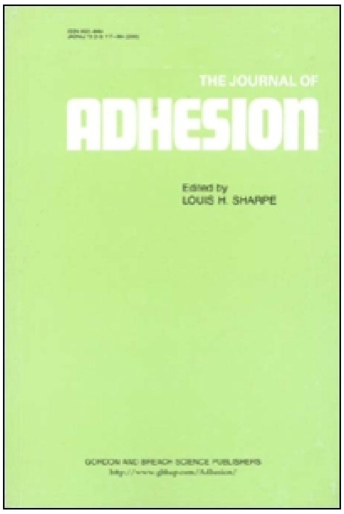

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Curing Behavior of Wood Adhesives Under High Steam Pressure*

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(In final form January 19, 1996)

Steam-injection pressing is a recent development for manufacturing wood products. The curing mechanism and behavior of wood adhesives during steam-injection heating and hot-platen heating may cause differences in both chemical and physical aspects. The curing of wood adhesives under high steam pressure using an especially designed reaction cell is discussed. The adhesives used in this study were phenol-formaldehyde (PF), urea-formaldehyde (UF), melamine-formaldehyde (MF), and isocyanate (IC) resins. At different curing times, the heating temperature (steam pressure) applied to cure the adhesives was 160°C (6 kgf/cm^2). Results were examined by analytical methods using FR-IR, ^{13}C-NMR, dynamic mechanical analysis and solvent extraction. (1) By steam-injection heating, PF resin immediately cured to some degree in a few minutes and maintained an equilibrium situation. In this case, the reaction was accompanied by the disappearance of the ether structure. (2) In UF resin, results from IR data clarified different reactions between hot-platen heating and steam-injection heating. During steam-injection heating, as heating time increased, UF resin returned to its liquid state under the influence of hydrolysis. (3) MF resin was almost cured under steam-injection in a short heating time compared with hot-platen heating. (4) IC resin foamed and cured in a short heating time under steam-injection. It was proved that steam-injection heating was more effective than by hot-platen heating for IC resin.

KEY WORDS: Steam-injection pressing; hot-platen pressing; curing behavior; wood adhesives; phenol-formaldehyde adhesive; urea-formaldehyde adhesive; melamine-formaldehyde adhesive; isocyanate adhesive; FT-IR; ^{13}C-NMR; dynamic mechanical analysis; solvent extraction.

1. INTRODUCTION

Steam-injection pressing technology was developed purposely for the manufacture of wood composite materials and other allied products. In the steam-injection pressing system, the particle mats are exposed to high steam pressure and temerature conditions, and the temperature of mat's core rises immediately compared with hot-platen

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pressing. Consequently, pressing time is anticipated to be shortened. Compared with the conventional hot-platen press, the steam-injection press with perforated platens, where steam is introduced, is intended to be applied for the curing of adhesive resins.

Almost all of the adehesives currently used to manufacture wood composite materials are synthetic polymer resins based on addition and condensation reaction of formaldehyde with compounds derived from either benzene or ammonia. The typical thermosetting resins are phenol-formaldehyde (PF), urea-formaldehyde (UF), resorcinol-formaldehyde (RF), melamine-formaldehyde (MF) and others. Recently, a new chemical bonding type of isocyanate adhesive (IC) is also being developed for wood production.

The curing reaction of the adhesives is very complex. The curing process of the adhesives is determined using differential thermal analysis (DTA)[1-4], torsional braid analysis (TBA)[5], differential scanning calorimetry (DSC)[6], infrared spectroscopy (IR)[7], etc. However, characterizing the curing process of adhesives has been done mainly under atmospheric pressure in the studies mentioned above, because wood products have been manufactured by using a hot-platen press.

Basic information on the curing process of adhesives under high steam pressure is necessary, especially for the development of steam-injection press technology. Chow and Mukai[8] reported the polymerization of phenolic resin at high vapor pressure. Shen[9] has reported that the mechanical properties of phenolic bonded particlebonds decreased with increase of the steam-injection time. Thoman and Pearson[10] suggested that polymerization of phenolic resin yields water as a by-product and that additional water by condensation of the steam injected shifts the chemical equilibrium. The combination of high temperature and steam possibly caused some hydrolysis of the cured resin and also of chemical components of wood such as hemicellulose. These are some of the factors that cause the reduction of adhesive bond and bonding strength which was observed in phenol-resin-bonded particleboards produced with excessive steam-injection. Subiyanto[11] measured the curing behavior of PF, UF, and other wood adhesives under high steam pressure using the hardness method. Besides these, few researches concerning the mechanisms of adhesive curing under high steam pressure were discussed in detail. Research on curing mechanisms under high steam pressure for several types of wood adhesives is necessary before their application to steam-injection pressing.

In this report, the curing mechanisms of several wood adhesives under high steam pressures, using a specially designed reaction cell, is discussed. Resins treated by hot-platen heating and steam-injection heating were analyzed using techniques such as FT-IR, ^{13}C CP/MAS NMR, dynamic mechanical analysis and solvent extraction. For the same methods of analysis, comparisons between hot-platen heating and steam-injection heating were also done.

2. MATERIALS AND METHODS

2.1. Materials

The adhesives used in this research were phenol formaldehyde (PF), urea formaldehyde (UF), melamine formaldehyde (MF), and polymeric type isocyanate (IC) resins.

These resins were obtained from Oshika Shinko Corp. Ltd. The properties of the resins are shown in Table I. The mole ratio of resins were as follows: PF resin with P:F mole ratio of 1:2.0; UF resin with U:F mole ratio 1:1.7; MF resin with M:F mole ratio 1:2.5. The IC resin was composed of crude diphenylmethane diisocyanate (MDI) and polyether polyol formulated to result in an isocyanate group (NCO) content of 31 %. In the case of hot-platen heating, water was added to the IC resin compound at 50% of the weight of resin. Ammonium chloride, as a catalyst, was added to UF resin at 1% based on solid resin weight.

2.2. Curing Methods

2.2.1. Steam-injection heating A specially-designed experimental apparatus used in this study is shown in Figure 1[11]. Each adhesive was weighed and contained in a poly(tetrafluoroethylene) film bag. The amount of resin was 0.1–2.5 g. The procedure followed the suggestion of Subiyanto *et al.*[11] That is to say, the poly(tetrafluoroethylene) film bag was tied loosely with thread immediately before putting it in the reaction cell so as to prevent the condensed water from penetrating

TABLE I
Properties of resins

Properties Resin	Specific gravity at 25°C	Viscosity at 25° C (poise)	pH	Resin content (%)
PF	1.177	0.88	10.5	45.9
UF	1.180	0.50	7.0	49.0
MF	1.186	0.70	9.0	53.8
IC	1.236	1.68	—	100.0

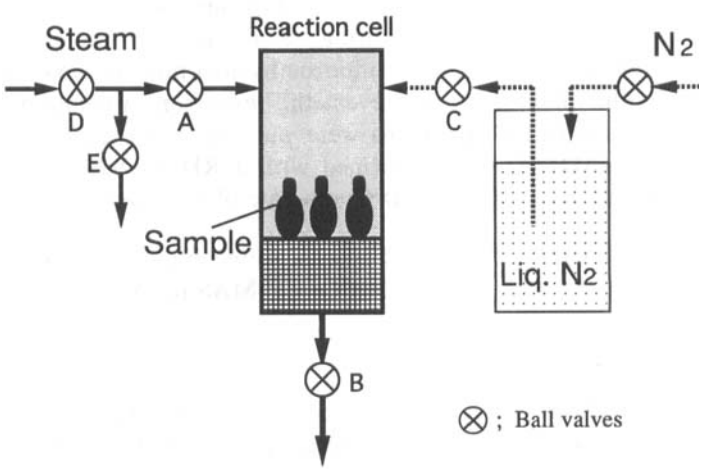


FIGURE 1 Apparatus for measurement of adhesives heated under high steam-pressure.

and also to prevent the bag from bursting from adhesive reaction or boiling. The temperature inside the reaction cell was recorded at certain time intervals. After a few seconds of warming, condensed water was drained in the steam line by opening the ball-valves D and E. Vavle E was then closed and high pressure steam was injected into the reaction cell by opening valve A. The target heating temperature was achieved by controlling the steam pressure from a steam generator. The heating temperature (steam pressure) was 160°C (6 kgf/cm^2) with steam-injection times from 10 sec to 60 min. After the steam was injected for the scheduled time, valve A was closed and valve B was opened to reduce the steam pressure for a few seconds followed immediately by opening valve C to inject liquid nitrogen (Liq.N_2) into the reaction cell until the adhesives were frozen. Frozen samples were taken out and kept in a freezer at -20 °C until analysis was done.

2.2.2. Hot-platen heating About 0.1–2.0 g of resin was placed between the platens (about 2.5 mm opening between upper and lower platen) and then heated at 160°C with heating times from 10 sec to 60 min. After the sample was heated for the scheduled time, it was dipped in liquid nitrogen and frozen to stop the reaction. After preparation, all the samples obtained also were kept in a freezer at -20 °C until analysis was done.

2.3. Analytical Methods

Frozen samples were vacuum-dried and ground to a powder before analysis.

2.3.1. Infrared spectral analysis The infrared absorbance spectra were obtained on a Nihon Bunko FT/IR-7000 using the KBr pellet technique. To observe the reaction quantitatively, the intensity ratio method was used for each obtained spectrum.

2.3.2. Dynamic mechanical analysis The specimens for dynamic mechanical analysis were prepared by soaking a strip (70 × 8 × 0.75 mm) of glass fiber filter in resin solution before each heat treatment. During steam-injection heating, the specimens were interposed between two poly(tetrafluoroethylene) films to hold, and were inserted into a thimble filter so as to prevent the resin from washing-out. Then, the thimble filter containing the specimens were put into the reaction cell. Dynamic mechanical analysis (DMA) was performed with a RHEO VIBRON DDV-25FP instrument, scanning from 20°C to 220°C at a rate of 3 °C/min and 10 Hz.

2.3.3. ^{13}C CP/MAS NMR ^{13}C NMR spectra were obtained at 50.3 MHz with a Varian XL-200 spectrometer equipped with a CP-MAS probe made by Doty Scientific Inc.

2.3.4. Solvent extraction In the case of the PF resin, the heat treated and pulverized dry resins (2.5 g) were extracted for 24 hr with methanol in a Soxhlet extractor. Thus, the amount of extracted resin was determined and the percentage residue was calculated.

3. RESULTS AND DISCUSSION

3.1. PF Resin

Generally, the cure of phenolic resoles involves substitution reactions of the methylol reactive group on a reactive site of an aromatic ring, yielding a methylene linkage between two aromatic rings, and/or a substitution reaction by a methylol reactive group on another methylol hydroxyl group to yield a methylene ether linkage. At temperatures above 140°C, methylene ether linkages can lose formaldehyde and convert to methylene linkages[12]. Furthermore, a carbonyl group is formed mainly through the oxidation of the methylene group. Therefore, the IR absorption bands of resins treated by hot-platen heating and steam-injection heating were observed. According to previous work[7], the absorbance ratio of the absorption bands at 1650 cm^{-1} (oxidation of methylene), 1050 cm^{-1} (dimethylene ether) and 1015 cm^{-1} (methylol) against that at 1610 cm^{-1} (benzene ring) were calculated. These results, plotted against the heating time, are shown in Figure 2. With hot-platen heating (a), 1650 cm^{-1}/1610 cm^{-1} gradually increased as the heating time increased while 1015 cm^{-1}/1610 cm^{-1} rapidly decreased for 3 min and then gradually decreased. 1050 cm^{-1}/1610 cm^{-1} slightly decreased over the whole heating time. With steam-injection heating (b), 1650 cm^{-1}/1610 cm^{-1} gradually increased and reached a constant value within 20 min, while 1015 cm^{-1}/1610 cm^{-1} decreased rapidly in the early stage (to 3 min), then maintained a constant value. 1050 cm^{-1}/1610 cm^{-1} also

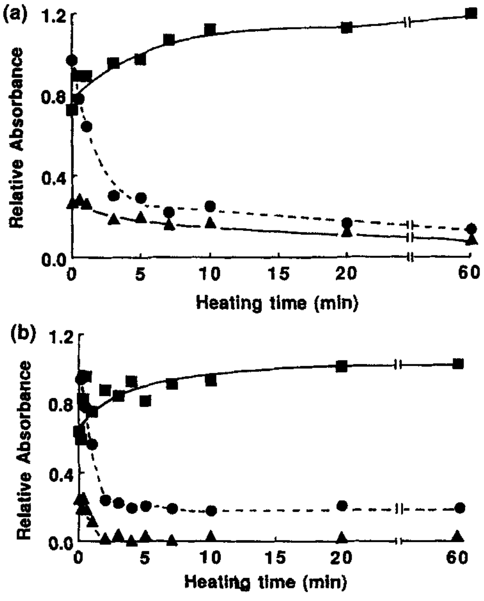


FIGURE 2 Infrared changes of PF resin during hot-platen heating (a) and steam-injection heating (b) at 160° C. Legend :■ ; 1650 cm^{-1}/1610 cm^{-1} (oxidation of methylene): ▲; 1050 cm^{-1}/1610 cm^{-1} (dimethylene ether): ● ; 1050 cm^{-1}/1610 cm^{-1} (methylol):

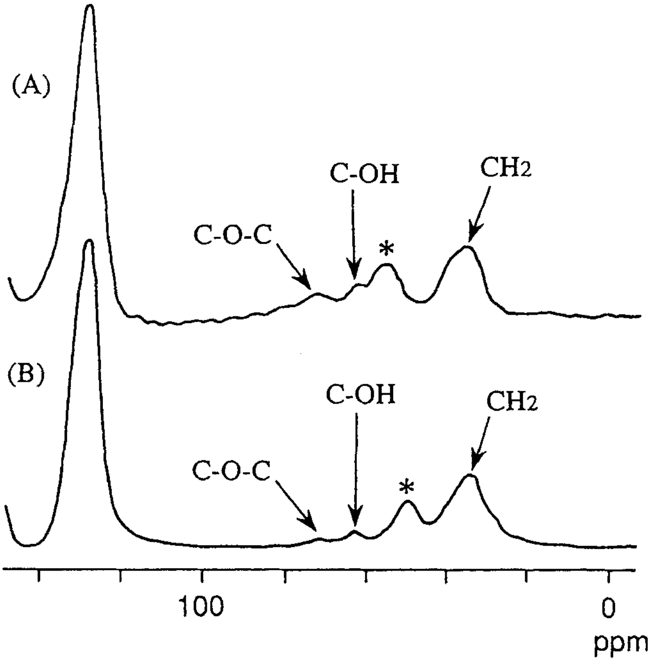


FIGURE 3 CP/MAS NMR spectra of heated PF resins. (A) Hot-platen heating at 160°C for 20 min. (B) Steam-injection heating at 160°C for 20 min. Asterisks indicate position of spining sidebands.

rapidly decreased, and finally almost reached a value of 0. Concerning the disappearance of dimethylene ether, ^{13}C NMR spectra were measured after heating each sample. Figure 3 illustrates the solid state ^{13}C NMR spectra of the PF resin hot-platen heated (A) and steam-injection heated (B) for 20 min. The structural assignments were derived from the literature[13]. In hot-platen heated PF resin (A), around 62 ppm of methylol and around 73 ppm of ether linkage were observed distinctly. In steam-injection heated PF resin (B), these peaks were of very weak intensity compared with the hot-platen heated. Especially, the peak of the ether linkage was rarely detected. This agreed with the IR data in Figure 2. That is to say, the reaction mechanism of PF resin under steam-injection heating at 160°C seems to be accompanied by the disappearance of the ether linkage.

Figure 4 shows the result of extraction tests with methanol on PF resins that were cured by hot-platen heating and steam-injection heating. For PF resin hot-platen heated, the methanol insoluble matter gradually increased for 2 min and soon reached almost 100 %, while in the resin heated by steam-injection it rapidly increased for 1 min and then stayed at approximately 95 %. These results suggest that in steam-injection heating, PF resin reacts much more quickly to grow to methanol-insoluble matter than in hot-platen heating, but a small quantity of methanol-soluble matter remains.

Figure 5 shows the changes in dynamic storage modulus (E') of PF resin samples during an oven temperature scan up to 220°C, after preheating consisting of 20 min

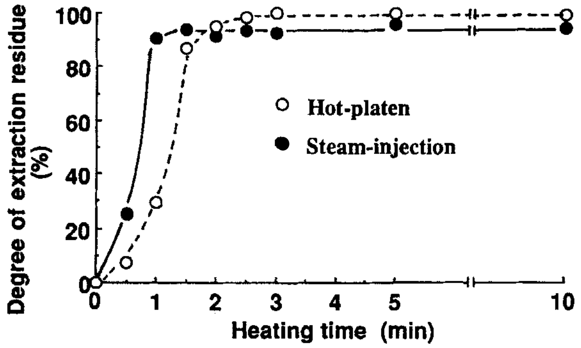


FIGURE 4 Percent extraction residue of PF resin during hot-platen heating and steam-injection heating at 160°C. Note : Solvent was methanol.

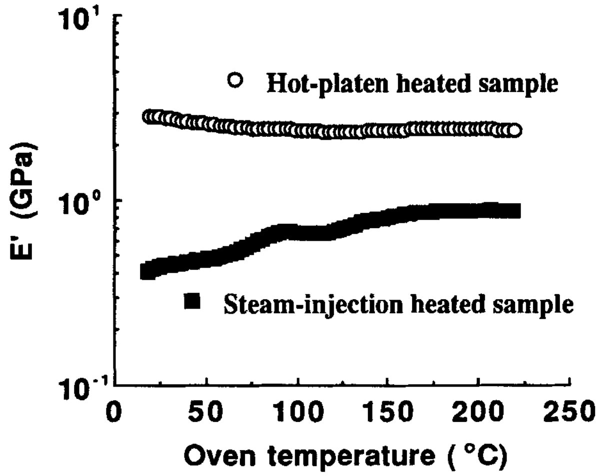
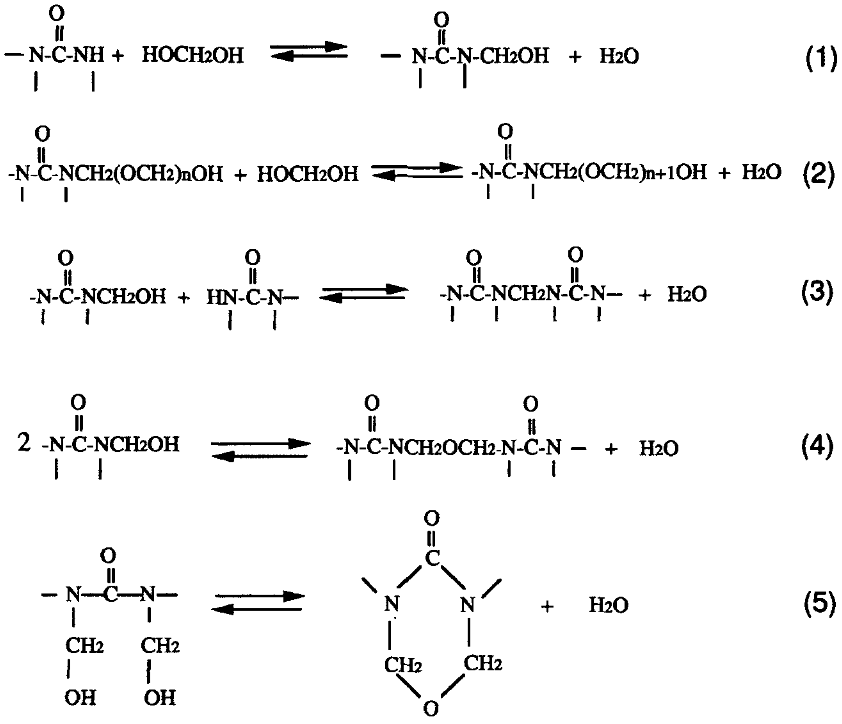


FIGURE 5 Dynamic storage modulus during scan at 3°C/min and 10 Hz for PF resins impregnated in glass filter after exposure to 160°C for 5 min in hot-platen and steam-injection.

at 160°C under hot-platen and steam-injection. For the hot-platen heated sample, an initial decrease was observed as the effect of thermal softening, and then the modulus reaches a plateau. This revealed that the PF resin had fully cured under this preheating condition before DMA measurement. For the steam-injection heated sample, *E′* gradually increased in the lower oven temperature range (20–100°C). This behavior seemed to be influenced by the evaporation of water that was contained in the resin and/or was foamed by the curing reaction of resin. Between 100 and 120°C, *E′* remained constant. Above 120°C, *E′* increased after curing, followed by constant values. It seems that PF resin did not cure completely in this preheating condition. It can be summarized that under steam-injection heating, PF resin immediately cured to some degree in the early stage for high. Pressure steam, accompanied by the disappearance of the ether structure, and soon become equilibrated.

3.2. UF Resin

As shown Scheme 1, the functionality of a UF polymer is believed to occur *via* some combination of the reactions. The reaction products between urea and formaldehyde can range from the simple one, mono methylolurea, $H_2NC(O)NHCH_2OH$, to a very complicated, widely crosslinked, three-dimensional product. Due to the complexity of the structure of UF resin and the presence of many components, the structure is still ambiguous. However, Myers tried to observe the changing of functional groups during cure using an IR technique[14]. So, using this technique, some of the infrared spectra were quantified on the same relative basis by normalizing the measured absorbances to that of the carbonyl ($1650\,cm^{-1}$) in each spectrum. Figure 6 shows the plot of changes in some of these absorbance against heating time on hot-platen heated (a) steam-injection heated (b) UF resins. These absorption bands are assigned as follows:[14–16] $1650\,cm^{-1}$ for carbonyl; $1540–1560\,cm^{-1}$ for secondary, linear amide; $1500–1520\,cm^{-1}$ for linear or cyclic tertiary amide; $1290–1300\,cm^{-1}$ for OH



SCHEME 1 Urea-formaldehyde polymerization and curing reaction.

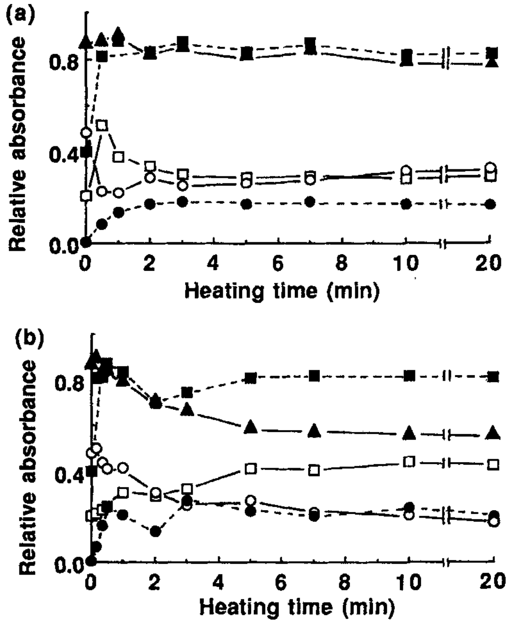


FIGURE 6 Infrared changes of UF resin during hot-platen heating (a) and steam-injection heating (b) at 160°C.Legend : ▲ 1540–1560 cm^{-1}; ■ 1500–1520 cm^{-1};□ 1290–1300 cm^{-1}; ○ 1020–1025 cm^{-1} ● 810 cm^{-1}.

and/or tertiary cyclic amide; 1020–1025 cm^{-1} for CH_2OH; 810 cm^{-1} for uronic ring. With hot-platen heating (a), 1540–1560 cm^{-1} slightly decreased, while 1500–1520 cm^{-1} rapidly increased immediately after heating and soon reached a constant value. 1290–1300 cm^{-1} rapidly increased and reached the maximum in 30 sec, followed by a gentle decrease. 1020–1025 cm^{-1} rapidly decreased for 30 sec and then slightly increased. 810 cm^{-1} began to appear immediately after heating and soon maintained a constant value. These behaviors were similar to those in Myers' report[14]. That is, during hot-platen heating of UF resin, tertiary amide may grow rapidly accompanied by the consumption of hydroxyl group and form a uronic ring. These changes are accounted for by processes such as reactions (3)–(5) (Scheme 1) in the forward direction[16]. With steam injection heating (b), 1540–1560 cm^{-1} slowly decreased, while 1500–1520 cm^{-1} rapidly increased immediately after heating, and slightly decreased for 2 min, then gradually increased. 1290–1300 cm^{-1} continuously increased, and 1020–1025 cm^{-1} gradually decreased. 810 cm^{-1} rapidly increased for 30 sec, and slightly decreased for 2 min, then somewhat increased.

In steam-injection heating of UF resin, the curing reaction seemed to occur rapidly immediately after heating, and the products cure to some degree because of high pressure steam. The reactions will be accounted for by processes such as reactions (3)–(5) (Scheme 1) in the forward direction[16]. After that, the UF resin may be partly subjected to hydrolysis as a by- product of the condensation reaction and condensed water from the steam under high pressure. In general, during hydrolysis reaction (1) and (2) will occur in the reverse direction, and they will be accompanied by the reverse of (3) and (4), succeeded by the loss of methylol as in (1) and (2)[16]. So, we supposed that the secondary amide will be formed by hydrolysis of tertiary amide, and cyclic tertiary amide may be formed by polymerization of secondary amide. The possible relative increase in the uronic ring during steam-injection heating indicates that the cyclic ether is a relatively stable entity.

Figure 7 illustrates the dynamic storage modulus (*E*′) of UF resin samples after exposure to 160°C at various heating times in the hot-platen mode. For these samples, the initial (20°C) *E*′ generally increased as the pre-heating time became longer in the hot-platen mode. In the sample of UF resin preheated for 30 sec, as the oven temperature increased, the sample softened somewhat, as shown by the drop in *E*′. Following this, further polymerization and crosslinking presumably occurred, whereby *E*′ eventually rose to a "plateau" value higher than the value at initial oven temperature. As the sample of UF resin preheated for 3 min has already fully cured, the *E*′ of sample maintained almost a constant value during DMA measurement. The results of the DMA measurement for the steam-injection-heated sample are shown in Figure 8. For the UF resin sample preheated for 30 sec, the modulus behavior was similar to that of the hot-platen-heated sample preheated for 30 sec. This revealed that the preheated sample under this condition has some degree of cure. Actually, this sample was somewhat rigid before measurement by DMA. However, in the sample of UF resin preheated for 3 min, the initial (20°C) *E*′ has a very low value compared with the sample preheated for 30 sec. The modulus curve of this sample during DMA measurement is similar to the non-heated (0 min) sample in Figure 7. In fact, the sample before DMA measurement was very soft and wet. Consequently, as the steam-injection time was increased, the UF resin returned to its liquid state. It can be supposed that the presence of excessive water under high steam pressure caused the acceleration of hydrolysis at 160°C.

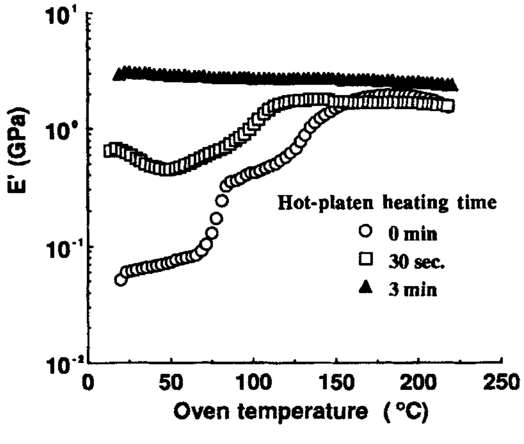


FIGURE 7 Dynamic storage modulus for UF resins after exposure to 160°C at various heating time in hot-platen.

3.3. MF Resin

The MF resin chemistry involves the same reaction of formaldehyde with amine groups to form methylene groups, which then condensed to methylene bridges as with urea. However, it is postulated that melamine imparts greater stability to the resulting linkages. The absorbance ratios of the absorption band at 1010 cm^{-1} (methylol) against that at 810 cm^{-1} (triazine ring) during hot-platen heating and steam-injection heating of MF resins were measured. The results are shown in Figure 9. With hot-platen heating, 1010 cm^{-1}/810 cm^{-1} slowly decreased for the 30 min of measurement. On the other hand, with steam-injection heating, it rapidly decreased in the early stage (to 7 min) and soon became constant. We noticed that the resin obtained by steam-injection heating for 5 min was a clear and rigid solid. Generally, MF resin has a structure of the triazine ring that is very stable and the three amine groups assure a three-dimensional cross-linked molecular structure when cured. Fully cured MF resin is very hard, and it is durable against heat and moisture. It is also colorless, being clear as glass. Thus, it seems that the MF resin almost fully cured under high steam pressure in a short heating time at 160°C without hydrolysis.

3.4. IC Resin

Isocyanate adhesives are based on the high reactivity of the isocyanate radical, —N=C=O. Coupled with strong polarity, compounds that carry this radical do not only have good adhesion potential, but also the potential for forming covalent bonds with substrates that have reactive hydrogens. Figure 10 shows the infrared spectral changes resulting from hot-platen heating (a) and steam-injection heating (b). These spectra were measured after heating the sample at 160°C for 30 sec, 3 and 5 min, respectively. With steam-injection heating, as the resin was heated, the inten-

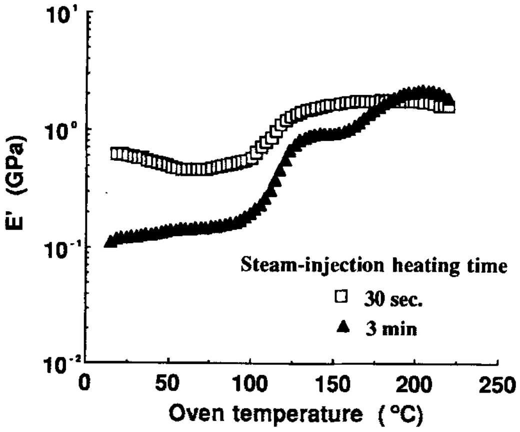


FIGURE 8 Dynamic storage modulus for UF resin after exposure to 160°C for 30 sec. and 3 min by steam-injection.

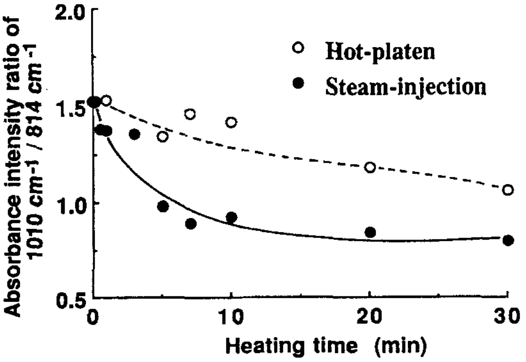


FIGURE 9 Infrared changes of MF resin during hot-platen heating and steam-injection heating at 160°C.

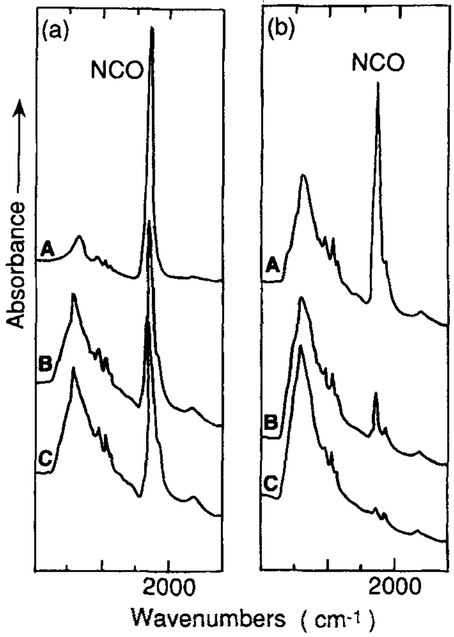


FIGURE 10 Infrared spectra of IC resin during hot-platen heating (a) and steam-injection heating (b) at 160°C. (A) 30 sec. (B) 3 min (C) 5 min.

sity of the band due to NCO streching at about 2278 cm^{-1} decreased considerably and 5 min later, this band had almost disappeared. On the other hand, with hot-platen heating, it was observed to be considerably in evidence even 5 min later. In accordance with a previous work[17], the absorbance at 2278 cm^{-1} (NCO) relative to that at 1610 cm^{-1} (benzene ring) was plotted as a function of heating time under hot-platen and steam-injection. The results are shown in Figure 11. For the steam injection heated resin, the ratio quickly reached a value of 0 within 2 min, whereas,

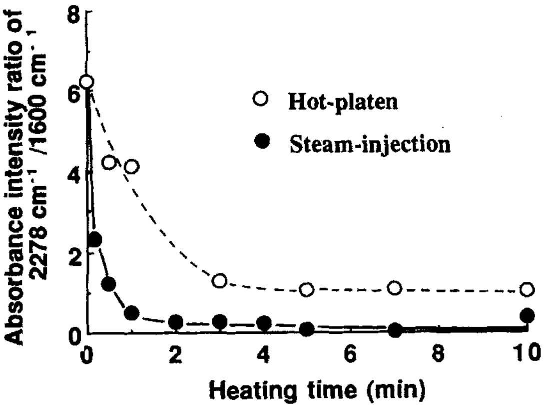


FIGURE 11 Infrared changes of IC resin during hot-platen heating and steam-injection heating at 160°C.

for hot-platen-heated resin, the ratio gradually decreased as the heating time was increased. However, the ratio did not reach a value of 0. This is natural for steam-injection heating because of the excessive moisture that reacted with the IC resin present in the reaction system under high steam pressure. Isocyanates can react with moisture, forming amines, which then can react with themselves to grow and cross-link, becoming thus a one-part adhesive system. So, the IC resin foamed and cured homogeneously in a short heating time under steam-injection heating. In the case of hot-platen heating, it seemed that the reaction of resin and water was heterogeneous although water was added to the resin at 50% by weight of resin before heating. Therefore, for IC resin, steam-injection heating is more effective than conventional hot-platen heating.

4. CONCLUSION

The curing behavior of wood adhesives under high steam pressure using an especially designed reaction cell was discussed. PF, UF, MF, IC resins were used as representatives of wood adhesives in this study. At different curing times, the heating temperature (steam pressure) applied to cure the adhesives were 160°C (6 kgf/cm^2). We characterized the curing behavior of each adhesive, using techniques as FT-IR, NMR, DMA, and solvent extraction. For each adhesive used, the comparison between hot-platen heating and steam-injection heating was also done. The results and conclusion are summarized as follows.

1. By steam-injection heating, PF resin immediately cured to some degree in a few minutes compared with hot-platen heating and, after that, it maintained a constant value. This heated PF resin contained methanol-soluble matter regardless of heating time. It was proved that PF resin did not cure completely and maintained an equilibrium situation under steam-injection heating. The reaction

of PF resin under steam-injection heating was accompanied by the disappearance of the ether structure.

2. UF resin immediately cured to some degree after steam-injection heating. After that, UF resin returned back to the gel and/or liquid state. Results from IR data indicated that secondary amide may have been formed from tertiary amide by hydrolysis and, furthermore, the secondary amide would form a cyclic tertiary amide by polymerization of the secondary amide, and cyclic ether as a uronic ring formed during steam-injection heating was not subject to hydrolysis because it was a relatively stable entity.
3. IR data show that MF resin cured almost completely under steam-injection in a short heating time almost without hydrolysis, because MF resin has a triazine ring structure that is very stable and the three amine groups assure a three-dimensional, cross-linked molecular structure when cured.
4. IC resin rapidly and fully cured under steam-injection. It seemed that excess moisture to react with IC resin was present and a homogeneous reaction occurred under steam-injection. On the other hand, in hot-platen heating, IC resin did not cure completely, becuase it was probably a heterogeneous reaction. So for IC resin, steam-injection heating is more effective than hot-platen heating.

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