論　文

Bonding of Surface-Activated Wood (Ⅰ)

Bonding Properties of Two-Ply Wood*

Erlinda L. MARI**

Tomoyasu SAKUNO**

Ikuo FURUKAWA**

Jun KISHIMOTO***

表面活性化木材の接着 (Ⅰ)

2プライ積層材の接着性

エルリンダ L. マリィ**

作 野 友 康**

古 川 郁 夫**

岸 本　 潤***

Summary

At moderate pressure and temperature, the suitability of two wood species and the effects of press time and the type and amount of crosslinking or binding agents were investigated in the bonding of wood activated by nitric acid. Mizume (*Betula grossa* Sieb. et Zucc.) yieded shear strength values higher than those of Giant ipil-ipil (*Leucaena leucocephala* Lam. de Wit.). Furfuryl alcohol was found to give the best bonds for Mizume and the only possible binding agent for Giant ipil-ipil. As to the quantity of crosslinking agent, a lesser amount gave better results for Mizume. Shorter pressing time also resulted in better bonding. With furfuryl alcohol-bonded Giant ipil-ipil, there was a tendency for better bonding with a greater amount of chemicals and a longer pressing time.

Ⅰ INTRODUCTION

Chemical modification of wood surfaces has been known for some time as a possible alternative in the bonding of wood. The method involves the preparation of active sites on the wood surface by oxidizing agents, followed by the application of crosslinking chemicals which react with these active sites. Bonding has to be completed by hot-pressing.

The significance attributed to this method is its non-dependence on petroleum-based synthetic resins. In addition, the oxidizing agents, such as acids, are inexpensive and easily available while the crosslinking chemicals, such as furfuryl alcohol, can be derived from agricultural or pulping residues. Moreover, fairly strong bonds have been reported.[4,5,10]

However, some reports suggest further studies due to the low water resistance obtained.[3,10] Also, the pressing conditions so far reported seem too severe causing great damage to the wood cells.[4,5,6,10] Moderate conditions, on the other hand, produced barely acceptable bond strength.[3,7] A practical method that would yield acceptable bond strength has yet to be established. In the meantime, use of nitric acid as the chemical activator seems to produce sufficient and consistent bonding.[4,10]

Using this surface-activation method, trial experiments revealed that it is possible to bond two-ply wood at low temperatures and pressures and still obtain acceptable bond strength values. With these results as a point of departure, this particular study was designed to investigate the effects of pressing time and the type and amount of crosslinking or binding agents on two wood species activated with nitric acid.

Ⅱ MATERIALS AND METHODS

1. Raw materials and chemicals used

The two wood species used were Mizume (*Betula grossa* Sieb et Zucc.) and Giant ipil-ipil (*Leucaena leucocephala* Lam de wit.), which have almost the same specific gravities of 0.67 and 0.68, respectively.

Radially sawn wood slats from both species were used. Mizume samples had a size of 180 (L)×25 (R) ×4.5 (T)㎜ after planing. Giant ipil-ipil samples were 260 (L)×50 (R)×5.5 (T)㎜ in size. The samples had about 11〜12 per cent moisture

content.

The surface activator was a 40 per cent solution of nitric acid (designated as N). The crosslinking chemicals were furfuryl alcohol (A), formaldehyde (B), and lignin (C).

2. Determination of the chemical composition of the raw materials

The chemical composition of both wood species was analyzed for basic comparison. The extractives content was calculated as percentage loss in weight (oven-dry basis) after sequential extraction with ethanol-benzene, ethanol, and hot water. The lignin content was determined by the Klason lignin 72 per cent sulfuric acid method. The holocellulose content was determined by the sodium chlorite method.

3. Preparation of two-plies and test for shear strength

Table 1 shows the experimental design used in this study. The surface activator was sprayed on first. The crosslinking chemicals were then applied after 15 minutes. For treatments using lignin, the lignin powder was carefully spread on the nitric acid-sprayed samples prior to the spraying of either furfuryl alcohol or formaldehyde. The treated samples were then assembled into two-plies and immediately hot-pressed. The bonded plies were then left at room condition for at least one week before cutting the test specimens.

Five tensile shear strength test specimens per treatment were prepared and tested at both dry (or normal) and wet conditions as specified in J I S - K 6851.[2] The wet condition test involves the immersion of specimens in hot water (60 ± 3℃) for 3 hours prior to testing while wet.

Table Ⅰ. Experimental design for the manufacture of two-plies (Factorial in completely randomized design)

Surface activator Spread,(g/cm^2) per two-ply	Nitric acid, 40% soln.(N) 0.025
Crosslinking chemicals Spread,(g/cm^2 per two-ply)	Furfury alcohol(A) Formaldehyde(B) Furfuryl alcohol+lignin(C) (7:3 parts by weight) Formaldehyde+lignin (7:3 parts by weight) 0.020 0.030
Press temp.,(℃)	100
Pressure,(kg/cm^2)	13
press time,(secs/mm of wood thickness)	90 135

4. Infrared (IR) analysis

To obtain a direct observation of the chemical modification effected by the treatments, scrapings of about 0.20 mm thickness were taken from the surface of both the untreated wood and the different bondlines. These scrapings were pounded into very fine powder and IR spectra were taken.

Comparison of the degree of reaction between furfuryl alcohol and formaldehyde was further observed through the IR spectra of scrapings taken until about 0.60 mm from the bondlines.

III RESULTS AND DISCUSSION

1. Chemical composition of the raw materials

Table 2 shows the chemical composition of Mizume and Giant ipil-ipil. Giant ipil-ipil was found to contain more extractives and a higher lignin content than Mizume. The lignin content of this Giant ipil-ipil is among the highest compared with several samples of Philippine Giant ipil-ipil.[1] It was at first considered that this high lignin content would be an advantage in this study. In contrast, however, the holocellulose content of Mizume was higher than that of Giant ipil-ipil. These differences in composition of the two materials may have had varying effects on the bonding mechanism each underwent, as the following shear strength data shows.

Table 2. Chemical composition of Mizume and Giant ipil-ipil

Component (%)	Wood species	
	Mizume	Giant ipil-ipil
Extractives	3.3	4.1
Lignin	20.7	26.1
Holocellulose	77.9	72.6

2. Tensile shear strength of two-plies

Table 3 is a summary of the results obtained from the tensile shear strength tests. Except for the unsuccessful bonding using only nitric acid without a crosslinking chemical, bonding by all treatments was apparently possible with Mizume. On the other hand, bonding of Giant ipil-ipil was only made possible with furfuryl alcohol. For this reason, statistical analysis of the effects of the treatments was based on the dry shear strength data of Mizume only.

Analysis of variance showed that the effects of all three main variables, namely, press time, type of crosslinking agent, and spread amounts, were significant (Table 4).

Table 3 Average shear strength of Mizume and Giant ipil-ipil two-plies

Wood Species	Press Time (sec/mm)	Spread (g/cm²)	Shear Strength				
			Dry		Wet		
			SS*1 (MPa)	WF*2 (%)	SS*1 (MPa)	WF*2 (%)	Ret.*3 (%)
Mizume			[A]				
	90	0.02	15.50	64	4.90	78	32
		0.03	12.65	44	4.32	52	34
	135	0.02	15.00	82	5.10	60	34
		0.03	10.40	40	3.53	96	34
			[A+C]				
	90	0.02	11.38	2	3.33	8	29
		0.03	8.73	0	3.04	0	52
	135	0.02	7.36	8	3.83	4	35
		0.03	8.24	2	3.63	20	44
			[B]				
	90	0.02	6.67	0	-	-	-
		0.03	5.50	0	-	-	-
	135	0.02	4.61	0	-	-	-
		0.03	4.90	0	-	-	-
			[B+C]				
	90	0.02	4.51	0	-	-	-
		0.03	6.18	0	-	-	-
	135	0.02	4.51	0	-	-	-
		0.03	4.90	0	-	-	-
Giant Ipil-ipil			[A]				
	90	0.02	6.67	14	-	-	-
		0.03	6.47	30	-	-	-
	135	0.02	7.75	28	-	-	-
		0.03	8.24	38	-	-	-

*1 SS-shear strength
*2 WF-Wood failure
A,B,C-Designations are as stipulated in Table 1

*3 Ret.-Strength retention
(wet SS/dry SS)×100

Table 4. Statistical Significance of Treatments by
Analysis of Variance Based on the Dry Shear
Strength Data of Two-Ply Mizume

Source of Variation	df	F
Treatments	(15)	31.468**
Press time, p	1	17.797**
Crosslinking agent, ca	3	134.816**
Spread, s	1	8.656**
p x ca	3	0.949ns
p x s	1	0.486
ca x s	3	9.001**
p x ca x s	3	3.597**
Error	64	

∗ ∗ - Significant at 1% level
ns - not significant

Referring to Table 3, furfuryl alcohol was found to effect the strongest bonds with average values between 10.40 and 15.50 MPa, which are comparable to those of some synthetic resin-bonded woods.[9] Such high strength may have been due to the black, tar-like substance which developed on the bondline.   This is believed to be a thermosetting resin.

The furfuryl alcohol-lignin combination yielded bond strength values averaging between 7.36 and 8.24 MPa. It is interesting to note that the values obtained are only about 70 per cent of those bonded with furfuryl alcohol only. It appears that the added lignin did not take part in the bonding mechanism. This result was thought to be basically due to the fact that the lignin was alkaline while the surrounding wood surface was highly acidic. To verify this, experiments using sodium hydroxide as the surface activator were also conducted, but none of these were successful. The wood surface only turned very soft but produced no interlocking after pressing. This, therefore, excludes the possibility of surface activation by alkaline treatments and by the simple methods and moderate conditions used in this study.

Back to Table 3, in the case of formaldehyde, lower strength values averaging between 4.61 and 6.67 MPa were obtained. The reaction was apparently much weaker compared with furfuryl abcohol.

On the other hand, the formaldehyde-lignin combination gave the lowest strength values averaging between 4.51 and 6.18 MPa, which were nearly equivalent to those bonded by formaldehyde alone—another indication that the added lignin did not contribute to the bonding system.

As to the effect of press time, strength values at longer pressing times were relatively lower than those at shorter pressing times. Longer press time might have caused further embrittlement of the bonds, and thus, a reduction in strength.

Likewise, the lesser amount of crosslinking chemical revealed higher strength values. This implies that a greater amount was not directly proportional to greater strength. Similarly to the case of ordinary plywood manufacture, an excessive amount caused a squeezing out of most of the chemical and consequently, starved joints, or in this case, a lesser degree of reaction due to the lack of polymerizing agents.

After the wet tests, strength retentions of furfuryl alcohol bonds ranged between 32 and 34 per cent ; the furfuryl alcohol-lignin bonds, between 29 and 52 per cent. In this case, lignin appeared to have had varying effects where the hot immersion test was involved. For both treatments, the wood failure values of the wet specimens were a little higher than the corresponding dry specimens. Such low strength retention but greater wood failure might have been due to the failure of crushed cells that swelled back after absorption of water.

In the case of the formaldehyde and formaldehyde-lignin bonds, all specimens completely separated during the water immersion period.

Going to the Giant ipil-ipil data, the highest strength value of 8.24 MPa was obtained from the treatment with the higher amount of furfuryl alcohol and the longer pressing time. Unlike Mizume, furfuryl alcohol-bonded Giant ipil-ipil did not show any water resistance. In other words, specimens separated during the water immersion period.

Several factors may have contributed to the poor response of Giant ipil-ipil to this type of bonding. The extractives content may suggest restriction of the reaction between the chemicals and the wood surface. Also, although the lignin content of Giant ipil-ipil is higher than that of Mizume, a different and faster reaction of Mizume lignin might have occurred. The color transfomation to green then finally to black when furfuryl alcohol was applied on the nitric acid-activated samples was faster with Mizume than with Giant ipil-ipil. Furthermore, the higher percentage of holocellulose in Mizume over Giant ipil-ipil might also suggest better bonding through enhanced plasticization of the bondline.

3. IR Spectral analysis

Through IR spectral analysis, further differences between the two wood materials and the effects of treatments were observed. In Figure 1 are the IR spectra of scrapings from the surfaces of the untreated materials. A striking difference can be observed within the band range $1590 \sim 1680$ cm^{-1}, which covers the ketones, aldehydes, amides, and carboxylates groups. Giant ipil-ipil shows a broad peak covering this whole range, while Mizume displays an intense peak at $1590 \sim 1610$ cm^{-1}band, which can be assigned to the aromatic groups.
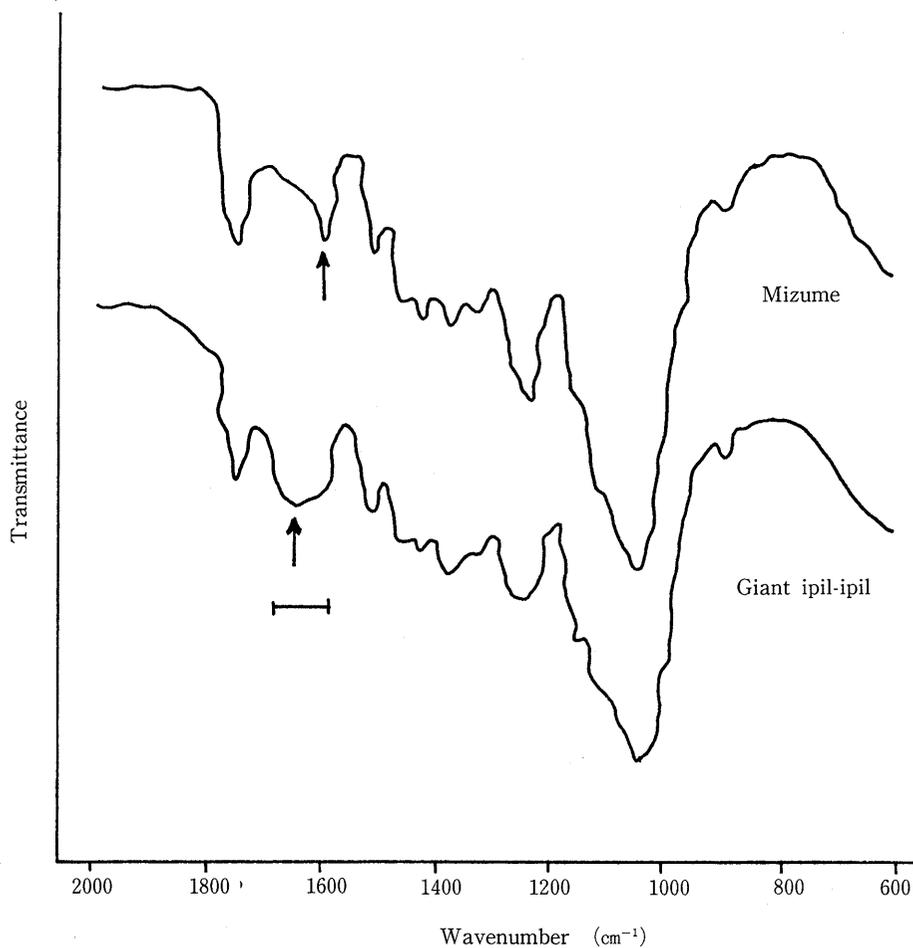

Fig.1 IR spectra of scrapings from untreated materials

As to the surface changes effected by the treatments, IR spectra of scrapings from the different bondlines of Mizume are shown in Figure 2. In all treatments, there is a clear indication of oxidation and modification of chemical components, especially the phenol and aromatic groups at 1500 and 1590 cm^{-1} bands. Compared with the untreated surface, the nitric acid and formaldehyde bondlines show similar broadening of peaks. The increased intensity of the band at about 1650 cm^{-1} can be attributed to the formation of nitrate esters on the polysaccharide component.[8] The spectra of furfuryl alcohol and furfuryl alcohol-lignin bondlines show more diffuse bands. The nitrate esters formed by the nitric acid treatment have been modified almost completely. The appearance of a new peak at 800 cm^{-1} in furfuryl alcohol and furfuryl alcohol-lignin bondlines implies vibrations of hydrofuranol rings.

The spectra of scrapings deeper into the bondlines indicate that furfuryl alcohol effected a very strong chemical reaction until about 0.60 mm from the bondline surface (Figures 3 and 4). Formaldehyde seemed to have reacted less as depicted by the almost identical spectra from the bondline surface extending to within the wood material. This may explain the lower strength values obtained with formaldehyde treatments. It can be observed also that Mizume and Giant ipil-ipil had different responses to both furfuryl alcohol and formaldehyde.

Ⅳ CONCLUSION

From the foregoing, it can be readily seen that furfuryl alcohol produces strong bonds with nitric acid-activated wood surfaces. The tensile shear strength values of furfuryl alcohol-bonded Mizume are comprable to those of synthetic resin-bonded wood. The pressing conditions used, which are very similar to those of conventional systems, proved sufficient to effect good bonding.

It was, however, disappointing that Giant ipil-ipil, which was hoped to respond well to bonding by chemical activation, did not perform as expected. It may be deduced that in bonding solid wood of this material, a higher pressure or longer pressing time may be required. As with other hard-to-control wood species, studies on bonding Giant ipil-ipil particles may give encouraging results. Variables such as particle size, treatment, and pressing conditions may prove worthy of investigation.
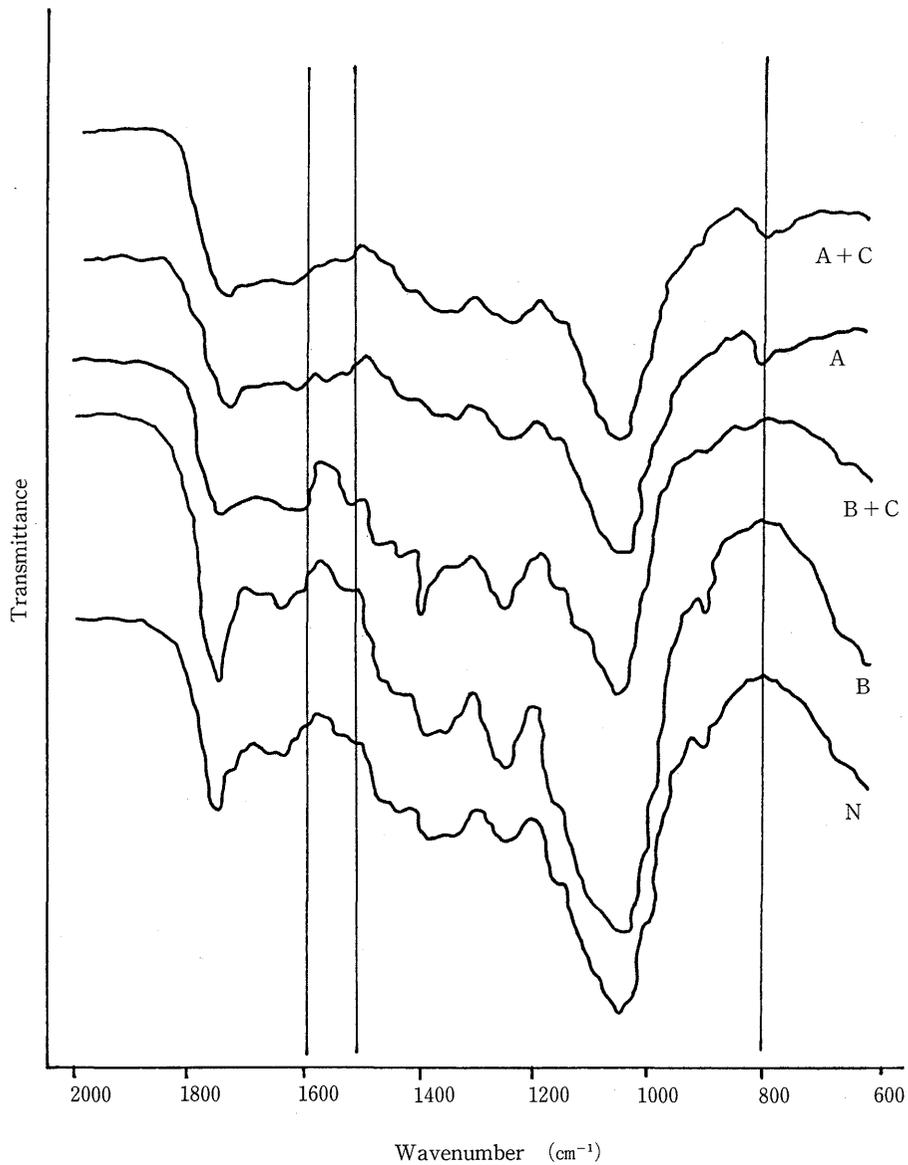
Fig.2 IR spectra of scrapings from the different bondlines
of Mizume
A, B, C, N-Designations are as stipulated in Table 1.

Transmittance

2000　1800　1600　1400　1200　1000　800　600

Wavenumber (cm⁻¹)
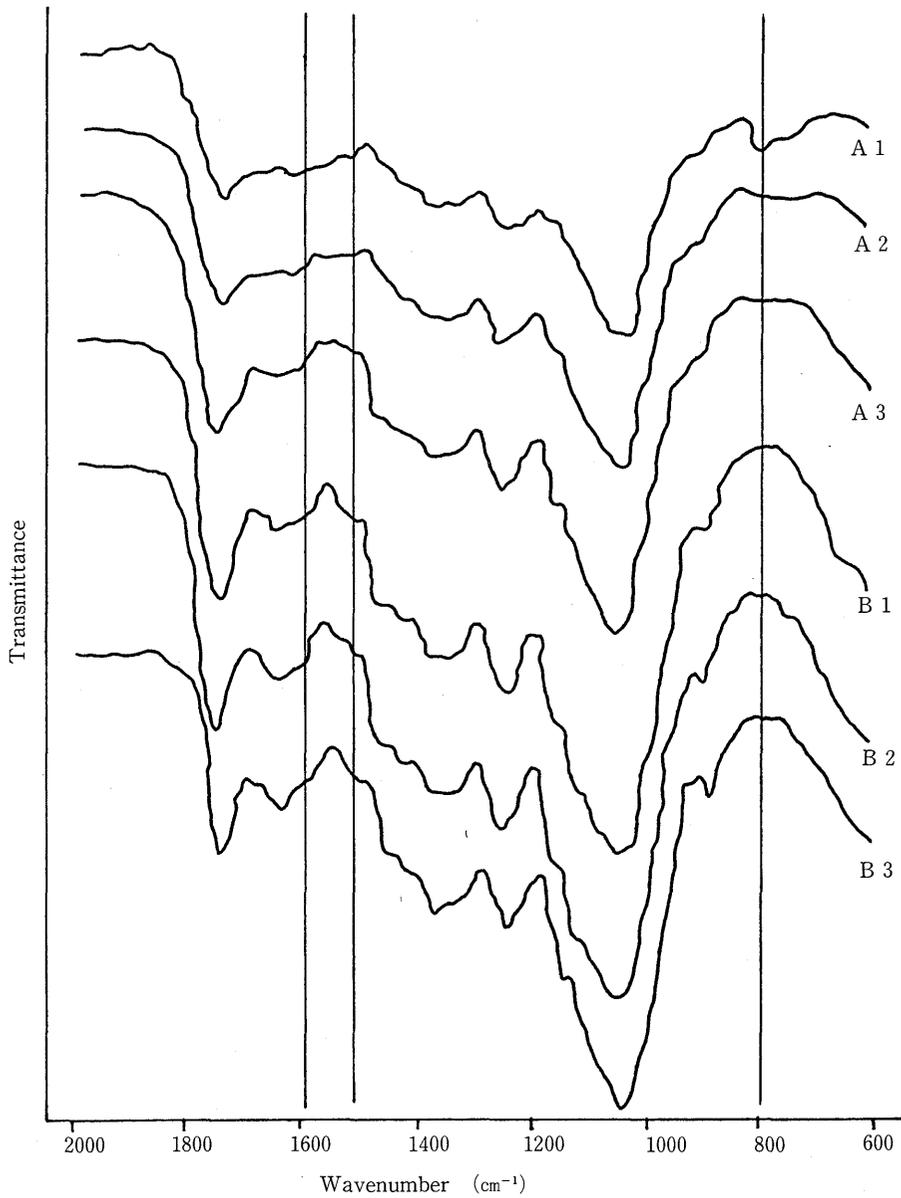
A 1
A 2
A 3
B 1
B 2
B 3

Fig.3 IR spectra of scrapings from furfuryl alcohol (A)
and formaldehyde (B) bondlines of Mizume
Note : Subscript numbers are for the 1 st, and
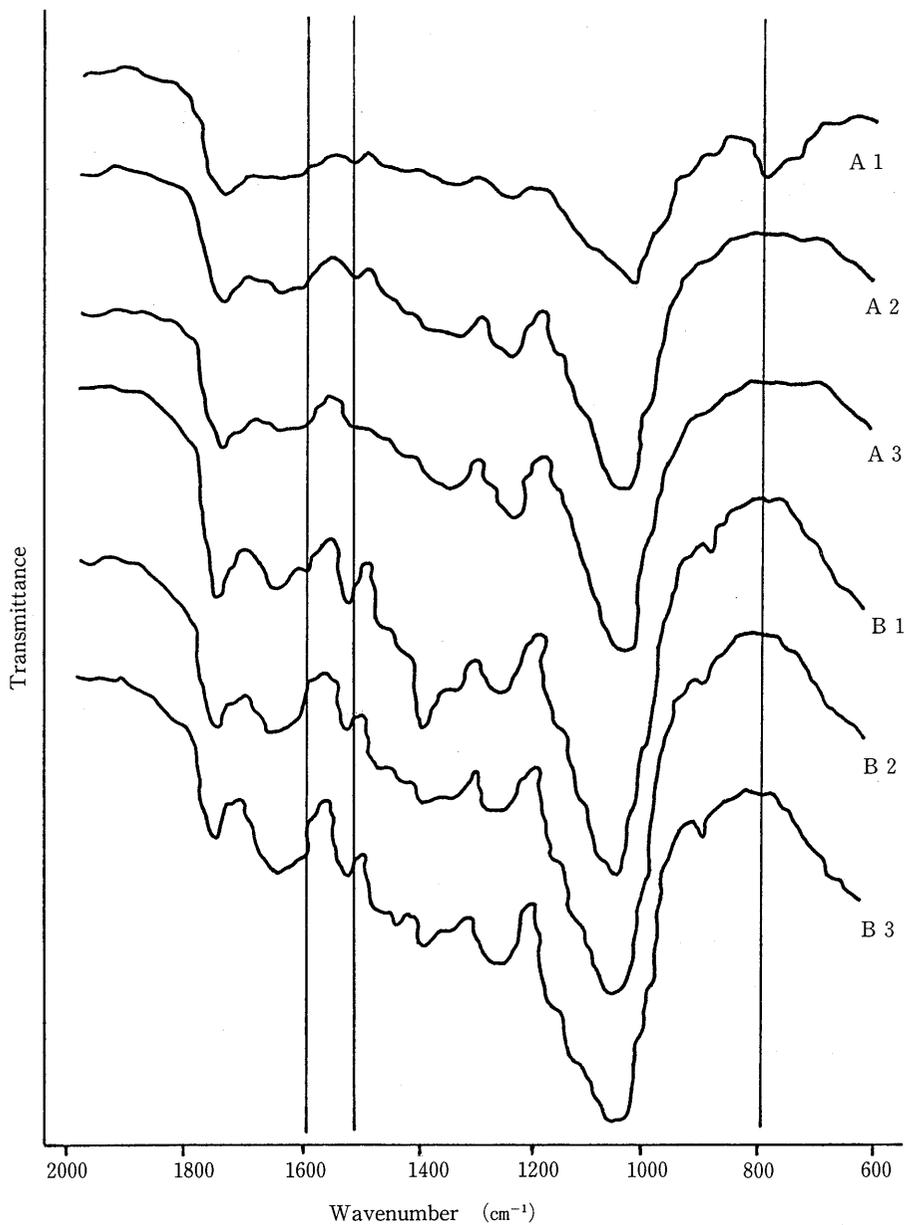3rd layers of 0.20mm-thick scrapings from
the bondline surface.

Fig.4 IR spectra of scrapings from furfuryl alcohol (A)
and formaldehyde (B) bondlines of Giant ipil-ipil
Note : Subscript numbers are for the 1 st, 2nd, and
3rd layers of 0.20mm-thick scrapings from
the bondline surface.

REFERENCES

1) Escolano, E. U., Gonzales, E. V., and Semana, J. A. : Proximate chemical composition of Giant ipil-ipil wood from different sources. Forpride Digest Ⅶ (1) : 18-22 (1978).

2) Japan Standards Association. JIS-K 6851. Tokyo

3) Johns, W. E. and Nguyen, T. : Peroxyacetic acid bonding of wood. For. Prod. J. **27**(1):17-23 (1977).

4) Kelley, S. S., Young, R. A., Rammon, R. M., and Gillespie, R. H.: Bond formation by wood surface reactions:Part Ⅲ-Parameters affecting the bond strength of solid wood panels. For. Prod. J. **33**(2):21-27 (1983).

5) Kelley, S. S., Young, R. A., Rammon, R. M., and Gillespie, R. H.: Bond formation by wood surface reactions: Part Ⅳ-Analysis of furfuryl alcohol, tannin, and maleic bridging agents. J. of Wood Chem. and Technol. **2**(3):317-342 (1982).

6) Murmanis, L. : Microscopy of acid-activated bonding in wood. Wood and Fiber Sci. **15**(3):203-221 (1983).

7) Philippou, J. L. : Applicability of oxidative systems to initiate grafting on and bonding of wood. J. of Wood Chem. and Technol. **1**(2):199-227 (1981).

8) Rammon, R. M., Kelley, S. S., Young, R. A., and Gillespie, R. H.: Bond formation by wood surface reactions:Part Ⅱ-Chemical mechanisms of nitric acid activation. J. Adhesion **14**:257-282 (1982).

9) Yamada, M., Sakuno, T., Furukawa, I., and Kishimoto, J.:Studies on the utilization of unused hardwoods(Ⅱ):Gluing durability of Konara, Kunugi, and Niseakashia. Bulletin of the Tottori Univ. Forests. No.16:149-158 (1986).

10) Young, R. A., Rammon, R. M., Kelley, S. S. and Gillespie, R.H.: Bond formation by wood surface reactions: Part Ⅰ-Surface analysis by ESCA. Wood Science **14**(3):110-119 (1982).