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## Durability of isocyanate resin adhesives for wood III: degradation under constant dry heating

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**Abstract** The durability of isocyanate resins consisting of emulsion-type polymeric diphenylmethane diisocyanate (EMDI) was investigated under constant dry heating. Two kinds of resin, water only-added resin and polyol/water-added resin, were used in this study. The kinetic studies based on the weight losses of the resins were carried out by isothermal thermogravimetry (TG) at temperatures ranging from 260° to 320°C. The apparent activation energies of the resins were calculated for weight losses of 5%, 10%, and 15%. The values of apparent activation energy of the resins increased with increasing weight loss. The bond-strength reductions of the specimens bonded with the resins were observed at various temperatures from 120° to 180°C. 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. According to the calculated values, the adhesion durability of polyol/water-added resin was superior to that of water only-added resin. To speculate on the changes in weight loss and the chemical structure of the resins in the glue lines under dry heating, changes in the cured resins were also observed.

**Key words** Isocyanate adhesives · Durability · Degradation · Dry heating · Wood adhesives

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### Introduction

Isocyanate resins consisting of polymeric diphenylmethane diisocyanate (PMDI) have been increasingly replacing traditional wood adhesives. In previous reports, the thermal properties of aqueous emulsion-type PMDI (EMDI) were studied under constant heating rates,<sup>1-3</sup> and it was found that the thermal properties of EMDI cured with water were improved by adding a small amount of polyol of relatively low molecular weight.

Because the durability of adhesive bonded wood composites is greatly affected by the durability of the resin adhesive used, there have been a number of studies on the adhesion durability of resins.<sup>4-6</sup> However, only limited research has been reported on the durability of isocyanate resins consisting of PMDI.<sup>7</sup> Generally, the durability tests can be divided into accelerated and exposure tests. In particular, the accelerated test has the advantage of being able to clarify the durability concerning a specific degradation factor. In this study, the durability of EMDI-based isocyanate resins when exposed to heat was investigated by an accelerated test. Kinetic studies based on the weight losses of the resins were carried out by isothermal thermogravimetry (TG). An evaluation of bond strength durability was also performed under constant dry heating. The changes in weight loss and the chemical structures of the resins in the glue lines were evaluated.

### Materials and methods

#### Materials

The EMDI and the propylene oxide-based polyether polyol used in this study were supplied by Mitsui Takeda Chemicals (Tokyo, Japan). The EMDI and polyol are now distributed under the commercial names Cosmonate M-201W and Diol-400, respectively. The properties of the materials were the same as described in previous papers.<sup>1,2</sup> 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 mixtures were blended by vigorous stirring. The control and the polyol-added resins are represented herein by the abbreviations ICW and ICWD4d, respectively. The thermal properties of ICW and ICWD4d under constant heating rates were described in previous papers.<sup>1-3</sup> The resol phenol-formaldehyde resin (PF) used in this study was obtained from the same company. The properties of PF were described in the previous paper.<sup>1</sup> For instrumental analyses, 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.

### Thermogravimetric analysis

The cured resins were ground to powder (<100 mesh) and vacuum-dried. The thermogravimetric analysis (TGA) was carried out using a TGA 2050 (TA Instruments Japan). The weight changes of the resins (10–15 mg) were scanned under air purging of 70 ml/min. In this study, isothermal experiments were performed at 260°, 280°, 300°, and 320°C. The furnace of the apparatus was preheated to the desired temperature, and the sample was then held in a platinum pan that slid into the furnace. Three replicates were conducted for each condition, and the average value was calculated.

### Fourier transform infrared spectroscopy

All infrared spectra were obtained with a fourier transform infrared (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<sup>-1</sup>.

### Bond strength measurement

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/cm<sup>3</sup> 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 the isocyanate resins (ICW and ICWD4d) and PF applied to the veneer were 200 and 300 g/m<sup>2</sup>, 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 being removed from the press. Test specimens were prepared according to the Japanese Industrial Standard (JIS) K6851. Before testing, the specimens bonded with isocyanate resins were subjected to constant dry heatings at 120°, 140°, 160°, and 180°C in an oven. For the specimen using PF, the heat treatment was conducted at only 160°C. The tensile shear bond strength was measured under a crosshead speed of 2 mm/min. The relative bond

strength reduction (r-bond strength) was calculated from the following equation.

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

where  $s$  is the bond strength of the specimen at an arbitrary heating time, and  $s_0$  is the bond strength of the unheated 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

### Weight changes of cured resins

To investigate the durability from a weight loss point of view, isothermal TG of ICW, ICWD4d, and PF were undertaken. Figure 1 shows the initial weight losses of the resins at 260°–320°C. Each plot indicates the average value. In the case of ICW at 260°C, the times required to reach weight losses of 5%, 10%, and 15% were 1.13, 48.1, and 319 min, respectively. The times required for ICWD4d at the same temperature were 6.88, 43.7, and 148 min, respectively. ICWD4d exhibited higher thermal stability than ICW until a weight loss of 5%. The opposite phenomena were observed at later stages. A similar tendency was indicated at other temperatures. For PF, the times at 260°C were 0.15, 0.33, and 9.13 min, respectively. The times required for each stage were short compared to that of the isocyanate resins.

Generally, the degradation rate can be described by the following equation:

$$da/dt = kf(\alpha) \quad (2)$$

where  $da/dt$  is the rate of degradation;  $f(\alpha)$  is a function of the degree of degradation;  $t$  is the time; and  $\alpha$  is the degree of degradation as expressed by Eq. (3).

$$\alpha = [(W_0 - W)/W_0] \times 100 \quad (3)$$

where  $W_0$  is the initial weight;  $W$  is the weight during the degradation; and  $k$  is the degradation rate constant, which can be expressed by the Arrhenius equation.

$$k = A \exp[-E/(RT)] \quad (4)$$

where  $A$  is the frequency factor;  $E$  is the activation energy;  $R$  is the gas constant; and  $T$  is the absolute temperature. Integration of Eq. (2) results in

$$g(\alpha) = \int [da/f(\alpha)] = kt \quad (5)$$

where  $g(\alpha)$  is the integrated expression of  $f(\alpha)$ . Equations (4) and (5) can be combined and rearranged as

$$\ln(t) = \ln[g(\alpha)/A] + E/(RT) \quad (6)$$

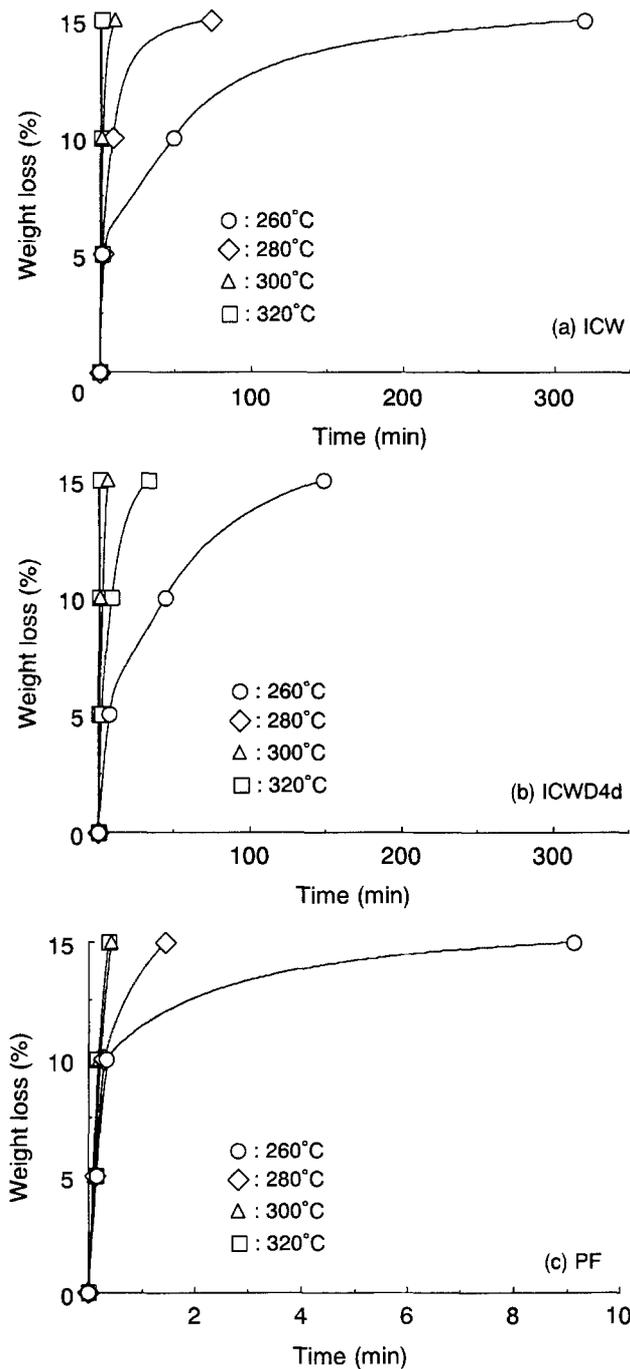


Fig. 1a-c. Weight losses of control isocyanate resin (ICW) (a), polyol added isocyanate resin (ICWD4d) (b), and phenol-formaldehyde (PF) (c) at several constant temperatures

According to the above equation, the activation energy ( $E$ ) can be obtained from the slope of  $\ln(t)$  versus  $1/T$  at a constant degradation stage.<sup>8</sup>

In all experimental data,  $\ln(t)$  was plotted versus  $1/T$ . The result is shown in Fig. 2. All regression lines showed a good correlation coefficient ( $\geq 0.90$ ) at each weight loss stage. The apparent activation energy of the each resin was calculated from the slopes. The results are shown in Table 1. The apparent activation energy of each resin increased with increasing weight loss. The changes in apparent activation

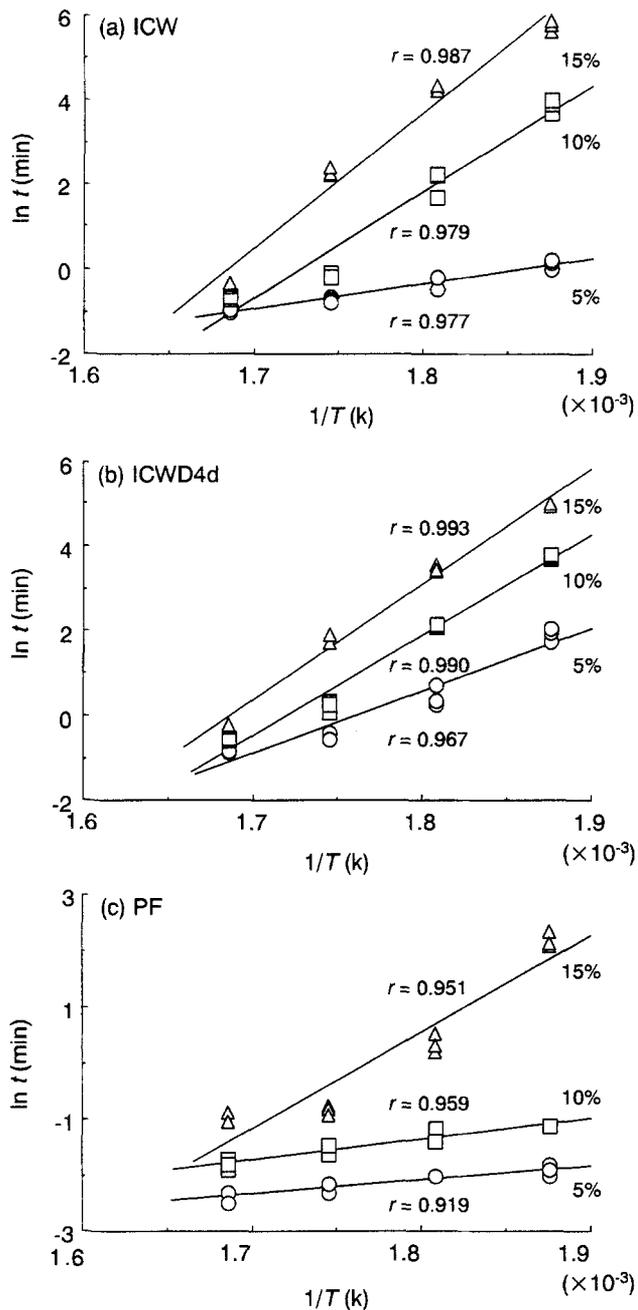


Fig. 2. Plots of  $\ln(t)$  as a function of  $1/T$  for three weight loss points for a ICW, b ICWD4d, and c PF

Table 1. Activation energy of ICW, ICWD4d, and PF at various weight losses

Resin	Activation energy ( $\times 10^5$ J/mol)		
	weight loss 5%	10%	15%
ICW	0.48	2.09	2.67
ICWD4d	1.23	1.96	2.28
PF	0.21	0.31	1.43

ICW, control isocyanate resin; ICWD4d, polyol-added isocyanate resin; PF, phenol-formaldehyde resin

Table 2. Adjusted  $R^2$  from several regression curves

Y	X	$n = 1$										$n = 2$									
		120°C		140°C		160°C		180°C		120°C		140°C		160°C		180°C					
		ICW	ICWD4d	ICW	ICWD4d	ICW	ICWD4d	ICW	ICWD4d	ICW	ICWD4d	ICW	ICWD4d	ICW	ICWD4d	ICW	ICWD4d	ICW	ICWD4d	ICW	ICWD4d
(a) r-Bond strength	t	0.771	0.856	0.617	0.741	0.645	0.584	0.680	0.793	0.901	0.926	0.868	0.929	0.819	0.754	0.851	0.972	0.864	0.864	0.972	0.864
(b) r-Bond strength	$\sqrt{t}$	0.935	0.978	0.897	0.961	0.897	0.851	0.917	0.966	0.981	0.991	0.994	0.996	0.986	0.970	0.989	0.962	0.959	0.959	0.962	0.959
(c) r-Bond strength	1/t	0.474	0.481	0.605	0.610	0.298	0.665	0.344	0.457	0.948	0.817	0.951	0.909	0.685	0.781	0.550	0.636	0.262	0.262	0.636	0.262
(d) r-Bond strength	log t	0.843	0.916	0.927	0.979	0.918	0.959	0.918	0.926	0.814	0.963	0.910	0.976	0.953	0.956	0.954	0.980	0.881	0.881	0.980	0.881
(e) (r-Bond strength) <sup>2</sup>	t	0.849	0.965	0.747	0.898	0.826	0.753	0.859	0.958	0.931	0.969	0.973	0.986	0.947	0.883	0.971	0.994	0.953	0.953	0.994	0.953
(f) 1/(r-Bond strength)	t	0.426	0.431	0.362	0.245	0.305	-	0.219	0.488	0.679	0.607	0.712	0.481	0.490	-	0.332	0.034	0.617	0.617	0.034	0.617
(g) log (r-Bond strength)	log t	0.845	0.989	0.915	0.948	0.929	0.781	0.954	0.854	0.807	0.986	0.919	0.988	0.913	0.926	0.946	0.961	0.856	0.856	0.961	0.856
(h) log (r-Bond strength)	t	0.491	0.659	0.453	0.465	0.461	0.161	0.452	0.792	0.702	0.786	0.820	0.728	0.660	0.185	0.639	0.992	0.798	0.992	0.798	0.798

Underlined values are above 0.950

energy imply that the degradation reaction of the resins does not proceed as a single elementary process. In a previous paper,<sup>3</sup> an investigation of the apparent activation energy of isocyanate resins was attempted using the results of TG under constant heating rates. However, it was impossible to calculate the apparent activation energy. This can be attributed to the complicated degradation process described above. At a weight loss of 5%, the apparent activation energy of ICWD4d was extremely high compared to that of ICW. However, the ICWD4d values were lower than those of ICW at weight losses of 10% and 15%. With PF, the apparent activation energy of each stage was extremely low compared to that of the isocyanate resins. Considering durability from a weight loss viewpoint, ICWD4d would be superior to ICW during the initial stage. In addition, PF was thought to be inferior to the isocyanate resins.

#### Adhesion durability

To investigate the durability of the resins from a bond strength viewpoint, the tensile shear bond strength of the specimen bonded with each resin was observed. Generally, there are two evaluation methods for analyzing bond strength reduction. One method is based on a rate equation. Gillespie and River<sup>9</sup> observed the shear bond strength of three-ply plywood bonded with several wood adhesives under constant dry heating. The degradation rate, apparent activation energy, and prediction of bond strength reduction at room temperature were investigated using a first-order rate equation. The other method is based on regression analysis. Sasaki et al.<sup>10</sup> observed the internal bond strength of three-ply plywood bonded with several wood adhesives under constant dry heating. Polynomial regression was performed to determine the behavior of each bond strength reduction. After determining the best fitting regression function, the service life and apparent activation energy were calculated. Because this method seemed to be useful for analyzing adhesive-bonded wood materials with a complicated degradation mechanism, polynomial regression was performed in the present study. First, the relation between r-bond strength reduction and heating time was investigated. The first- and second-order polynomials of the following general equation were applied to the regression.

$$Y = \sum_{i=1}^n A_i X^i \quad (7)$$

According to the report,<sup>10</sup> expressions (a) to (h) in Table 2 were used as the fitting regression functions, where  $Y$  is the r-bond strength,  $X$  is the heating time ( $t$ ),  $A$  is a constant, and  $n$  is the order ( $\leq 2$ ). No intercept model was adopted for expressions (a), (b), and (e). To determine the best fitting regression function, the coefficient of determination adjusted for the degree of freedom (adjusted  $R^2$ ) was calculated. The results are shown in Table 2. Underlines indicate a value of 0.950 or above. Based on the results obtained, the best fitting function was found to be the second order of expression (b). Sasaki et al.<sup>10</sup> reported that the best fitting

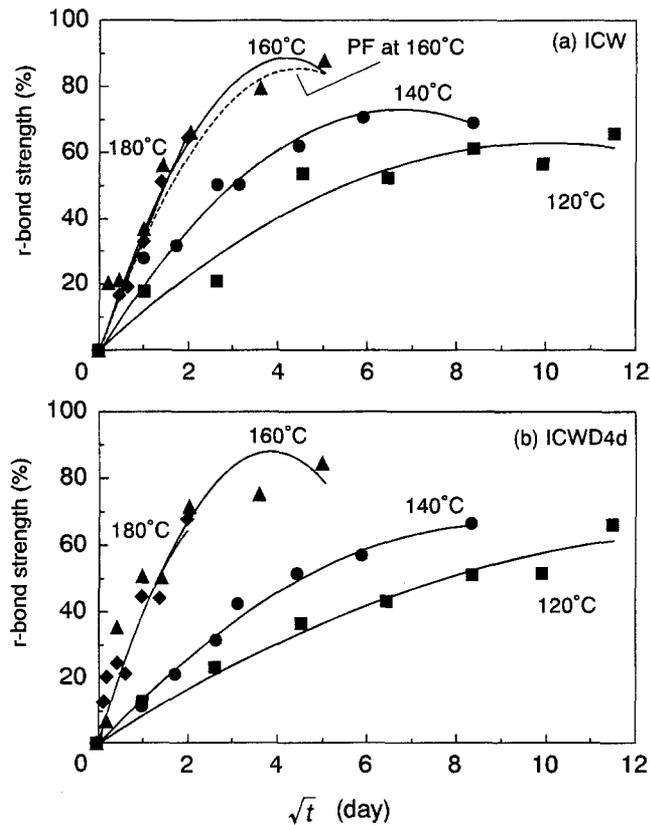


Fig. 3. Relative bond strength reduction (*r-bond strength*) of a ICW, and b ICWD4d as a function of heating time at various temperatures

regression for the internal bond strength of plywood under constant dry heating was expression (d). Northcott and Colbeck<sup>11</sup> reported the durability of plywood bonded with various phenolic resins. The relation between the bond strength reduction and the number of cyclic boiling tests was regressed using the first-order expression (b). Gillespie and River<sup>9</sup> analyzed the bond strength reduction using the first-order expression (h) based on the first-order rate equation, as mentioned above. Therefore, the various regression functions would be fitted, depending on the experimental conditions. The *r-bond strengths* were plotted against the square root of the heating time, as shown in Fig. 3, and the changes in wood failure during the bond strength test are shown in Fig. 4. The wood failures of the specimens bonded with ICWD4d exhibited relatively high values, indicating that more degradation took place in wood than in the adhesive under dry heating. In the case of ICW, a large variation was observed at 180°C. This could be due to the melting of ICW.<sup>13</sup> As a whole, however, the adhesiveness of the resins seemed good. The half-lives were calculated from the regression curves in Fig. 3. The half-lives using ICW, ICWD4d, and PF at 160°C were 1.97, 1.70, and 2.47 days, respectively. The adhesion durability of the specimens bonded with ICW and ICWD4d at 160°C was somewhat inferior to that of the specimens bonded with PF. Figure 5 shows the relation between the reciprocal absolute temperature of the heat treatment and the natural logarithm of the half-lives when using ICW and ICWD4d. Regression

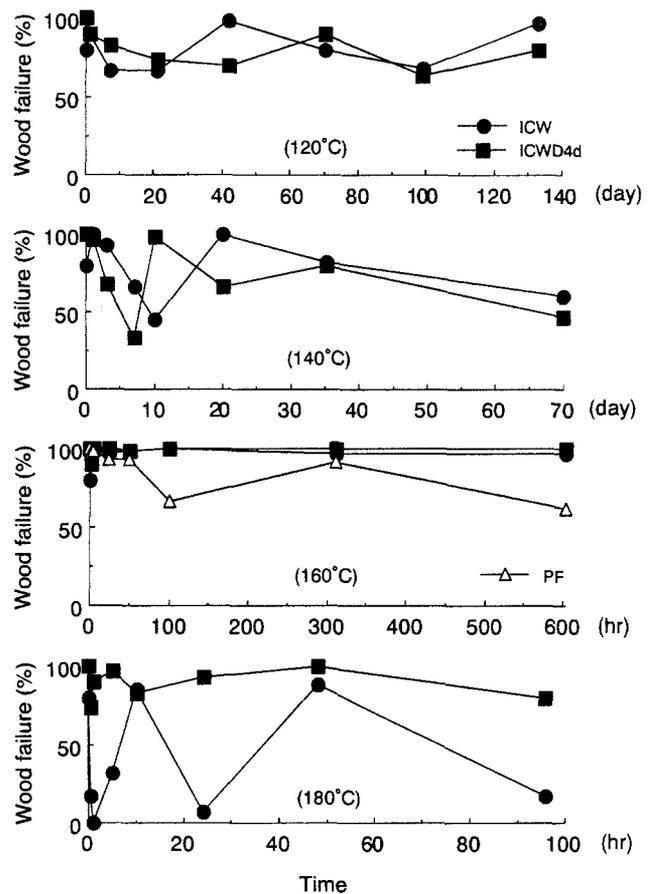


Fig. 4. Changes of wood failure in the bond strength test after various heat treatments

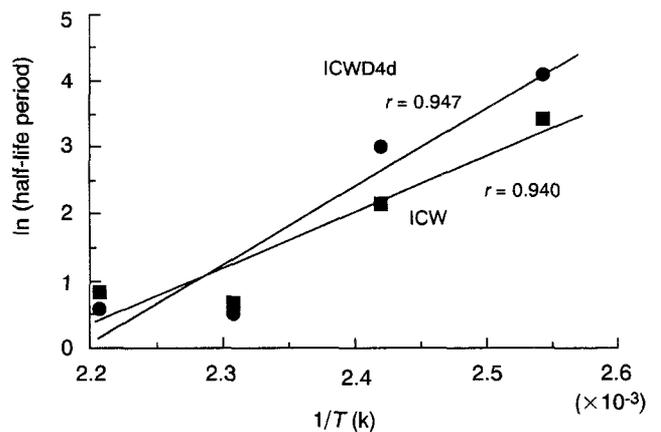


Fig. 5. Plots of  $\ln(\text{half-life period})$  as a function of  $1/T$

lines showing good correlation coefficients ( $\geq 0.940$ ) were observed. The values of apparent activation energy using ICW and ICWD4d were  $6.90 \times 10^4$  and  $9.73 \times 10^4$  J/mol, respectively. In addition, we attempted to predict the half-lives of the specimens at 20°C. The calculated times of the specimens using ICW and ICWD4d were 92 and 4189 years, respectively.

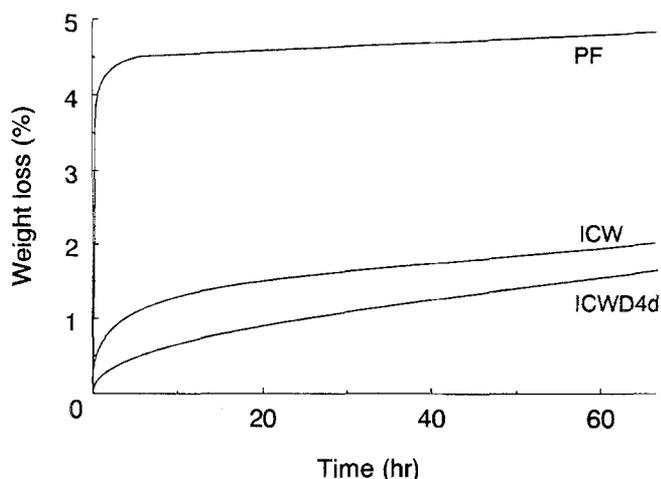


Fig. 6. Weight changes of ICW, ICWD4d, and PF at 160°C

#### Changes in the resins in the specimen

To speculate the changes in weight loss and chemical structure of the resins in the glue lines under the dry heating condition, changes in the cured resins were observed using TG and FT-IR. Figure 6 shows the weight changes of the resins at 160°C. The weights of ICW and ICWD4d decreased gradually with increasing heating time, but the extent of the weight losses was small. The times required to reach 1% weight loss for ICW and ICWD4d were 4.3 and 22.3h, respectively. The weight of PF decreased rapidly within a short time and then decreased gradually. Considering the half-lives of the specimens bonded with ICW and ICWD4d calculated from the regression curves, the weight losses of the resins in the specimens were expected to be less than 2%. Therefore, the weight losses of the isocyanate resins seemed to have little effect on the bond strength reductions. Figure 7 shows the infrared spectra of ICW and ICWD4d under dry heating at 160°C. For ICW the infrared spectrum of the unheated specimen recorded a strong peak of  $2276\text{ cm}^{-1}$ , showing that the resin contains a considerable amount of unreacted isocyanate groups. The isocyanate absorption band decreased markedly with increasing heating time. The absorption band at  $2100\text{ cm}^{-1}$  appeared as a shoulder to the isocyanate absorption band in 15h. This absorption band was assigned to the carbodiimide ( $-\text{N}=\text{C}=\text{N}-$ ) based on the condensation of two isocyanate groups.<sup>12,13</sup> The marked change in the absorption peak at  $1661\text{ cm}^{-1}$  attributed to urea carbonyl groups<sup>14,15</sup> was scarcely observed over the entire heating time. For ICWD4d similar spectral changes were observed. Consequently, based on the reaction of unreacted isocyanate groups, the after cure took place, rather than degradation, until the bond strength reached its half-life point.

#### Conclusions

The durability of isocyanate resins consisting of EMDI was investigated under constant dry heating. Based on to the

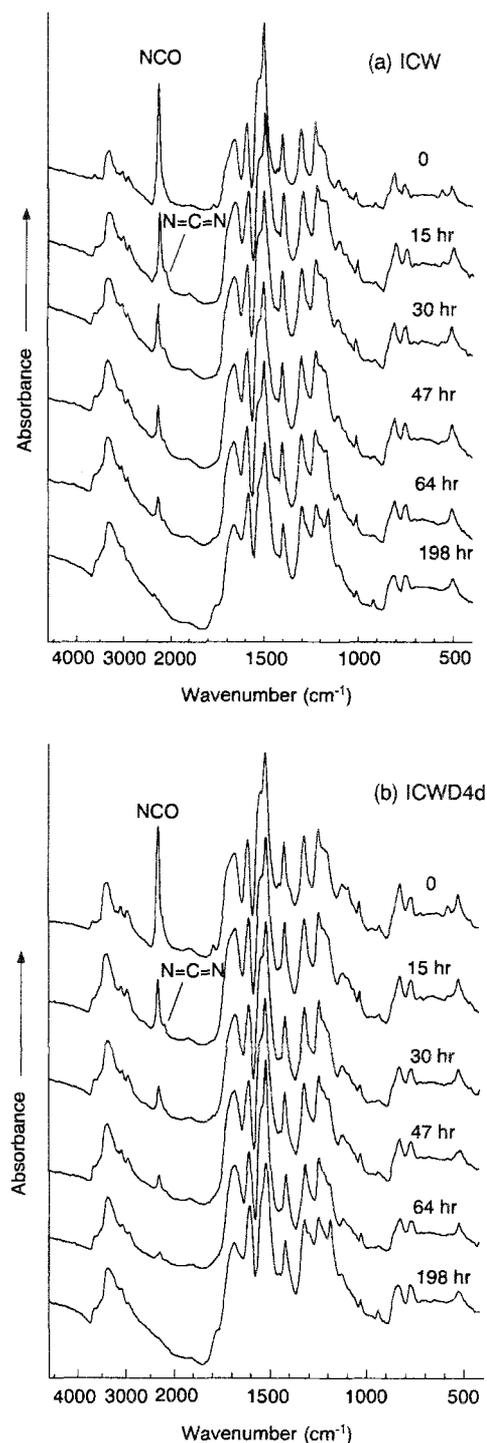


Fig. 7. Infrared changes of a ICW and b ICWD4d at 160°C

results of isothermal TG, it took longer to reach a weight loss of 5% for ICWD4d than for ICW. An opposite tendency was observed at higher weight losses. PF exhibited rapid weight loss compared to ICW and ICWD4d. For all resins, the values of apparent activation energy increased with increasing weight loss, showing that the degradation reactions of the resins were complicated. The adhesion durability of the specimens bonded with ICW and ICWD4d at 160°C was somewhat inferior to that of the specimens

bonded with PF. The values of apparent activation energy using ICW and ICWD4d for the half-life period were  $6.90 \times 10^4$  and  $9.73 \times 10^4$  J/mol, respectively. Considering the high wood failure of the specimens, the adhesiveness of the ICW and ICWD4d seemed good. Good adhesiveness was also observed when using PF. The weight losses of ICW and ICWD4d in the glue lines of the specimens were expected to be only a few percent under the dry heating condition. In addition, the after cure was more marked than degradation until the bond strength reached its half-life point.

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