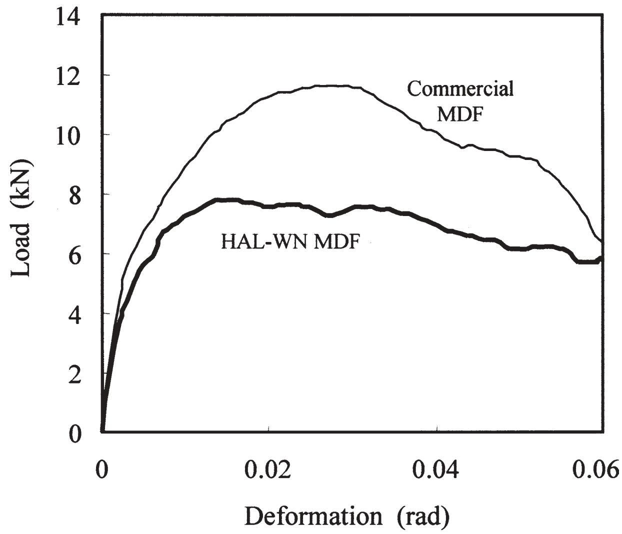

Fig. 7. Simulated load–deformation curves of nailed shear walls of commercial MDF and HAL–WN MDF

superior IB to the commercial one, but the MOR was half that of the commercial material. Thus, HAL was found to be more suitable than KL as adhesive, but the properties did not appear satisfactory.

Allowable lateral resistance of the shear walls with prepared MDF

Figure 6 shows the averaged load–slip curves of the nailed joints with the prepared and commercial MDF used in the analyses. The averaged moduli of rigidity (G) of the prepared and commercial MDF are 1.09 GPa and 1.95 GPa, respectively. Figure 7 shows the lateral load-deformation curves, which were simulated based on these basic data. From Fig. 7, the average lateral resistance of the shear wall sheathed on one side per unit wall width was evaluated to be 4.91 kN/m for the prepared MDF and 6.37 kN/m for the commercial MDF. These values, however, do not give an exact comparison between two kinds of MDF because of the incompatibility in their density and thickness. Although allowable lateral resistance of the shear wall is generally determined as the 50th percentile value with 75% confidence of the lateral resistance, it cannot be determined directly here. However, we may be able to roughly estimate it as follows. The shear wall factor given for commercial MDF used in this study is 3.0, which ensures that its lowest allowable lateral resistance is equal or more than 5.88 kN/m. Then, the allowable lateral resistance of the shear walls with prepared MDF is roughly estimated as 4.50 kN/m if the variance of it is not much larger than the variance of the resistance of the walls with commercial MDF. A more conservative estimation may give 4.00 kN/m.

At any rate, an allowable resistance of 4.50 or 4.00 kN/m for the prepared MDF seems practically available. Internal shear walls are usually sheathed on both sides with the same sheet material. Their lateral resistance, then, becomes twice the resistance of shear walls sheathed on one side. The resultant allowable resistance of 9.00 or 8.00 kN/m for the prepared MDF is sufficient for ordinary residential constructions. This is because the ultimate resistance of timber constructions is determined not only by the lateral resistance of shear walls but also by the resistance of structural joints which must transmit the lateral forces from shear walls to foundations. In most of the practical design of internal shear walls, the expected lateral resistance is usually 6.0 to 8.0 kN/m, even in the regions of strong winds and earthquakes.

When the prepared MDF is used on the internal sides of external shear walls, the external sides of them can be sheathed with stronger sheet materials.

Practical potential of the prepared MDF for structural use

A disadvantage of the prepared MDF is relatively low water resistance. This disadvantage, however, seems not to be serious in actual use of the prepared MDF. The principal advantage of it, that is its harmlessness to the human body, must lead it to proper use for internal walls. The material for internal use has less risk of degradation due to high moisture in comparison with the external sheathing materials of external walls or roofs. Relatively inferior bending properties of prepared MDF are not so critical when used for interior walls. Bending properties are more important for floor or roof materials, or external sheathing materials of external walls.

An expected performance of sheathing materials of internal walls may be satisfactory resistance of nailed or screwed joints. For residential constructions in an aging society, internal walls that allow handrails to be fixed easily with nails or screws are very convenient. The lateral resistance of nailed joints with prepared MDF shown in Fig 6 was practically available for this purpose. Of course, it is better if the sheathing material that satisfies this need is also harmless to the human body and is environmentally friendly.

Conclusions

Isolated lignins and waste paper can be converted to boards that are considered to be regenerated wood materials. AL was a suitable source of lignin for board production because it acted as a hydrophobic and hot-melt type adhesive.[5] The high-density HB completely fulfilled the HB regulation of JIS. Unfortunately, the density of the HB was relatively high. When the density was decreased, the board property deteriorated. However, this problem was overcome by the addition of inorganic salts and prolonged molding time. In particular, the water resistance was remarkably improved.

We prepared MDF in this study. Most of the parameters of the MDF concerning the board properties except for the internal bonding were inferior to those of the commercial MDF. However, as a construction material, the MDF had sufficient mechanical strength to be used as sheet material for internal shear walls.

The FBs, HB and MDF, have an advantage over the traditional FB; the FBs are environmentally friendly boards because they use recycled paper and pulping byproduct without formaldehyde-based adhesive. Accordingly, the FB can be utilized as internal wall that does not pollute the residential atmosphere.

In this study, we showed one example of direct lignin utilization for board making. The molding technique will be applied to produce not only HB and MDF but also other paper-based materials, for instance paper receptacles.

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