

Kenji Umemura · Akihiro Takahashi · Shuichi Kawai

Durability of isocyanate resin adhesives for wood IV: degradation under constant steam heating

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Abstract The durability of isocyanate resins consisting of emulsion-type polymeric diphenylmethane diisocyanate (EMDI) was investigated under constant steam heating. Two kinds of resin, water only-added resin and polyol/water-added resin, were used in this study. The degradation of the resins under steam heating was observed using Fourier transform infrared spectroscopy (FT-IR), weight changes, and thermogravimetric analysis (TGA). FT-IR analysis showed that the degradation reaction of the resins scarcely proceeded for a few hours and then increased significantly. The weights of the resins decreased linearly during steam heating. The thermal stability of steam-treated resins was made clear by TGA. The bond strength reductions of the specimens bonded with the resins were also observed. The best fitting regression function for the behavior of bond strength reduction was determined statistically. The apparent activation energy of each resin was calculated from the regression function, for the half-life period. Considering the calculated values, the adhesion durability of using polyol-added resin was superior to that of using water only-added resin. It was clarified that the durability of the isocyanate resins under steam heating was markedly inferior to that under dry heating.

Key words Isocyanate adhesives · Durability · Bond strength · Steam heating · Wood adhesives

K. Umemura (✉)
Forestry and Forest Products Research Institute, PO Box 16,
Tsukuba Norin Kenkyu Danchi-nai, Ibaraki 305-8687, Japan
Tel. +81-298-73-3211 (ext. 532); Fax +81-298-73-3797
e-mail: kumemura@ffpri.affrc.go.jp

A. Takahashi
Mitsui Takeda Chemicals, Tokyo 100-6009, Japan

S. Kawai
Wood Research Institute, Kyoto University, Kyoto 611-0011, Japan

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Introduction

As non-formaldehyde-based wood adhesives, isocyanate resins consisting of polymeric diphenylmethane diisocyanate (PMDI) have received much attention, but only limited research has been reported on the durability of PMDI.¹ In a previous paper,² the durability of emulsion-type PMDI (EMDI) was studied under constant dry heat. The degradation behavior and adhesion durability of EMDI were determined at temperatures above 100°C.

The durability of adhesive-bonded wood composites is greatly affected by the durability of the adhesives used. A number of studies have been conducted on the durability of conventional adhesives.³⁻⁵ In particular, heat and moisture have been thought to be important degradation factors concerning the durability of wood adhesives.⁶⁻¹⁰ In many cases, durability tests with heating have been performed at temperatures above 100°C, whereas tests for moisture have been thought at temperatures below 100°C. Therefore, it is difficult to investigate the interaction of these degradation factors. To resolve this problem, the use of high-pressure steam was adopted. It was then possible to investigate the effect of moisture at temperatures above 100°C.

In this study the durability of two kinds of resin, water only-added EMDI and polyol/water-added EMDI, was studied under constant steam heating. The degradation properties of the resins were investigated using Fourier transform infrared spectroscopy (FT-IR), weight changes, and thermogravimetric analysis (TGA). The adhesion durability of the resins was also clarified.

Materials and methods

Materials

The EMDI and propylene oxide-based polyether polyol used in this study were supplied by Mitsui Takeda Chemicals (Tokyo, Japan). The EMDI and polyol are now distrib-

Table 1. Preparation of resins

Resin	E-MDI (g)	Polyol (g)	Water (g)	NCO/polyol-OH	Total NCO/OH
ICW	100	0	12.63	–	0.5
ICWD4d	100	5.61	12.38	25	0.5

ICW, control isocyanate resin; ICWD4d, polyol-added isocyanate resin; E-MDI, emulsion-type polymeric diphenylmethane diisocyanate

uted under the commercial name Cosmonate M-201W and Diol-400, respectively. The properties of the materials were the same as described in previous papers.^{11,12} To cure the EMDI, the polyol was added at an NCO/polyol-OH ratio of 25, and water was added to obtain a final NCO/OH ratio of 0.5. For the control, only water was added at an NCO/OH ratio of 0.5. The details of the formulations of the resins are shown in Table 1. The mixtures were blended by vigorous stirring. As in previous studies,^{2,13} the control and polyol-added resins were represented by the abbreviations ICW and ICWD4d, respectively. The resol phenol-formaldehyde resin (PF) used in this study was obtained from the same company. The properties of PF were described in previous papers.¹¹ The isocyanate resins (ICW and ICWD4d) and PF were cured at 40°C for 24 h and at 160°C for 50 min, respectively, in an oven. The cured resins were ground to powder (less than 100 mesh) and vacuum-dried.

Steam heating for cured isocyanate resins

The steam heating was performed using a specially designed reaction cell.¹⁴ Cured resin 3.0 g was placed in an extraction thimble, which was placed in a reaction cell. The detailed operation of the reaction cell was described in a previous paper.¹⁴ The steam heating was conducted at 160°C (0.63 MPa). After steam heating, the extraction thimble was removed from the reaction cell quickly and was cooled using liquid nitrogen. The cooled resin was lyophilized and kept in a desiccator. The amount of residue was determined, and the weight loss was calculated. For comparison purposes, the ICWD4d samples were subjected to constant dry heating at 160°C in an oven.

Fourier transform infrared spectroscopy

All infrared spectra of the treated resins were obtained with an FT-IR 7000 spectrometer (JASCO) using the KBr pellet method; and were each recorded as an average of 16 scans at a resolution of 4 cm⁻¹. The isocyanate and carbonyl groups of the resins were observed using absorption peaks at 2274 and 1670 cm⁻¹, respectively. The height of the peak [H(2274)] was calculated with respect to a baseline drawn between the points at 2400 and 1800 cm⁻¹. The height of the peak [H(1670)] was calculated with respect to a baseline drawn between the points at 1820 and 1570 cm⁻¹. The C=C absorption peak of the aromatic ring at 1599 cm⁻¹ was used as a reference.¹⁵ The height of this peak [H(1599)] was also calculated with respect to a baseline drawn between the points at 1820 and 1570 cm⁻¹. The absorption intensity

ratios of the isocyanate and carbonyl groups of treated resins were obtained.

Thermogravimetric analysis

The TGA was carried out using a TGA 2050 (TA Instruments Japan). The treated resin (10–15 mg) was scanned from room temperature to 700°C at a rate of 6°C/min in air and nitrogen purging of 70 ml/min.

Preparation of bond strength test specimen

Two-ply parallel veneer-laminated specimens (5 × 16 cm) were prepared using lauan (*Shorea* spp.) veneer of 5 mm thickness. The average air-dried density and moisture content of the veneer were 0.62 g/cm³ and 11.2%, respectively. EMDI and polyol, as well as water, blended under the same conditions as described above, were used as the isocyanate resin adhesives. The amount of isocyanate resins (ICW and ICWD4d) and PF applied to the veneer were 200 and 300 g/m², respectively. In the case of PF, oven-dried veneers were used and an open time of 10 min was adopted. The assembled veneers were hot-pressed for 10 min under a pressure of 1.08 MPa at 160°C. They were held for another 2 min before they were removed from the press. The specimens for tensile shear test were prepared according to the Japanese Industrial Standard (JIS) K6851.

Steam heating for bond strength test specimens

The steam heating was performed using a steam injection press. Aluminum frame packing was placed around the press platen to prevent steam from escaping during the steam injection heating. The specimens bonded with isocyanate resins were inserted into the press, and the steam heating was conducted at 120°, 140°, 160°, and 180°C (0.2–1.0 MPa). For the specimen using PF, steam heating was conducted at only 160°C (0.63 MPa).

Bond strength measurement

The tensile shear bond strength of the steam-treated specimens was measured under a crosshead speed of 2 mm/min. The relative bond strength reduction (r-bond strength) was calculated from the following equation;

$$\text{r-bond strength (\%)} = [(s_0 - s)/s_0] \times 100 \quad (1)$$

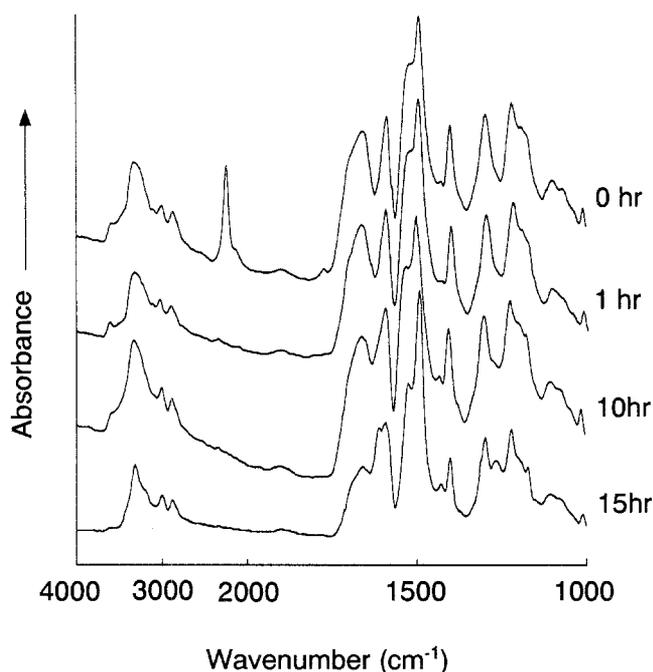


Fig. 1. Infrared changes of polyol-added isocyanate resin (ICWD4d) under steam heating at 160°C

where s is the bond strength of the specimen at arbitrary steam heating time; and s_0 is the bond strength of the untreated specimen. Three test specimens were used for each condition, and the average value was calculated. The regression analyses were performed with commercially available statistical software (StatView Version 5.0).

Results and discussion

Change of chemical structure under steam heating

Figure 1 shows the infrared spectral changes of ICWD4d under steam heating at 160°C. The infrared spectrum of untreated resin (0h) recorded a strong peak at 2274 cm⁻¹, showing that the resin contains a considerable amount of unreacted isocyanate groups. In addition, the absorption bands at 3360 cm⁻¹ attributed to N—H stretching vibration and at 1670 cm⁻¹ attributed to C=O stretching vibration¹² were clearly identified. These spectra are ascribed to urea linkage arising from the reaction between isocyanate and water. The isocyanate absorption band at 2274 cm⁻¹ was not observed at 1h. The intensity of the band detected at 1670 cm⁻¹ decreased with increasing heating time. The absorption peaks at 1624 and 1274 cm⁻¹ appeared at 15h. In this study, the resins form a urea crosslinked network to react with water. Generally, amide-type linkages between nitrogen atoms and carbon of carbonyl groups would be cleaved in the presence of water. The cleavage leads to the formation of amino and carboxyl groups, and the latter is rather unstable when attached to a nitrogen atom. This unstable carbamic acid decomposes to

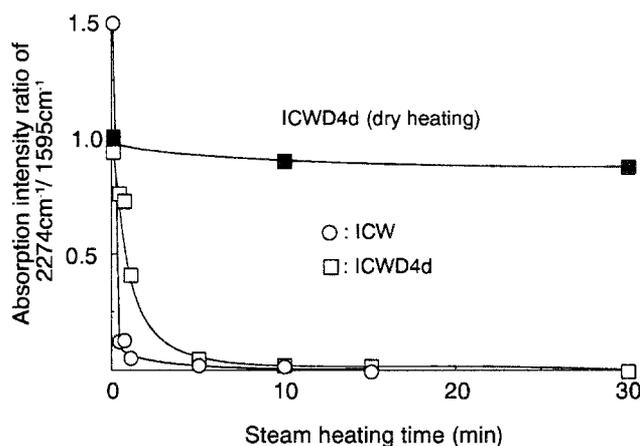
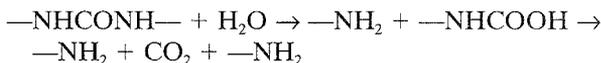


Fig. 2. Changes in unreacted isocyanate groups of control isocyanate resin (ICW) and ICWD4d under steam heating at 160°C

amine and CO₂, a hydrolysis reaction that can be described as follows.



Kresta et al.¹⁶ studied the decrosslinking of polyurea-urethane reaction injection molding using transesterification with low-molecular-weight diol. They confirmed the absorption peaks at 1624 and 1276 cm⁻¹ could be attributed to amine, which was formed by cleavage of urea groups. Therefore, the absorption peaks at 1624 and 1274 cm⁻¹ seemed to be attributed to N—H bending and stretching vibrations arising from the formation of amine, respectively. In ICW, those absorption peaks were also observed at 15h. To observe the degradation behavior of the resins quantitatively, the absorption intensity ratios of isocyanate and carbonyl groups were plotted against the steam heating time.

Figure 2 shows the changes of unreacted isocyanate groups of ICW and ICWD4d. The value for untreated ICWD4d was less than that for untreated ICW, indicating that the unreacted isocyanate group content in ICWD4d was low compared to the content in ICW. This means that the reactivity of the isocyanate group was enhanced by the addition of polyol.¹³ When heating was performed, the relative amounts of the isocyanate groups in both ICW and ICWD4d decreased rapidly, then reached a value of 0 within a short time. On the other hand, the value for ICWD4d under dry heating at 160°C scarcely decreased during this period. It was found that after-cure based on the isocyanate group took place rapidly in the presence of moisture.

Figure 3 shows the changes in the carbonyl groups of ICW and ICWD4d. The value for untreated ICWD4d was higher than that for untreated ICW, indicating that ICWD4d contained a larger number of carbonyl groups than did ICW. The relative number of carbonyl groups in ICW increased just after heating and then decreased slightly for a short time, suggesting that urea linkage arising from the reaction between isocyanate and moisture increased

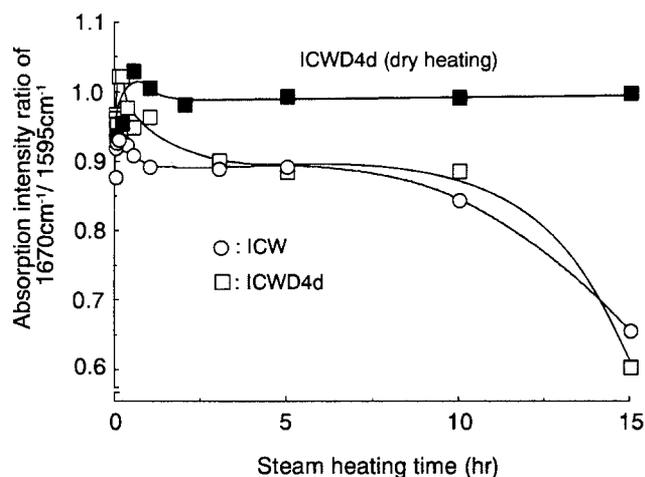


Fig. 3. Changes in carbonyl groups of ICW and ICWD4d under steam heating at 160°C

rapidly and then decreased slightly. After that, the value remained constant for 5 h and then decreased gradually. The degradation reaction scarcely proceeded up to 5 h (the value was nearly equal to that of untreated resin). When the heating time is prolonged further, a marked degradation reaction was believed to take place. In ICWD4d, the value increased rapidly just after heating, then decreased by 90% compared with that of untreated resin. This indicates that degradation occurs to some degree. After that, there was no remarked change for a few hours, indicating that the degradation reaction scarcely proceeded. However, at a later time, the reaction seemed to increase significantly. The behavior exhibited from 5 to 15 h was similar to that of ICW. The carbonyl group of ICWD4d under dry heating increased just after heating and then maintained a constant value over the entire heating time. Therefore, the resin would be much more subject to degradation under the wet condition than under the dry condition.

Weight change under steam heating

Figure 4 shows the weight changes of ICW and ICWD4d under steam heating at 160°C. There was little weight loss of ICW at the beginning of heating. After that, however, the weight decreased markedly up to 5 h and then decreased linearly. The weight of ICWD4d decreased linearly over the entire heating time. The proportion of weight loss from 5 to 15 h was similar to that of ICW. Considering the results shown in Fig. 3, resin degradation is not likely to be the main cause of the continuous weight loss. For example, the absorption intensity ratio of the carbonyl groups in ICW indicated a constant value from 1 to 5 h. Nevertheless, a marked weight loss of ICW was observed. Judging from the above result, ICW and ICWD4d cured at 40°C for 24 h seemed to be susceptible to elution under steam heating at 160°C. Especially ICW was believed to contain a large steam-soluble fraction. The weight losses of ICW and ICWD4d at 15 h were 55% and 41%, respectively. In a previous paper,² the weight changes of the resins under dry

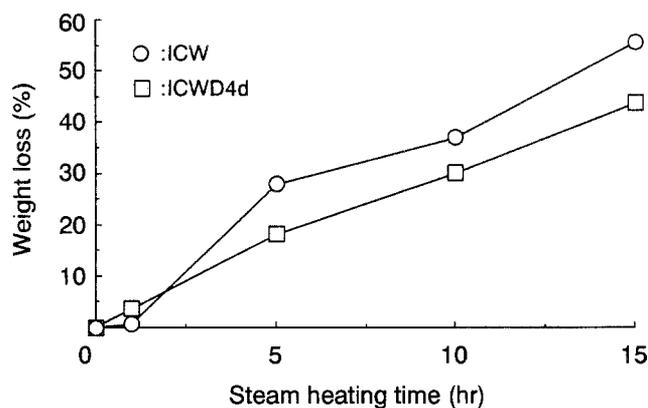


Fig. 4. Weight loss of ICW and ICWD4d under steam heating at 160°C

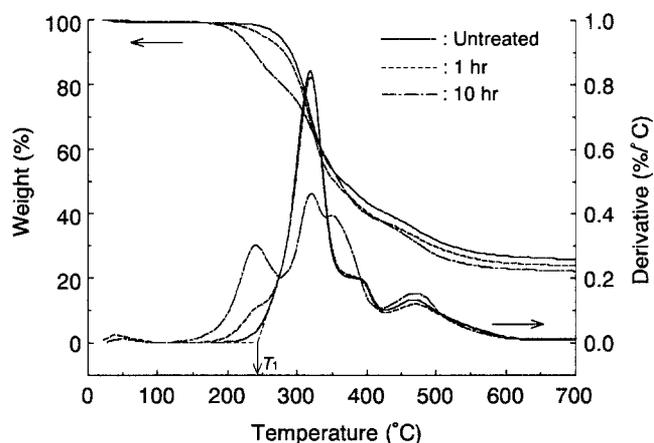


Fig. 5. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of steam-heated ICWD4d in a nitrogen atmosphere

heating at 160°C were studied using TGA. The times required to reach the 1% weight losses for ICW and ICWD4d were about 4 and 22 h, respectively. Consequently, it was found that the weight of the resins decreased markedly under steam heating compared to that under dry heating.

Thermal stability of steam-treated resins

Figure 5 shows the thermogravimetric (TG) and derivative TG (DTG) curves of steam-treated ICWD4d in a nitrogen atmosphere. The weight of untreated resin decreased significantly at temperatures above 250°C. One-step weight reduction was observed in the temperature range 200–400°C, as reflected in the DTG curve. In the case of resin steam-treated for 1 h, the weight reduction started at about 200°C, and a shoulder in DTG appeared at about 230°C. In resin steam-treated for 10 h, the weight reduction started below 200°C, and a peak in DTG was observed at about 230°C. Therefore, the thermal stability of ICWD4d was believed to decrease with increasing steam heating time.

To evaluate the thermal stability of steam-treated resins, the extrapolated onset temperature of weight reduction (T_1) derived from DTG was plotted against the steam heat-

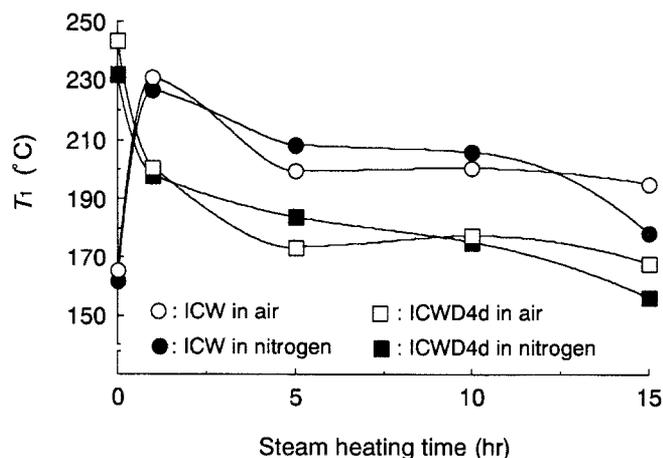


Fig. 6. Onset temperature (T_1) of the weight reduction of ICW and ICWD4d

ing time. In this study, the evaluation was based on TGA data derived from measurements in air and nitrogen atmospheres. The result is shown in Fig. 6. In the case of ICW in an air atmosphere, T_1 increased significantly for 1h, decreased slightly for 5h, and then maintained a constant value. In a nitrogen atmosphere, T_1 increased for 1h and then decreased gradually. The reason for the rise of T_1 at an early stage seems to be that the ICW underwent after-cure by steam heating and formed a stable structure. The reduction in T_1 would be due to degradation. On the other hand, the T_1 value of untreated ICWD4d was high compared to that of untreated ICW. This means that the thermal stability of untreated ICWD4d is superior to that of untreated ICW. The reason is that the curing reaction of resin proceeds smoothly when a small amount of the polyol is added.¹³ The T_1 of ICWD4d decreased for 5h in both atmospheres. After that, T_1 maintained a constant value in an air atmosphere and decreased gradually in a nitrogen atmosphere. The behavior of T_1 showed a trend similar to those of ICW from 1 to 15h. As a whole, however, the thermal stability of steam-treated ICWD4d was inferior to that of steam-treated ICW. Considering the changes in chemical structure shown in Figs. 2 and 3, the part played by after cure of ICW formed by steam heating is a contribution to good thermal stability. However, further investigation is necessary to confirm this hypothesis.

Adhesion durability

The relation between relative bond strength reduction and steam heating time was investigated. To analyze the results obtained, polynomial regression was performed as for the previous report.² In other words, first- and second-order polynomials of the following general equation were applied to the regression.

$$Y = \sum_{i=1}^n A_i X^i$$

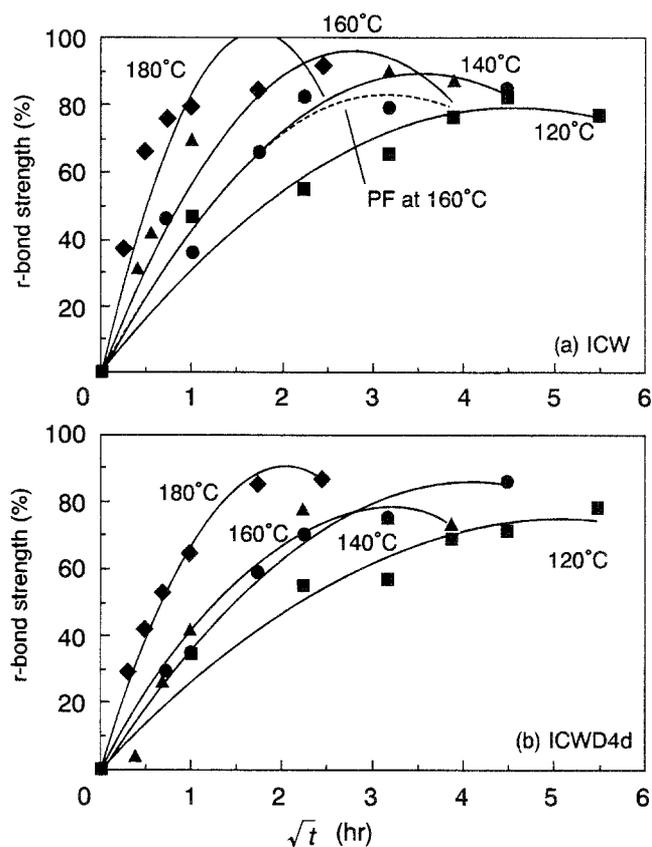


Fig. 7. Relative bond strength reduction (r -bond strength) of a ICW and b ICWD4d as a function of the steam-heating time at various temperatures

where Y is r -bond strength; X is steam heating time (t); A is a constant; and n is order (≤ 2).

As the fitting regression functions, expressions (a) to (h) listed in Table 2 were used. In expressions (a), (b), and (e), no intercept model was adopted. To determine the best fitting regression function, the coefficient of determination adjusted for the degrees of freedom (adjusted R^2) was calculated. The results are shown in Table 2. The values with underlines indicate the values above 0.960. Judging from the values obtained, the best-fit function was found to be the second order of expression (2). The r -bond strength were plotted against the square root of the heating time, as shown in Fig. 7. In a previous paper,² the bond strength reduction of the specimens bonded with the same resin was observed under dry heating at the same temperature range. The best-fit function was also the second order of expression (2). Therefore, the relation between relative bond strength reduction and heating time obeyed the same regression function, irrespective of whether moisture was present. Based on the regression curves, the adhesion durability of ICWD4d was somewhat superior to that of PF. The calculated half-lives for ICW, ICWD4d, and PF at 160°C were 0.71, 1.51, and 1.38h, respectively. The times required for each resin were markedly short compared to the time under dry heating.² This indicated that the adhesion durability under the wet condition was much lower than that under the dry condition. The changes in wood failure in the

Table 2. Adjusted R² from several regression curves

Y	X	n = 1										n = 2									
		120°C	140°C	160°C	180°C																
(a) r-Bond strength	t	0.765	0.807	0.691	0.607	0.725	0.637	0.497	0.497	0.905	0.914	0.842	0.894	0.905	0.780	0.833	0.842	0.842			
(b) r-Bond strength	√t	0.932	0.957	0.934	0.879	0.913	0.859	0.799	0.799	0.985	0.990	0.982	0.997	0.979	0.983	0.982	0.968	0.968			
(c) r-Bond strength	1/t	0.584	0.737	0.790	0.572	0.788	0.775	0.538	0.538	0.929	0.883	0.942	0.974	0.968	0.976	0.979	0.976	0.976			
(d) r-Bond strength	log t	0.866	0.959	0.974	0.774	0.916	0.893	0.908	0.908	0.851	0.959	0.710	0.971	0.957	0.926	0.879	0.956	0.975			
(e) (r-Bond strength) ²	t	0.855	0.918	0.841	0.711	0.841	0.749	0.616	0.616	0.973	0.972	0.920	0.969	0.961	0.903	0.896	0.577	0.974			
(f) 1/(r-Bond strength)	t	0.664	0.591	0.399	0.294	0.028	0.324	0.448	0.448	0.999	0.795	0.528	0.717	-	0.429	0.552	0.092	0.575			
(g) log (r-Bond strength)	log t	0.904	0.973	0.940	0.710	0.714	0.846	0.841	0.841	0.882	0.965	0.629	0.974	0.977	0.940	0.792	0.933	0.992			
(h) log (r-Bond strength)	t	0.690	0.710	0.515	0.364	0.245	0.412	0.216	0.216	0.996	0.861	0.622	0.797	0.320	0.568	0.677	0.226	0.775			

Underlined values are higher than 0.950

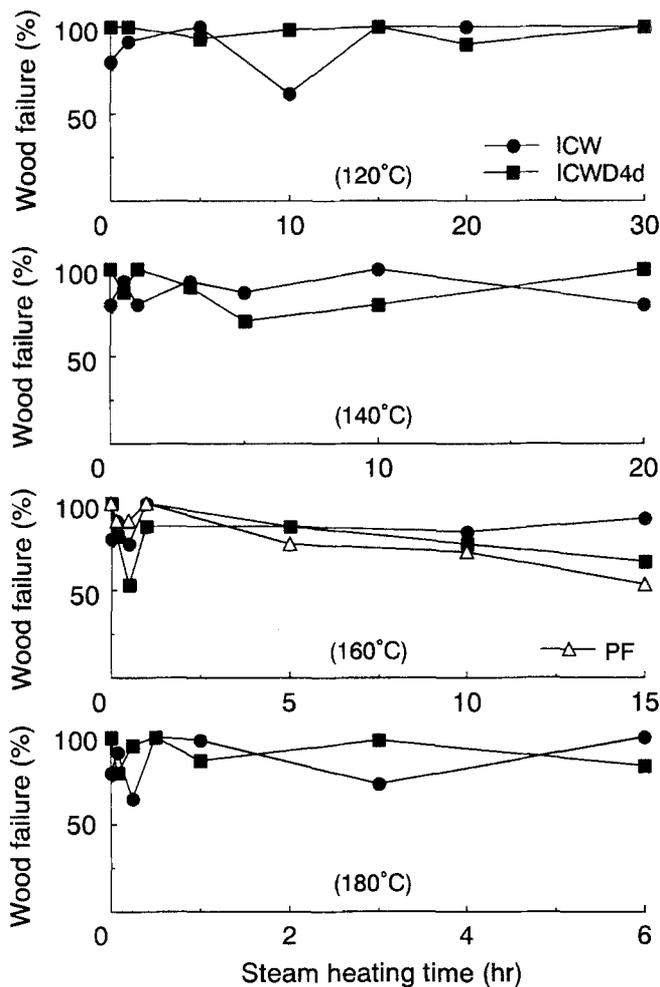


Fig. 8. Changes of wood failure in the bond strength test after various steam treatments

bond strength test are shown in Fig. 8. The wood failures of the specimens bonded with each resin exhibited a relatively high value. In many instances the specimens were broken at the upper part of the glue line. It seemed that more degradation in wood took place compared to that of the adhesives under steam heating. Figure 9 shows the relation between the reciprocal absolute temperature of the steam treatment and the natural logarithm of the half-lives when using ICW and ICWD4d. The regression lines showed a good correlation coefficient (>0.930). The values of apparent activation energy using ICW and ICWD4d were 4.85×10^4 and 6.82×10^4 J/mol, respectively. The apparent activation energy decreased by 30% compared to that under dry heating.² We also attempted to predict the half-lives of the specimens at 20°C. The calculated times of the specimens using ICW and ICWD4d were 19.6 and 294.1 days, respectively.

Conclusions

The durability of isocyanate resins consisting of EMDI was investigated under constant steam heating. FT-IR analysis

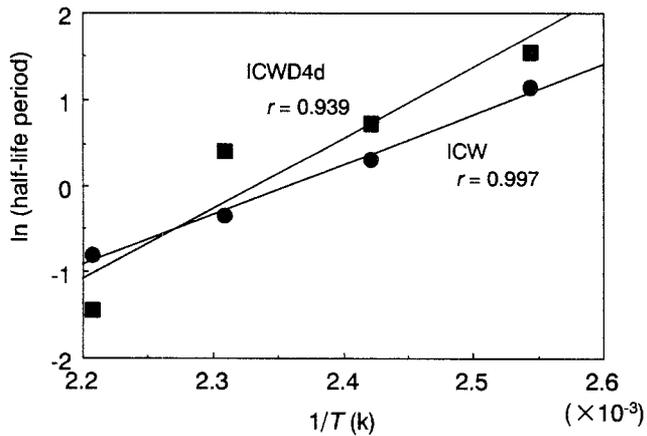


Fig. 9. Plots of $\ln(\text{half-life})$ as a function of $1/T$

showed that the after-cure arising from unreacted isocyanate groups took place rapidly. The degradation reaction scarcely proceeded for a few hours but then increased significantly. The absorption peaks, regarded as the formation of amine due to the hydrolysis reaction of urea linkages, were observed at 160°C for 15h. The resins seemed to be susceptible to elution under steam heating at 160°C. According to the TGA results, the thermal stability of steam-treated ICW was superior to that of steam-treated ICWD4d. The adhesion durability of the specimen bonded with ICWD4d under steam heating was superior to that of ICW. Considering the high wood failure of the specimens, however, the adhesiveness of the ICW and ICWD4d seemed to be good. The apparent activation energy of using ICW and ICWD4d for the half-life period were 4.85×10^4 and 6.82×10^4 J/mol, respectively.

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