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Effect of polyol on thermo-oxidative degradation of isocyanate resin for wood adhesives

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Abstract The thermo-oxidative degradation of various polyol-added isocyanate resins for wood adhesives was studied using differential scanning calorimetry and thermogravimetry. The degradation of the resin cured with water began at 150°C. When a certain polyol was added to the resin at an NCO/OH ratio of 25 in addition to water, the cured resin began to degrade at 200°C. To clarify the cause of the good thermal stability in polyol-added resins, the effect of various polyols on the reactivity of isocyanate was investigated. It was found that the reactivity of isocyanate was enhanced by the addition of a dipropylene glycol and glycerin-type polyols. In addition, the effect of the NCO/polyol-OH ratio was investigated using dipropylene glycol-type polyol. The reactivity of isocyanate increased with increasing polyol content. The thermal stability of the resin was improved to a certain degree by addition of a small amount of the polyol but deteriorated when a large amount of the polyol was added.

Key words Isocyanate adhesives · Thermo-oxidative degradation · Differential scanning calorimetry · Thermogravimetry · Wood adhesives

Introduction

In wood composite board industries, isocyanate (IC) adhesives have been used increasingly as replacements for traditional formaldehyde-based adhesives. Polymeric diphenylmethane diisocyanate (PMDI) has especially been used as an isocyanate adhesive for wood. When PMDI is used for board manufacture, it is usually diluted and sprayed on materials. The isocyanate is believed to react with wood components and water. In particular, the isocyanate–water reaction is considered to be one of the most important curing reactions.[1–3] PMDI has been also used as a component of polyurethane and is reacted with polyols. In a previous paper[4] the effect of polyether polyols on the thermal property of the aqueous emulsion-type PMDI (EMDI) cured with water was studied using dynamic mechanical analysis (DMA). The thermal property of EMDI cured with water was improved by adding a small amount of polyol with relatively low molecular weight. In this study the thermal stability of EMDI cured with polyol in addition to water was investigated in detail using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The improvement mechanism of thermal stability in the resin is also discussed.

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Materials and methods

Materials

The EMDI and six types of propylene oxide-based polyether polyols used in this study were the same as described in a previous paper.[4] The properties of polyols are shown in Table 1. To cure the EMDI these polyols were added at various NCO/polyol-OH ratios. The final NCO/OH ratios of the resins were adjusted to 0.5 and 1.0 with water. For the control, only water was added at an NCO/OH ratio of 0.5. The mixtures were blended by vigorous stirring. The detailed formulations and abbreviations are shown in Table 2. The resins were cured at 40°C for 24 h in an oven. The cured resins were ground to powder (less than 100 mesh) and vacuum-dried.

Differential scanning calorimetry

The DSC experiments were conducted using a DSC 2910 (TA Instruments Japan). Indium, biphenyl, and mercury

were used for calibration. Prior to preparing the sample, a small hole was made in the cover of aluminum pans using tweezers to release the decomposed gas arising from the resin at high temperature. The samples (about 5 mg) were encapsulated in the aluminum pans and scanned from −100° to 400°C at a rate of 6°C/min under air and nitrogen purging.

Thermogravimetric analysis

The TGA was carried out using a TGA 2050 (TA instruments Japan). The sample (10–15 mg) was scanned from room temperature to 700°C at rates of 4°–10°C/min under air and nitrogen purging.

Fourier transform-infrared spectroscopy

All infrared spectra were obtained with a FT-IR 7000 spectrometer (JASCO) using the KBr pellet method and were recorded by averaging 16 scans at a resolution of 4 cm^{-1}. The unreacted isocyanate group of the resin was obtained by use of the isocyanate (NCO) stretching absorption peak at 2274 cm^{-1}. The height of this peak [H(2274)] was calculated with respect to a baseline drawn between the points at 2400 and 1900 cm^{-1}. The C=C stretching absorption peak of the aromatic ring at 1600 cm^{-1} was used as a reference.[5] The height of this peak [H(1600)] was also calculated with respect to a baseline drawn between the points at 1630 and 1570 cm^{-1}. The relative amount of unreacted isocyanate group of the resin was obtained from the following expression.

$$\frac{\text{H(2274)/H(1600) of polyol added resin}}{\text{H(2274)/H(1600) of resin cured with only water}}$$

Three replicates were employed for each condition.

Table 1. Properties of polyols

Polyol	Constituents	No. of functional groups	Molecular weight[a]
Diol400	DPG + PO	2	400
Diol1000	DPG + PO	2	1000
Diol3000	DPG + PO	2	3000
KB 280	Bisp + PO	2	380
MN 400	Gly + PO	3	400
PE 600	PE + PO	4	370

DPG, dipropylene glycol; PO, propylene oxide; Bisp, bisphenol A; Gly, glycerin; PE, pentaerythritol
[a] Theoretical value

Results and discussion

Thermal properties of ICW

To investigate the change in heat quantity of the resin cured with only water (ICW) in an air atmosphere, DSC was applied. The result is shown in Fig. 1a. The endothermic peak and the small peak change were observed at 50°–60°C and 180°–200°C, respectively. In addition, the large exothermic peak appeared at above 200°C. This large exothermic peak would be due to the thermo-oxidative degradation of ICW. In a previous study[6] the mechanical degradation of ICW was confirmed at above 200°C. The DSC was also scanned in a nitrogen atmosphere to eliminate the effect of oxidation. The result is shown in Fig. 1b. The thermal behavior until 200°C was similar to that in air. Some endothermic and exothermic peaks were found above this temperature. Figure 2 shows DSC curves obtained from the ICW subjected to the following thermal treatment in an air atmosphere. The sample was heated to 200°C (first scan), cooled to −100°C, and then heated again (second scan). On the second scan the endothermic peak was observed at 50°–60°C, but the small change at 180°–200°C was not observed. The similar tendency was also recognized in a nitrogen

Table 2. Abbreviations and formulations of IC resins

Abbreviation	Composition of resin	NCO/polyol-OH ratio	Final NCO/OH ratio (water addition)	Polyol content (wt%)[a]
ICW	EMDI + water	–	0.5	0
ICD4	EMDI + Diol 400	1	1.0	58.4
ICWD4a	EMDI + Diol 400 + water	1	0.5	56.9
ICWD4b	EMDI + Diol 400 + water	5	0.5	20.1
ICWD4c	EMDI + Diol 400 + water	12	0.5	9.4
ICWD4d	EMDI + Diol 400 + water	25	0.5	4.8
ICWD4e	EMDI + Diol 400 + water	50	0.5	2.4
ICWD1	EMDI + Diol 1000 + water	25	0.5	11.1
ICWD3	EMDI + Diol 3000 + water	25	0.5	27.2
ICKB	EMDI + KB 280	1	1.0	57.3
ICWKB	EMDI + KB 280 + water	25	0.5	4.6
ICMN	EMDI + MN 400	1	1.0	48.3
ICWMN	EMDI + MN 400 + water	25	0.5	3.2
ICPE	EMDI + PE 600	1	1.0	39.6
ICWPE	EMDI + PE 600 + water	25	0.5	2.3

[a] Polyol content (wt%) = [polyol/(EMDI + polyol + water)] × 100

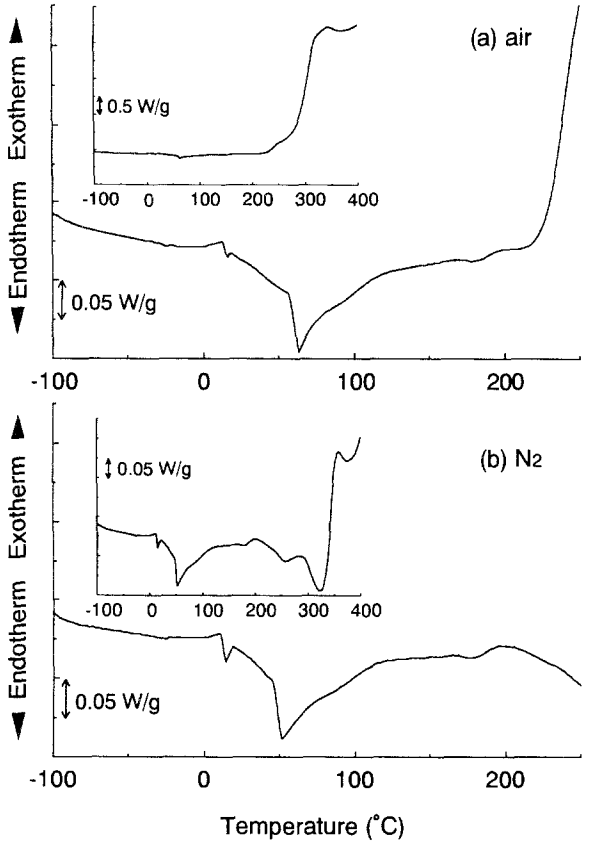

Fig. 1. Differential scanning calorimetry (DSC) curves of emulsion-type polymeric diphenylmethane diisocyanate (EMDI) plus water (ICW) in air (**a**) and N_2 (**b**) atmospheres

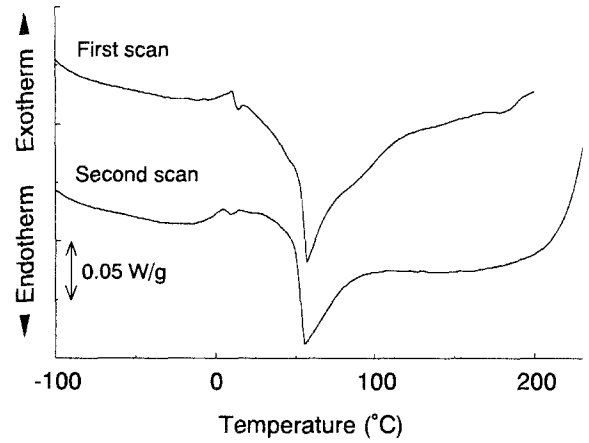

Fig. 2. DSC curves of the first and second scans for ICW in an air atmosphere

atmosphere. Therefore, the small change was not ascribed to the oxidation.

Generally, polyureas based on diisocyanate/diamine exhibit no change at around 50°–70°C in DSC,[7–10] but there are several reports concerning the change at around 200°C.[9,11] Coleman et al. reported that 2-methylpentane-1,5-diphenylurea exhibited the endothermic peak for melting at 172°C.[9] Yadav et al. prepared poly(hexamethylene) ureas

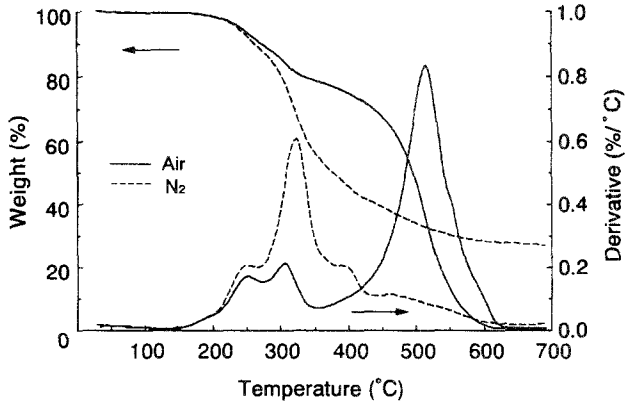

Fig. 3. Thermogravimetric analysis (TGA) curves of ICW in air and N_2 atmospheres

produced by the technique of interfacial polycondensation. The polymer exhibited an endothermic peak at 240°C, regarded as the melting of imperfect crystals, and an exothermic peak at 250°C due to the cold-crystallization transition.[11] On the other hand, polyurethane-ureas exhibit endothermic peaks at around 60°C and 180°C.[12–14] Seymour and Cooper[12] have reported that the endothermic peaks at around 70°C and 180°C were the breakup of short- and long-range orders in a hard segment of polymer, respectively. However, Luo et al.[15] prepared the segmented polyether poly(urethane urea) copolymer based on diphenylmethane diisocyanate (MDI), ethylene oxide-capped poly(propylene oxide) diol, 3,5-diethyltoluenediamine. The endothermic peak was not observed, but the exothermic peak due to formation of ordered urea hydrogen bonds was observed clearly in the temperature range 130°–220°C. Therefore, the endothermic and exothermic peaks of polyureas and polyurethane-ureas are greatly influenced by the composition, preparation condition, and other factors. Considering the above reports, the endothermic peak of DSC at 50°–60°C in this study seems to be a breakup of short-range order in the resin. The small change at 180°–200°C seems to be due to melting and rearrangement of the resin. The inference for the change supports the result of the DMA measurement in the previous study.[4]

Figure 3 shows the weight loss curves and derivative weight loss curves of ICW at a heating rate of 6°C/min under air and nitrogen atmospheres. The weight loss started slowly at 150°C regardless of the atmosphere. In an air atmosphere the weight loss behavior showed two-step degradations, at 200°–300°C and 450°–600°C. The first part of the degradation showed two derivative weight loss peaks at 250°C and 300°C, illustrating the complexity of the process. On the other hand, the one-step degradation at 200°–450°C was observed in the nitrogen atmosphere. This indicates that the thermo-oxidative degradation mechanism in air is different from the thermal degradation mechanism in nitrogen. Based on the derivative weight loss curve in nitrogen atmosphere, the degradation was able to split into three peaks: at 250°C, 320°C, and 400°C.

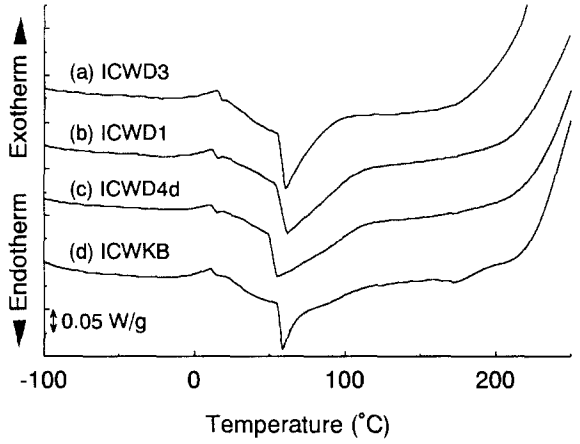

Fig. 4. DSC curves of ICWD3, ICWD1, ICWD4d, and ICWKB (see Table for compositions) in an air atmosphere

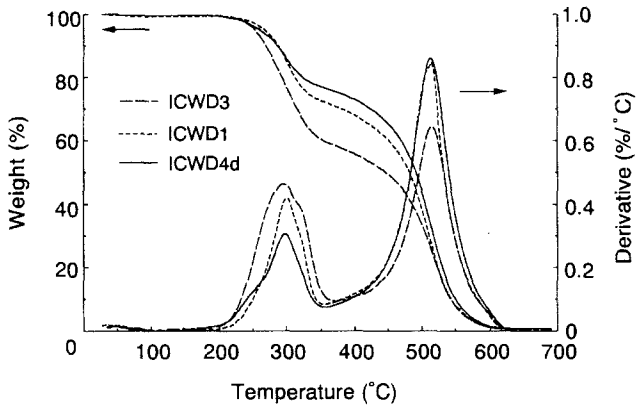

Fig. 5. TGA curves of ICWD3, ICWD1, and ICWD4d in an air atmosphere

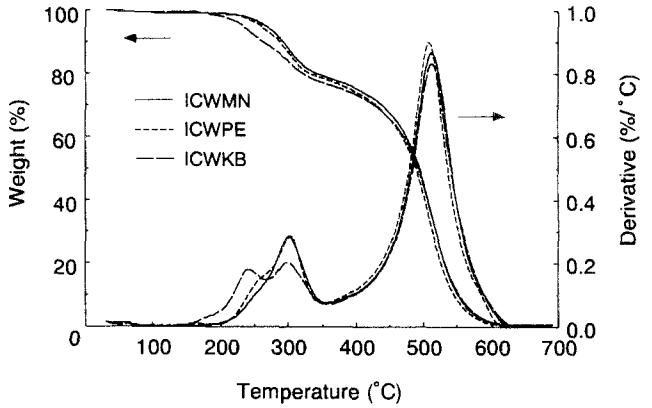

Fig. 6. TGA curves of ICWMN, ICWPE, and ICWKB in an air atmosphere

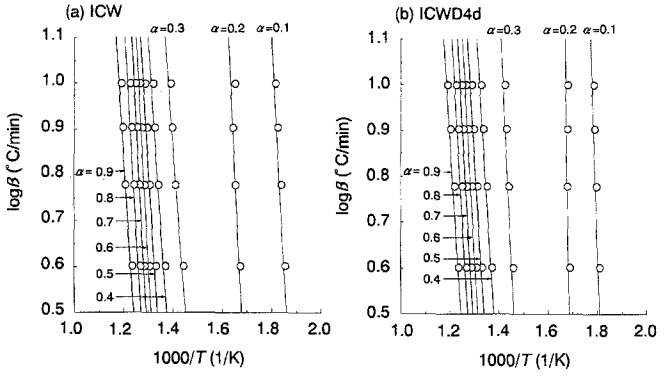

Fig. 7. Dependence of the logarithm of the heating rate ($\log\beta$) versus the reciprocal absolute temperature ($1/T$) for the Ozawa method at indicated conversions (α) of decomposition of ICW (**a**) and ICWD4d (**b**)

Thermal properties of polyol-added resins

Figure 4 shows the DSC curves of dipropylene glycol-type polyol-added resins (ICWD3, ICWD1, ICWD4d) and bisphenol A-type polyol-added resin (ICWKB) in an air atmosphere. For all resins the endothermic peak was observed at 50°–60°C. There was no peak change at 180°–200°C except for ICWKB, which showed the change at the same temperature range during DMA measurement.[4] It is well known that a broad change regarded as glass transition of polyol soft segment in polyurea and polyurethane-urea is detected in the temperature range −50°C to −20°C.[10,16,17] However, polyol-added resins in this study exhibited no change due to the glass transition. The DSC curves of glycerin-type polyol (MN400)- and pentaerythritol-type polyol (PE600)-added resins (ICWMN and ICWPE) had patterns similar to that of ICWD4d.

Figure 5 shows the weight loss curves of ICWD3, ICWD1, and ICWD4d in an air atmosphere. The weight loss behavior showed two-step degradations, at 200°–350°C and 350°–600°C. The onset of degradation was observed at 200°C regardless of the molecular weight of the polyol and was higher than that of ICW shown in Fig. 3. The weight loss during the first step increased with increasing molecular weight of the polyol. Figure 6 shows the weight loss curves for ICWMN, ICWPE, and ICWKB in an air atmosphere. Though the weight loss behavior of these resins was also in two steps, the behaviors of the first step were somewhat different. Judging from the derivative weight loss curves, the weight loss behaviors of ICWKB and ICWPE were similar to those of ICW and ICWD4d, respectively.

The kinetics of thermal degradation of the resins were attempted using Ozawa's method.[18] This method requires several TGA curves at different heating rates (β). The logarithms of the heating rate ($\log\beta$) are plotted against the reciprocal absolute temperature ($1/T$) with regard to each degree conversion (α), defined as the weight loss at a given temperature divided by the total weight loss. Usually α was taken to be 0.1, 0.2 . . . 0.9. From the slope of the lines, the activation energy of degradation can be calculated for each conversion and the average value for the whole range of conversion. However, this method is assumed to be the constant activation energy during degradation of the polymer. Figure 7 shows the plots of $\log\beta$ versus $1/T$ for each α of ICW and ICWD4d. Though the plots of each conversion gave a straight line, the slopes of the lines during the initial conversions (α = 0.1–0.3) were different from those of the lines during later conversions. It seems as if the

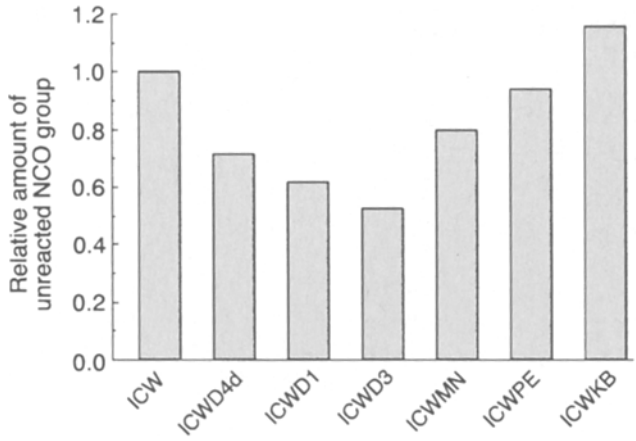

Fig. 8. Relative amount of the unreacted NCO group in various IC resins

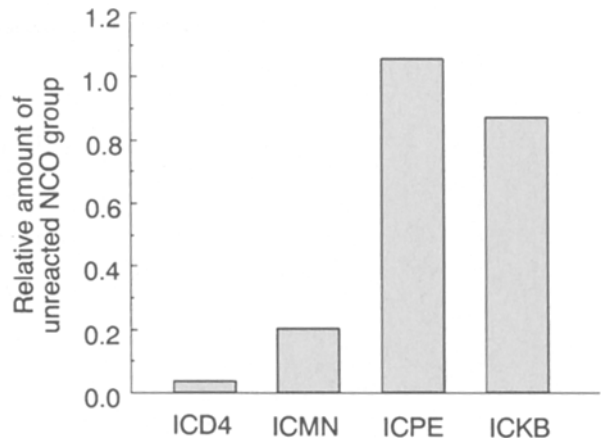

Fig. 9. Relative amount of the unreacted NCO group in IC resins cured by polyols without adding water

activation energy is changing during the initial degradation. Similar results were obtained for the other polyol-added resins. Therefore, the activation energy could not be calculated because of a deviation from the assumption. This seems to be due to the preparation method of the resins as wood adhesives. The activation energy in the initial degradation will be discussed and clarified in the next report.

Reactivity of isocyanate and polyol

To elucidate the cause of good thermal stability of some polyol-added resins, the effects of polyols on the reactivity of isocyanate were investigated. Figure 8 shows the relative amount of unreacted NCO group in the polyol-added resins. In dipropylene glycol-type polyol-added resins (ICWD3, ICWD1, ICWD4d), each unreacted NCO group content was less than that of ICW. The values decreased with increasing the molecular weight of the polyol. Especially the value of ICWD3 was about half that of ICW. For other polyol-added resins the values of ICWMN and ICWPE were somewhat lower than that of ICW, but that of ICWKB was higher than the ICW.

Figure 9 shows the relative amount of unreacted NCO groups in the resins cured by polyols only. Though the molecular weights of these polyols were about 400, there was a marked difference in the reactivity of isocyanate. The unreacted NCO group content of ICD4 and ICMN was low compared to the contents of ICPE and ICKB. Tabor et al.[19] reported that the unreacted NCO group content increased with increasing polyol functionality in water-blown rigid foams. They suggested that as the polymer network develops, diffusion of molecular species becomes more difficult with increasing polyol functionality. Although KB280 had two hydroxyl groups in this study, the resultant value for ICKB was markedly higher than the value for ICMN prepared from MN400 with three hydroxyl groups. The reason seems to be that the bisphenol structure of KB280 prevents diffusion and mobility of molecular species.

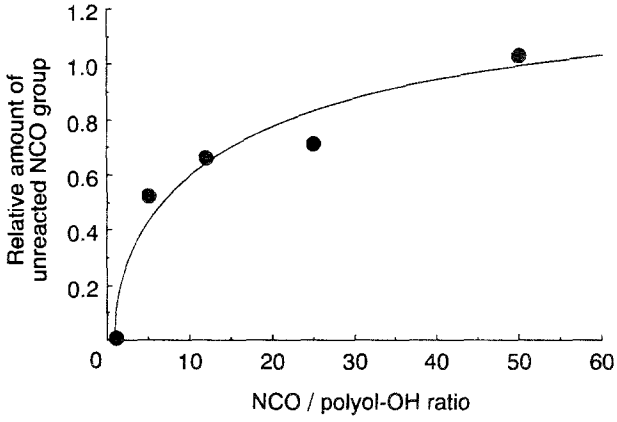

Fig. 10. Relation between the NCO/polyol-OH ratio and the relative amount of the unreacted NCO group of water and Diol400 addded resin

The effect of the NCO/polyol-OH ratio on unreacted NCO group content was investigated using Diol400. The result is shown in Fig. 10. The final NCO/OH ratio of the resins was adjusted to 0.5 with water. The unreacted NCO group content increased markedly up to the ratio of 25 and then increased slightly. This means that the reactivity of the NCO group was enhanced with increasing polyol content. Figure 11 shows the infrared spectra of carbonyl group in the polyol-added resins. The final NCO/OH ratio of the resins (except ICD4) was adjusted to 0.5 with water. Generally, the isocyanate reacts with hydroxyl group to form a urethane linkage, which is indicated as a peak of urethane carbonyl group detected at around 1700–1730 cm^{-1}.[20] The isocyanate also reacts with water. The condensation between the isocyanate and water produces unstable carbamic acid, which rapidly decomposes to carbon dioxide and amine. The latter rapidly react with another isocyanate to form a urea linkage, which is indicated as a peak of urea carbonyl group detected at around 1640–1715 cm^{-1}.[20] With an NCO/polyol-OH ratio of 50 (ICWD4e), the absorption band at 1660 cm^{-1} attributed to disordered urea carbonyl

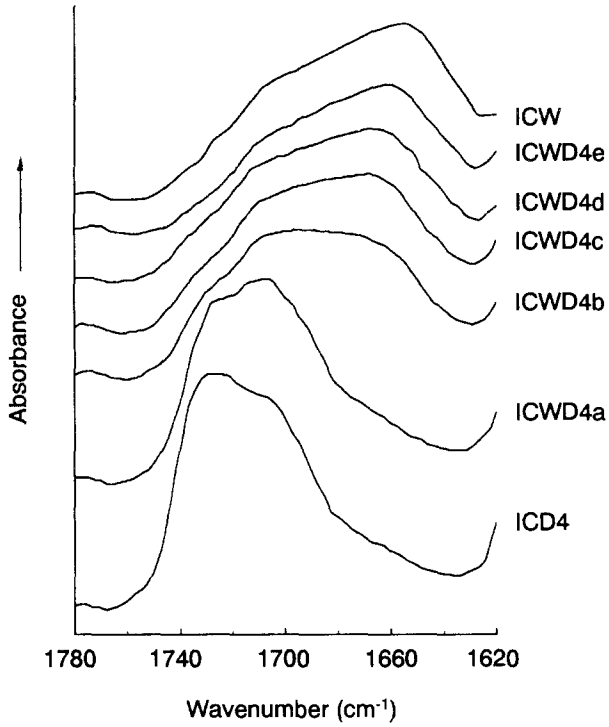

Fig. 11. Infrared spectra of carbonyl group with various polyol contents

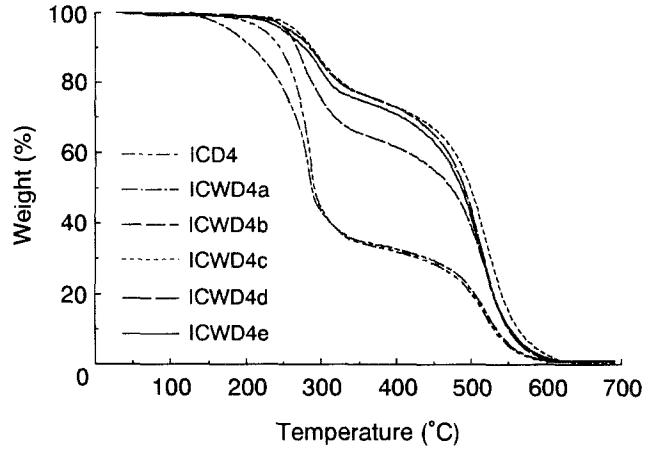

Fig. 12. TGA curves of Diol400 added resins in an air atmosphere

group[21,22] was clearly identified. The peak form was similar to that of ICW, which was cured with water only. The peak of the carbonyl group broadened up to a NCO/polyol-OH ratio of 5 (ICWD4b) with increasing polyol content. The absorption band at 1660 cm^{-1} disappeared, and only a strong absorption band at 1710 cm^{-1} was observed at an NCO/polyol-OH ratio of 1 (ICWD4a). Considering the results in Fig. 10, formation of the carbonyl group would increase gradually with increasing polyol content. However, it is difficult to distinguish between the carbonyl group arising from urea linkage and the carbonyl group arising from urethane linkage because of overlap of the two peaks. Judging from the carbonyl peak of ICD4 without adding water, urethane linkage would be formed mainly in ICWD4a.

Figure 12 shows the weight loss curves of the above resins in an air atmosphere. All curves showed two-step degradations at 200°–300°C and 400°–600°C. A marked difference was observed at the first step of degradation. ICWD4c and ICWD4d exhibited higher thermal stability than ICWD4e. On the other hand, ICWD4b and ICWD4a showed lower thermal stability than ICWD4e. This indicates that addition of an excess amount of polyol to the resin lowered the thermal stability. The onset of degradation temperature of ICWD4a was especially lower than that of ICD4 without adding water. It seems to be caused by the presence of unreacted polyol in the resin.

Based on the above results, the cause of good thermal stability of the resins cured with some polyols in addition to water can be explained as follows. In the case of the ICW cured with water only, the primary curing reactions proceed by the formation of urea linkages, but the curing reaction does not fully proceed because the polyurea structure has a strong intermolecular force. When a small amount of a certain polyol is added to the resin, the polyol weakens the intermolecular force to some degree. Therefore, the curing reaction proceeds smoothly and the cured resin has good thermal stability. When the polyol is further added to the resin, not only the introduction of polyol as soft segment but also a residue of unreacted polyol occurs. Consequently, the thermal stability of the resin seems low.

Conclusions

The thermo-oxidative degradation of polyol-added isocyanate resins for wood adhesives was investigated using DSC and TGA. ICW showed a small peak change due to melting and rearrangement of the resin at 200°C during DCS. The temperature of the onset of weight loss was 150°C in TGA. The polyol-added resins (except ICWKB) did not show a small peak change at 200°C in DSC, and the onset temperature of weight loss was 200°C. This improved thermal stability is attributed to the stimulation of reactivity of isocyanate by addition of polyol. The effect of the NCO/polyol-OH ratio on the reactivity of isocyanate was also investigated using Diol400. The reactivity was improved with increasing polyol content, and the formation of urethane linkage was confirmed. The thermal stability increased to some degree after addition of a small amount of polyol but decreased when the polyol content was large.

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