Durability of Isocyanate Resin Adhesives for Wood. II. Effect of the Addition of Several Polyols on the Thermal Properties

KENJI UMEMURA,[1] AKIHIRO TAKAHASHI,[2] SHUICHI KAWAI[1]

[1] Wood Research Institute, Kyoto University, Gokasho Uji, Kyoto 611, Japan

[2] Mitsui Chemicals, Inc., Yokohama, Kanagawa 247, Japan

Received 13 January 1999; accepted 1 March 1999

ABSTRACT: The thermal properties of isocyanate (IC) resins prepared with a small amount of polyether polyols and water were investigated using dynamic mechanical analysis (DMA). The bond strengths of 3-ply plywoods glued with these polyol-containing IC resins were also measured. The thermal stability was dramatically improved by addition of dipropylene glycol-type polyols with molecular weights of 400 and 1000. In addition, the bond strengths in a dry condition and after aging at 250°C for 10 min exhibited high values compared with that of an IC resin cured with water alone. However, addition of the same polyol type with a molecular weight of 3000 resulted in low heat stability and low bond strength. In the case of glycerin-type polyol with a molecular weight of 400, good thermal stability and slightly higher bond strength were obtained. When bisphenol A and pentaerythritol-type polyols were used, not much improvement in thermal stability was achieved. The bond strengths were similar or inferior to that of an IC resin cured with water only. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1807–1814, 1999

Key words: isocyanate resin; thermal properties; dynamic mechanical analysis; polyols; wood adhesives

INTRODUCTION

Over the past few years, there has been increasing concern over the formaldehyde emission from wood products utilizing formaldehyde-based resin adhesives. As one of the ways to overcome the above problem, the utilization of isocyanate (IC) resin adhesives has increased. Especially, polymeric diphenylmethane diisocyanate (P-MDI) has been commonly used as isocyanate adhesives for wood.[1–6] A previous paper[7] described the thermal properties of an IC resin cured with water using an aqueous emulsion-type polymeric diphenylmethane diisocyanate (E-MDI). The IC resin cured only with water exhibited lower thermal properties than those of the cured phenol formaldehyde (PF) resin. Heat treatments at high temperatures were not very effective for improving the heat resistance. On the other hand, isocyanates are reacted with polyols in the syntheses of urethane and urethane–urea polymers. Therefore, many types of polymers can be manufactured according to different formulations of isocyanates and polyols. In this paper, the effects of different polyether polyols on the thermal proper-

A part of this article was presented at the 35th Symposium on Adhesion of the Adhesion Society of Japan at Tokyo, June 19–20, 1997.

Correspondence to: K. Umemura (m54318@sakura.kudpc.kyoto-u.ac.jp).

Contract grant sponsor: Japanese Ministry of Education; contract grant number: 2626, 1997–2000.

Journal of Applied Polymer Science, Vol. 74, 1807–1814 (1999)
© 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/071807-08

Table I Properties of Polyols

Polyols	Constituent	No. Functional Group	Molecular Weight[a]	OH Value	Viscosity at 25°C (Pa S)
Diol400	DPG[b]+PO[b]	2	400	280	0.08
Diol1000	DPG+ PO	2	1000	112	0.15
Diol3000	DPG+ PO	2	3000	37.4	0.57
KB280	Bisp[b]+ PO	2	380	293	90.0
MN400	Gly[b]+ PO	3	400	420	0.70
PE600	PE[b]+ PO	4	370	600	7.70

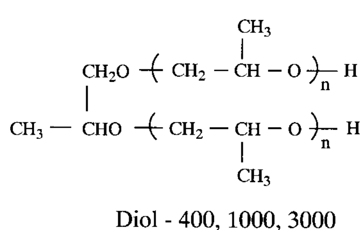
[a] Theoretical value.
[b] DPG: dipropylene glycol; PO: propylene oxide; Bisp: bisphenol A; Gly: glycerin; PE: pentaerythritol.

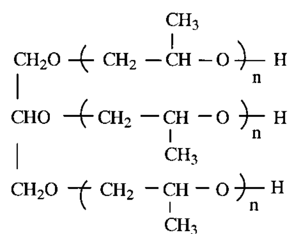
ties and bond strengths of an IC resin were investigated.

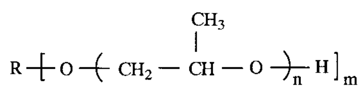
EXPERIMENTAL

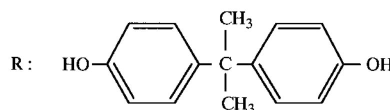
Materials

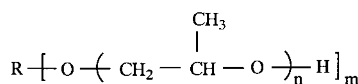
The E-MDI used in this study was the same as that described in our previous paper.[7] Six types of propylene oxide-based polyether polyols were supplied by Mitsui Chemical Inc. (Kanagawa, Japan). The properties and chemical structures of these polyols are shown in Table I and Figure 1, respectively. The functional group number of dipropylene glycol-type polyols was kept constant with varied molecular weights. For the other polyols with varied chemical structures and functional group number, the molecular weight was maintained at about 400. To cure the resin, these polyols were added at an NCO/OH ratio of 25, and water was added to obtain a final NCO/OH ratio of 0.5. For a control, only water was added at an


Diol - 400, 1000, 3000


MN-400




KB-280



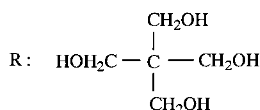

PE-600

Figure 1 Chemical structures of polyols.

Table II Preparation of IC Resins

Resin	E-MDI (g)	Polyol (g)	Water (g)	Polyol Content (wt %)[a]
IC	100	0	12.63	0
IC + Diol400	100	5.61	12.38	4.8
IC + Diol1000	100	14.03	12.38	11.1
IC + Diol3000	100	42.02	12.38	27.2
IC + KB280	100	5.36	12.38	4.6
IC + MN400	100	3.74	12.38	3.2
IC + PE600	100	2.62	12.38	2.3

[a] Polyol content (wt %) = polyol/(E-MDI + polyol + water) × 100.

NCO/OH ratio of 0.5. The mixtures of resin and additives were blended by stirring. The detailed formulation of the resins are shown in Table II. Resol PF resin was also used as described in the previous paper.[7]

Dynamic Mechanical Analysis (DMA)

The DMA was carried out using a RHEO VIBRON DDV-25FP instrument, with the scanning temperature ranging from ambient temperature to 360°C. The heating rate and frequency were 6°C/min and 10 Hz, respectively. The specimens for DMA were prepared in a similar manner as described in the previous paper.[7] The resins were cured at 40°C for 24 h in an oven.

Fourier Transform Infrared Spectroscopy (FTIR)

The specimens were removed from the dynamic mechanical measurement apparatus immediately after the temperature reached the IR measurement points. The specimens were then cooled and cut into two. The inner portion of the middle of the specimens were scraped off using a pair of tweezers. All infrared absorbance spectra were obtained with a Nihon Bunko FTIR 7000 spectrometer using the KBr pellet technique.

Bond Strength Measurement

Three-ply plywoods (size 25 × 25 cm) were prepared using rotary-peeled Apitong (*Dipterocarpus grandiflorus* Blco.) veneers of 1.6 mm thickness. The oven-dried density of the veneers was 0.66 g/cm^3. E-MDI and polyol, as well as water, blended under the same conditions as described above, were used as the IC resin adhesives. The IC and PF resin adhesives were applied to the core veneer at a spread rate of 160 g/m^2. Hot-pressing temperatures adopted for the IC and PF resin adhesives were 140 and 160°C, respectively. The assembled 3-ply plywood was hot-pressed for 5 min under a press pressure of 0.98 MPa. Test specimens were prepared according to the Japanese Industrial Standard (JIS) K6851. Heat-aging of the specimens at 250°C for 10 min, as well as under normal dry conditions, was performed. The tensile shear strengths of the adhesive bonds were measured under a crosshead speed of 2 mm/min. A total of 10 test specimens were used for each fabricating condition. The average value, standard deviation, and wood failure were calculated for each condition.

RESULTS AND DISCUSSION

Effect of Molecular Weight of Dipropylene Glycol-type Polyols on Thermal Properties

Figure 2 shows the dynamic mechanical properties of the IC resin cured by the addition of water and Diol400. The value of storage modulus (E') decreased gradually with increasing temperature, up to about 285°C, and then decreased rapidly. In the previous paper,[7] the IC resin cured with only water showed a rapid decrease of E' due to the degradation above 220°C. Therefore, the thermal stability of the IC resin was improved dramatically by the addition of a small amount of dipropylene glycol-type polyether polyol with a molecular weight of 400. The tan δ showed small and broad transitions at about 100, 200, and 260°C, respectively. In addition, a sharp peak was also observed at about 314°C. The low intensity transition between 50 and 150°C has been attributed to the breakdown of hydrogen bonding between polyurea groups and the ether oxygen of the polyol in copolyureas and polyurethane–urea.[8–10] Therefore, a transition could have oc-

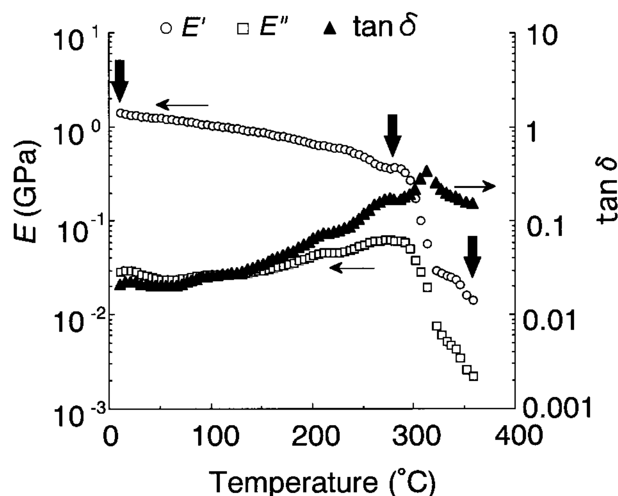


Figure 2 Dynamic mechanical properties of IC resin cured by adding water and Diol400. Arrows indicate IR measurement points.

curred at around 100°C in the Diol400 containing the IC resin. Considering the dynamic mechanical properties of the IC resin cured only with water,[7] the transition at 200°C could be due to the rearrangement of urea groups. In addition, the transitions at 260 and 314°C in the Diol400 containing IC resin would be due to degradation reactions.

To investigate the change in chemical structure of the IC resin cured with water and Diol400 during DMA measurement, IR spectra were obtained at 10, 285, and 360°C. The results are shown in Figure 3. The IR spectrum recorded a strong peak of 2276 cm^{-1} at 10°C, showing that the IC resin contained a considerable amount of unreacted isocyanate groups. The absorption bands at 3340 cm^{-1}, attributed to hydrogen-bonded N—H groups, and at 1669 cm^{-1}, attributed to disordered urea carbonyl groups,[11,12] were clearly identified at 10°C. The addition of Diol400 is expected to produce urethane linkages, indicated as a peak of the urethane carbonyl group, which are detected at around 1700–1730 cm^{-1}.[13] However, in this study, the above mentioned absorption band was not shown clearly and only appeared as a shoulder at 1669 cm^{-1}. The shoulder was a little higher compared to the IC resin cured with only water.[7] The reason seems to be that the amount of polyol added to the resin was very little. During the DMA measurement, the peak of 2276 cm^{-1} decreased with increasing temperature. Although the peak of 2100 cm^{-1} attributed to carbodiimide was observed at 290°C in the

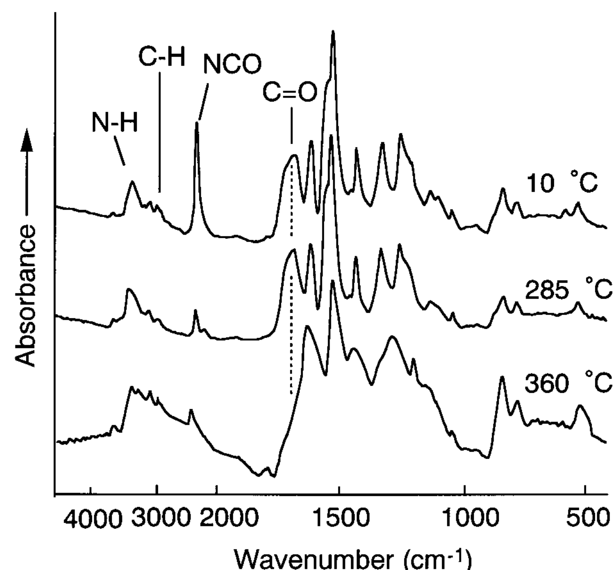


Figure 3 Infrared spectra changes of IC resin cured by adding water and Diol400 during DMA measurement.

water-cured IC resin,[7] the peak did not appear in the Diol400-added IC resin. On the other hand, the peak of 1669 cm^{-1} was observed clearly up to 285°C, then decreased with increasing temperature. This tendency was similar to that of the water-cured IC resin.[7]

Figure 4 shows the dynamic mechanical properties of the IC resin cured by the addition of water and Diol1000 with a molecular weight of 1000. The thermal stability of the IC resin was

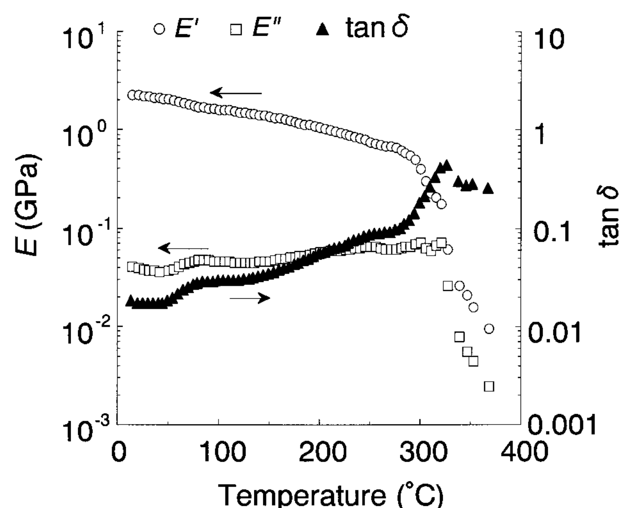


Figure 4 Dynamic mechanical properties of IC resin cured by adding water and Diol1000.

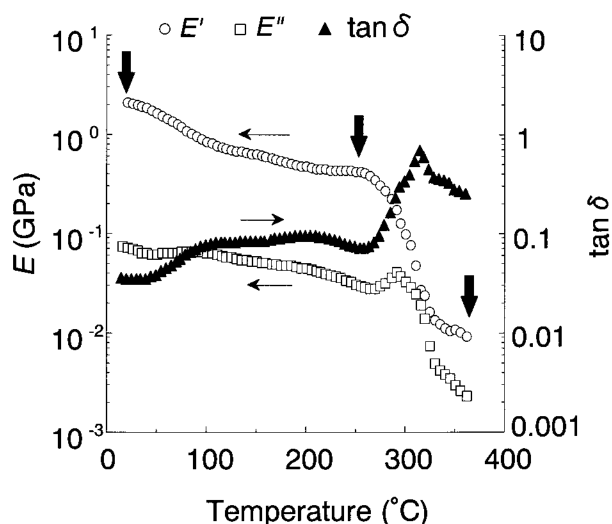


Figure 5 Dynamic mechanical properties of IC resin cured by adding water and Diol3000. Arrows indicate IR measurement points.

also improved dramatically. The value of E' decreased gradually with increasing temperature up to about 285°C and then decreased rapidly. The tan δ transition was only observed at around 90 and 325°C. The IR spectra of the Diol1000-added IC resin at 10°C was also similar to that of the Diol400-added IC resin, as shown in Figure 2. Generally, the reactions of water and polyol with IC resins lead to the formations of urea and urethane bonds, respectively. The thermal stability of urethane bonds is a little inferior to that of urea bonds.[14] It is well known that the polyol with a molecular weight between 500 and 5000 imparts a flexibility to the resin. Therefore, the thermal stability of the IC resin is believed to decrease with increasing polyol content. However, the opposite tendency was recognized in this study.

When water and Diol3000 with a molecular weight of 3000 were added to the resin, the dynamic mechanical properties were different from those with Diol400 and -1000 added. The result is shown in Figure 5. The E' exhibited a nonliner behavior and decreased rapidly at above 250°C, that is, the thermal stability seemed to be reduced by the addition of Diol3000. The tan δ had a broader transition over the temperature range of 50–250°C. This might be due to the marked breakdown of hydrogen bonding between polyurea groups and ether oxygens of polyol with increasing polyol content.[8] To investigate the change of the chemical structure during the DMA measurement, infrared spectra were obtained at 10, 255, and 360°C. The results are shown in Figure 6. Like the spectra of Diol400 in Figure 3, the bands of N—H groups at 3346 cm^{-1} and unreacted isocyanate groups at 2278cm^{-1} were observed at 10°C. The absorption bands at about 2870 cm^{-1}, regarded as CH_2 stretching, and about 1091 cm^{-1}, regarded as C—O—C[15,16], appeared clearly. These spectra were ascribed to the polyol structure of Diol3000. In addition, the small peak at 1711 cm^{-1}, regarded as hydrogen-bonded urethane carbonyl groups,[17,18] was observed, that is, the absorption peaks due to the additional polyol could be detected. The peaks of isocyanate and urethane carbonyl groups decreased at high temperature. In contrast, the peak of C—O—C was observed clearly at high temperature. This could be due to the presence of residual ether groups of polyol, as the ether groups are markedly heat stable in polyurethanes.[19,20]

Effects of Polyol Chemical Structures on Thermal Properties

Based on the above results, the addition of a small amount of dipropylene glycol-type polyol with a relatively low molecular weight was effective to improve the thermal stability of the IC resin. In this part, the effects of other polyols with a molecular weight of 370–400 on the thermal properties were investigated at the same NCO/OH

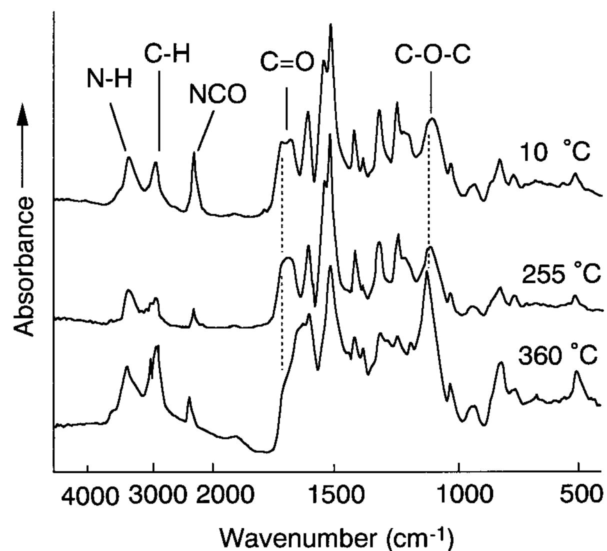


Figure 6 Infrared spectra changes of IC resin cured by adding water and Diol3000 during DMA measurement.

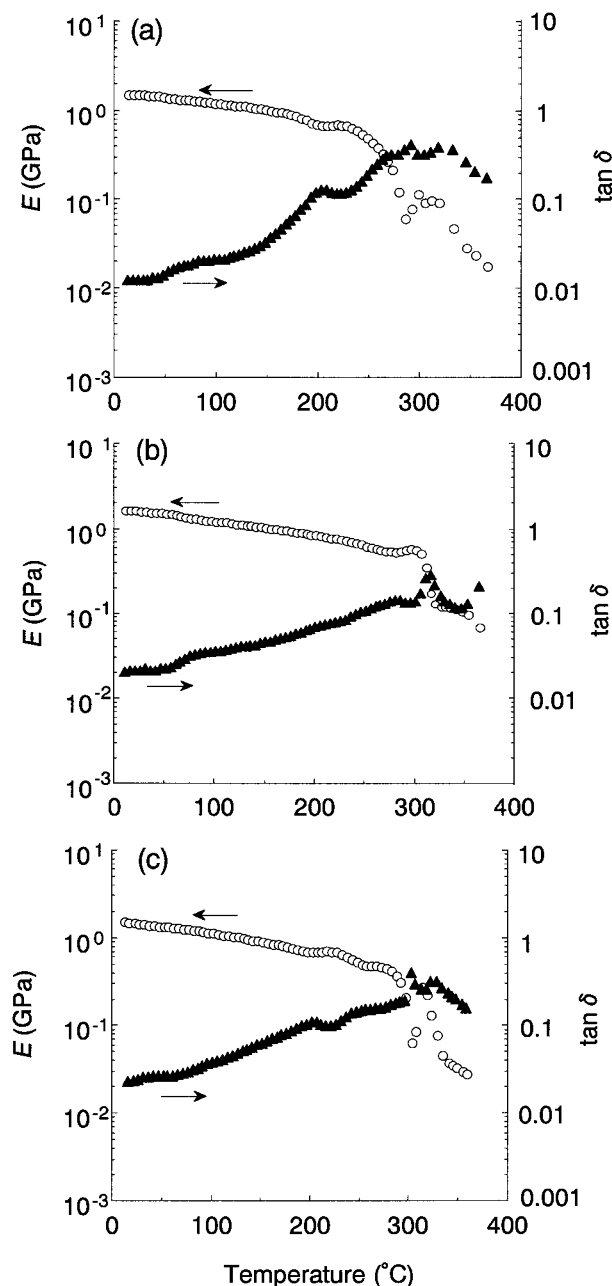


Figure 7 Dynamic mechanical properties of IC resin cured by adding water and (a) KB280, (b) MN400, and (c) PE600.

ratio. Figure 7 shows the dynamic mechanical properties of the IC resin cured with water and (a) KB280, (b) MN400, and (c) PE600 additions, respectively. In the case of KB280, E' decreased gradually when the temperature increased up to 180°C. A small sudden dip was observed at about 200°C, after which E' decreased rapidly. This behavior was similar to that of the IC resin cured with only water.[7] The tan δ showed transition points at around 90, 200, and 300°C. Generally, the thermal stability of the polymer would be improved by the introduction of a rigid structure such as an aromatic ring. However, the addition of KB280 with an aromatic structure was not effective for improving the thermal stability of the IC resin in this study. In the case of MN400, good thermal stability was observed up to about 300°C. It is clear that the addition of glycerin-type polyol could also improve the thermal stability of the IC resin. On the other hand, the E' of PE600 decreased gradually until 280°C. The tan δ transition was observed at about 200 and 300°C. Although PE600 had a pentaerythritol structure with four hydroxyl groups, the resultant thermal stability seemed to be inferior to that of MN400. The infrared spectra of these polyol-containing IC resins were also measured. Similar to the case of Diol400, the peak of the urethane carbonyl groups was barely detectable. The above results show that the functionality and chemical structures of polyol had an effect on the thermal stability of the IC resin.

Bond Strength of Polyol-added IC Resins

Figure 8 shows the dry bond strengths of 3-ply plywoods glued with the polyol-added IC resins. The dry bond strength of the PF resin is also shown for comparison with those of the IC resins. The average bond strengths of only-water-added IC and PF resins were 2.17 and 2.68 MPa, respectively. In the case of the Diol400- and -1000-containing IC resins, the average bond strength recorded was 2.56 MPa, similar to that of the PF resin. The bond strength therefore increased by 18% compared with that of the only-water-added IC resin. These differences were also statistically significant at the 95% significance level. Milota and Wilson[21] reported on the effect of various polyols on the performances of particleboard glued with P-MDI resins. The addition of polyethylene glycol with a molecular weight of 1000 was found to result in a higher internal bond compared to that of neat P-MDI.

In contrast, the bond strength and the percentage of wood failure of the Diol3000-added IC resin were 1.98 MPa and 100%, respectively. Considering the percentage of wood failure, the Diol3000-added IC resin was considered to have good adhesiveness. However, high polyol content in the resin could result in a high flexibility and energy-absorbing capacity of the resin. Consequently, a

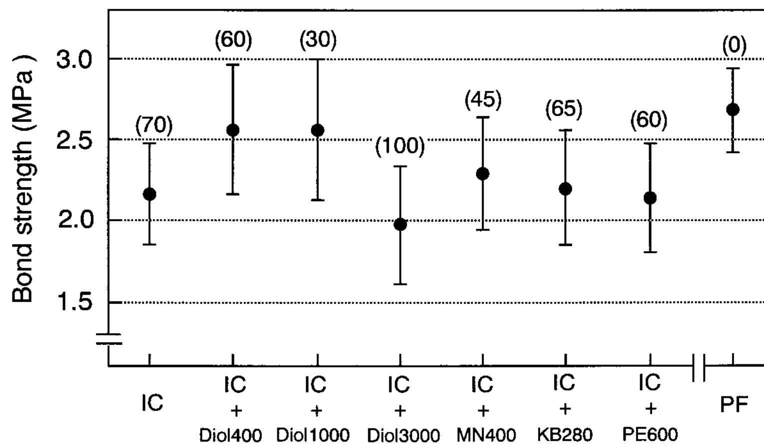


Figure 8 Dry bond strengths of some polyol-added IC resins. The numbers in the parentheses show the average values of the percentage of wood failure.

relatively low bond strength was recorded. In the case of the MN400-added resin, the bond strength was improved, but to a lesser extent. When the KB280- and PE600-added resins were used, the bond strengths were similar to that of the only-water-added IC resin.

Figure 9 shows the bond strengths after heat aging at 250°C for 10 min. In the case of the only-water-added IC and PF resins, the average values were 1.51 and 1.80 MPa, respectively. The bond strengths decreased by about 30% compared to the unaged specimens. Although the heat aging caused the bond strengths of Diol400 and -1000 to decrease, their bond strengths after heat aging were higher than that of the only-water-added IC resin after heat aging, by more than 15%. The MN400-added resin was also more resistant to heat aging compared to only-water-added IC resin. In the case of Diol3000, KB280, and PE600, the bond strengths after heat aging were similar or inferior to that of the only-water-added IC resin. The cause and mechanism of the good thermal stability and high bond strength of IC resins by the addition of some kinds of polyols will be discussed in the next report.

CONCLUSIONS

The effects of polyether polyols on the thermal properties of the IC resin were investigated at a NCO/OH ratio of 25. When the dipropylene glycol-

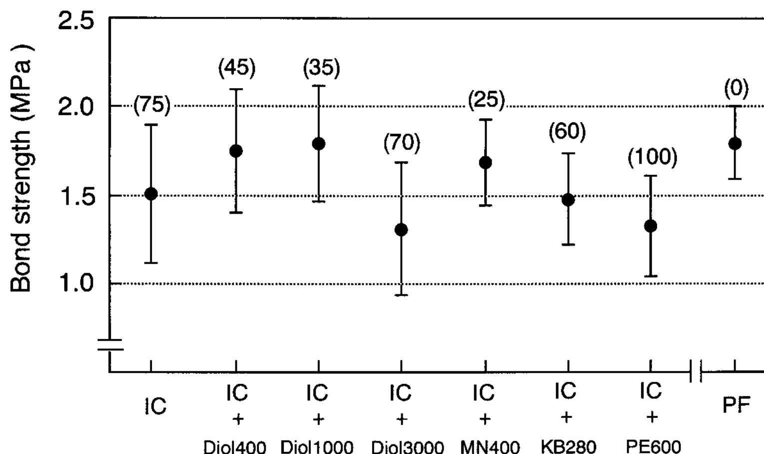


Figure 9 Bond strengths of some polyol-added IC resins after heat aging at 250°C for 10 min. The numbers in the parentheses show the average values of the percentage of wood failure.

type polyether polyols with relatively low molecular weight (Diol400 and -1000) were added to the IC resin in addition to water, the E' decreased gradually until about 280°C, followed by a rapid drop. Compared to the resin cured with only water, the thermal stability was dramatically improved. When the polyol with molecular weight of 3000 (Diol3000) was added to the IC resin, the thermal stability decreased. The addition of the glycerin-type polyol with a molecular weight of 400 (MN400) resulted in good thermal stability of the resin. When the bisphenol A- and pentaerythritol-type polyols (KB280 and PE600) were used, the improvement of the thermal stability was not so significant.

The bond strengths of 3-ply plywoods glued with the Diol400- and -1000-added IC resins showed higher values compared to that of the only-water-added IC resin, both before and after heat aging. The bond strengths were also similar to that of the PF resin. When the other polyol-added IC resins were used, the bond strengths were similar or inferior to that of the only-water-added IC resin.

This work was supported, in part, by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education (Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists No. 2626, 1997–2000). The authors thank Ms. Wong Ee Ding of the Wood Research Institute, Kyoto University, for her critical reading of this manuscript.

REFERENCES

1. Hawke, R. N.; Sun, B. C.; Gale, M. R. Forest Prod J 1993, 43, 15.
2. Johns, W. E.; Maloney, T. M.; Huffaker, E. M.; Saunders, J. B.; Lentz, M. T. In Proceedings of the 15th International Particleboard Symposium W.S.U., 1981; Maloney, T. M., Ed.; p 213.
3. Sun, B. C.; Hawke, R. N.; Gale, M. R. Forest Prod J 1994, 44(3), 34.
4. Sun, B. C.; Hawke, R. N.; Gale, M. R. Forest Prod J 1994, 44(4), 53.
5. William, E. J.; Thomas, M. M.; John, B. S.; Huffaker, E. M.; Lentz, M. M. In Proceedings of the 16th International Particleboard Symposium W.S.U., 1982; Maloney, T. M., Ed.; p 71.
6. Saito, F.; Taniguchi, T. Mokuzai Gakkaishi 1984, 30, 921.
7. Umemura, K.; Takahashi, A.; Kawai, S.; J. Wood Sci 1998, 44, 204.
8. Ryan, A. J.; Stanford, J. L.; Wilkinson, A. N. Polym Bull 1987, 18, 517.
9. Ryan, A. J.; Stanford, J. L.; Still, R. H. Polymer 1991, 32, 1426.
10. Stanford, J. L.; Still, R. H.; Wilkinson, A. N. Polym Int 1996, 41, 283.
11. Luo, N.; Wang, D.-N.; Ying, S.-K. Polymer 1996, 37, 3577.
12. Coleman, M. M.; Sobkowiak, M.; Pehlert, G. J.; Painter, P. C. Macromol Chem Phys 1997, 198, 117.
13. Priester, R. D.; McClusky, J. V., Jr.; O'Neill, R. E.; Turner, R. B. J. Cell Plast 1990, 26, 346.
14. Wang, C. L.; Melby, E. G.; Schmucker, A. E.; Sandels, F. V.; Harshbarger, R. H.; Spencer, R. L. Adhes Age 1994, 37(Dec.), 24.
15. Kaminski, A. M.; Urban, M. W. J Coat Technol 1997, 69(873), 113.
16. Lnig, L.; Ning, W. D.; Kang, Y. S. Macromolecules 1997, 30, 4405.
17. Teo, L.-S.; Chen, C.-Y.; Kuo, J.-F. Macromolecules 1997, 30, 1793.
18. Luo, N.; Wang, D.-N.; Ying, S.-K. Polymer 1996, 37, 3045.
19. Woolley, W. D. Br Polym J 1972, 4, 27.
20. Ravey, M.; Pearce, E. M. J Appl Polym Sci 1997, 63, 47.
21. Milota, M.; Wilson, J. B. Forest Prod J 1985, 35(7), 44.