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ORIGINAL ARTICLE

Kenji Umemura · Akihiro Takahashi · Shuichi Kawai

Durability of isocyanate resin adhesives for wood I: Thermal properties of isocyanate resin cured with water*

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Abstract The thermal properties of isocyanate (IC) resin cured with water were studied using dynamic mechanical analysis (DMA) and Fourier transform infrared spectroscopy. The thermal properties of cured phenol formaldehyde (PF) resin were also studied for comparison purposes. The DMA specimens were prepared using a unique technique. The relation between the mechanical and chemical changes of the resin during DMA was clarified. The cured PF resin had better thermal stability than the IC resin cured with water. The improvement of thermal stability in cured IC resin by heat treatment was considered to be less effective. The effect of the heating rate on the mechanical properties was also investigated. The apparent activation energy in the thermal degradation of cured IC resin was calculated based on the results obtained.

Key words Isocyanate resin adhesives · Thermal properties · Dynamic mechanical analysis · Fourier transform infrared spectroscopy · Wood adhesives

Introduction

Formaldehyde emission from wood products utilizing formaldehyde resin adhesives has become a public concern. Consequently, instead of formaldehyde resin adhesives, the utilization of isocyanate (IC) resin adhesives has increased. When IC resins are used as a binder for wood materials, the resins are believed to react with wood components and water.[1,2] However, if water is present in the wood materials, IC resins would react with the water in preference to the wood components.[3] Therefore the IC resin–water reaction is considered one of the most important reactions when bonding wood composite materials with IC resins.

The durability of wood composite products has become a topic of interest in recent years. The durability of adhesive is of great importance, as it determines the durability of resin-bonded wood-based products. Generally, the thermal properties of adhesives are thought to have a significant influence on durability. Several analytical methods, such as infrared spectroscopy (IR), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), have been used to investigate the thermal properties of the adhesives. In particular, DMA is useful for investigating the mechanical properties of the adhesives and significantly reflects the bonding performance. Only a few studies have been conducted on the mechanical properties of IC resin cured with water.[4] This could be attributed to the fact that the type of IC resin normally used for wood composite materials is polymeric diphenylmethane diisocyanate (PMDI), which is a hydrophobic resin. Furthermore, the IC resin cured with water is brittle, making preparation of the specimen for DMA difficult. An aqueous emulsion-type polymeric diphenylmethane diisocyanate (EMDI) has been developed recently.[5–7]

In the present study the specimens of IC resin cured with water for DMA were prepared using a unique preparation technique with EMDI. The thermal properties of IC resin cured with water were determined using DMA and Fourier transform infrared spectroscopy (FT-IR). The thermal properties of cured PF resin were also studied for comparison with those of the cured IC resin. The effect of heat treatment and the apparent activation energy in the thermal degradation were investigated as well.

K. Umemura (✉) · S. Kawai
Wood Research Institute, Kyoto University, Uji 611-0011, Japan
Tel. +81-774-38-3677; Fax +81-774-38-3678
e-mail: umemura @ kuwri.kyoto-u.ac.jp

A. Takahashi
Mitsui Chemicals, Yokohama 247, Japan

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Table 1. Properties of IC resin

Molecular weight ($\overline{M}_w$)	360–400
Viscosity (25°C, Pa · S)	0.1–1.0
Specific gravity (25°C)	1.23–1.25
NCO (%)	29–30

Table 2. Properties of PF resin

F/P ratio	2.0
pH (25°C)	11.2
Viscosity (25°C, Pa · S)	0.8
Specific gravity (25°C)	1.2
Gelation time (min) (boiling water)	28.5
Nonvolatile component (%) (135°C, 1 h)	40.0

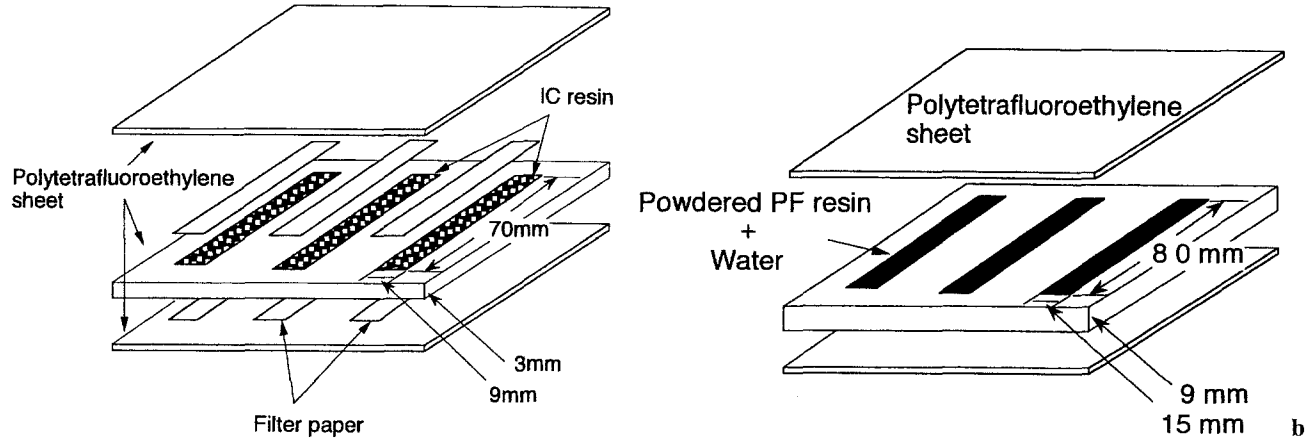

Fig. 1. Preparation of samples for DMA measurement. **a** Cured IC resin. **b** Cured PF resin

Materials and methods

Materials

The EMDI used in this study was supplied by Mitsui Chemical (Yokohama, Japan). This IC resin is distributed under the trade name UR-4000. The properties of the IC resin are shown in Table 1. To cure the IC resin, water was added at an NCO/OH ratio of 0.5 and stirred well. The resol phenol-formaldehyde (PF) resin used in this study was obtained from the same company. The properties of the PF resin are shown in Table 2.

Measurement of dynamic mechanical properties

The DMA was carried out with a Rheo Vibron DDV-25FP instrument, and the scanning temperature ranged from ambient temperature to 360°C. Heating rates were varied from 1° to 9°C/min. The oscillation frequency was 10 Hz, and the data were recorded at 5°C intervals.

Preparation of specimens

When preparing the specimens for DMA, resin is usually poured into a molding frame and cured. For water-added IC and resol PF resins, it is difficult to prepare the specimens using the above method because of the formation of cracks in brittle cured resins. Therefore for IC resin filter papers were used to prepare the specimen, as shown in Fig. 1a. The filter papers were placed in a molding frame prior to pouring the resin. After the resin was poured, more filter papers were placed on the resin to prevent formation of cracks. The IC resin was cured at 40°C for 24 h in an oven. The specimens with filter papers were then removed from the molding frame, and the filter papers were sanded out using a belt sander. The specimens obtained were about 70 × 9 × 2 mm.

In the case of resol PF resin, the specimens were prepared as follows: PF resin was first freeze-dried and pulverized to less than 100 mesh. About 4 g water was poured in each molding frame, as shown in Fig. 1b, followed by about 5 g powdered PF resin. The PF resin was cured at 80°C for 24 h in an oven. The cured PF resin obtained was sanded using a belt sander and was further heated at 160°C for 30 min to attain complete cure. The specimens obtained were about 65 × 9 × 2 mm. The apparent average densities of cured IC and PF resins were 0.85 and 1.25, respectively.

Fourier transform infrared spectroscopy

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

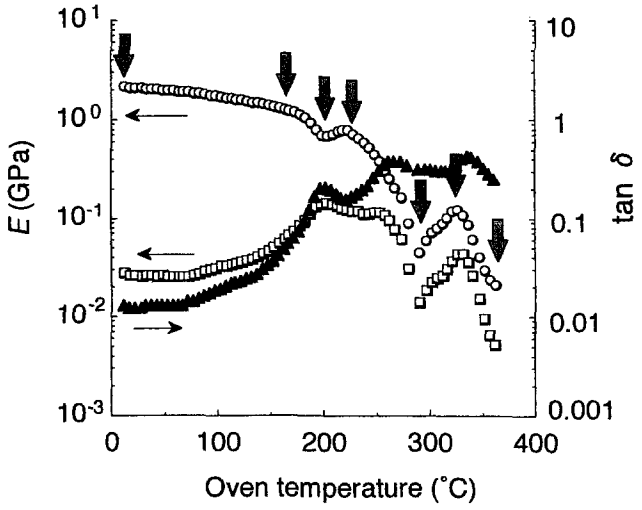

Fig. 2. Dynamic mechanical properties of cured IC resin observed at 6°C/min and 10Hz. *Arrows* indicate IR measurement points. *Open circles, E'; open squares, E''; filled triangles,* tan δ

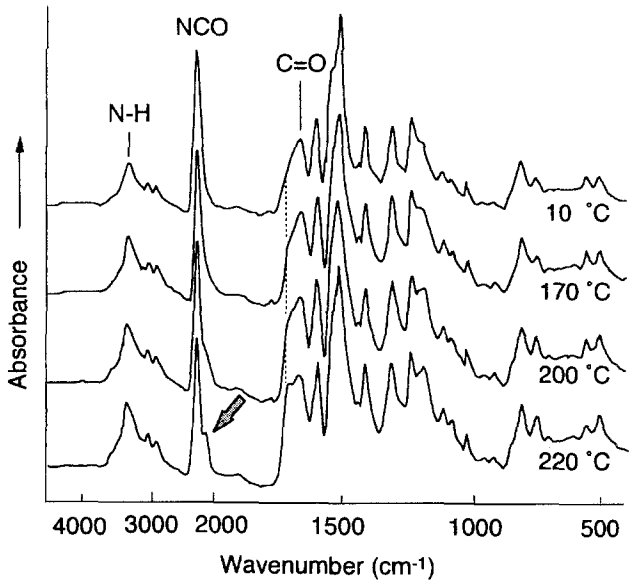

Fig. 3. Infrared spectra changes of cured IC resin during DMA measurement from 10° to 220°C

Results and discussion

Thermal properties of cured IC resin

Figure 2 shows the dynamic mechanical properties of cured IC resin observed at 6°C/min. The value for the storage modulus (E') decreased gradually with increasing temperature up to about 180°C. A sudden dip was observed at about 200°C, after which there was a rapid decrease, followed by a temporary increase from 300°C to 325°C. Tan δ had peaks at 200°C, 267°C, and 335°C. To investigate the change in chemical structure of cured IC resin during the measurement, infrared spectra were observed at several temperatures (Fig. 2). Figs. 3 and 4 show the IR spectral changes of cured IC resin from 10°C to 220°C and from 290°C to 360°C during the measurement, respectively. Numerous studies have reported IR measurement of polyurethanes and polyureas.[8–23] According to these works, the bands of primary interest are 3200–3500 cm^{-1} for the N—H stretching region, 2270–2280 cm^{-1} for isocyanate absorbance, and 1600–1800 cm^{-1} for the C=O stretching region.

In Fig. 3 the infrared spectrum recorded a strong peak of 2276 cm^{-1} at 10°C, showing that IC resin cured with water at 40°C for 24h may contain a considerable amount of unreacted isocyanate groups. In addition, the absorption bands at 3340 cm^{-1} attributed to hydrogen bonded N—H groups, and at 1661 cm^{-1} attributed to disordered urea carbonyl groups,[11,16] were clearly identified. The isocyanate absorption band decreased slightly with increasing heating temperature. The absorption band at about 2100 cm^{-1} appeared as a shoulder to the isocyanate absorption band at 220°C. This absorption band was assigned to the carbodiimide (—N=C=N—) based on the condensation of two NCO groups.[9,20] When the heating temperature was increased, the absorption band at 3340 cm^{-1} shifted toward the higher frequency of 3400 cm^{-1}. In polyurethane ureas, as the temperature is increased the average strength of the hydrogen bonds decreases, which is observed as a shift in the IR absorbance peak to a higher frequency.[14,22] This occurrence could be due to dissociation of the hydrogen bonding. The absorption band at 1707 cm^{-1} increased gradually, as indicated by a shoulder to the band at 1661 cm^{-1}. The band was observed clearly at 220°C. The absorption band at 1690–1710 cm^{-1} is generally assigned to urethane or urea carbonyl groups, but the detail assignment is still not clear. In this study, because IC resin reacted only with water, the resultant structures formed were mainly urea.

Merten et al.[20] reported that the biuret group was formed when heated at 200°C for 5 min, which was observed as an IR absorbance peak at 1695–1724 cm^{-1}. The absorption band at 1705 cm^{-1} in 2-methylpentane-1,5-diphenylurea exposed to temperatures above 160°C was regarded as the formation of monourea.[16] Luo et al.[24] reported that the ordered urea hydrogen bonds formed at 130°C–220°C in segmented polyurethane urea. Although clear assignment of the absorption band at 1707 cm^{-1} is difficult, it is thought to be due to the segmental motion of IC resin polymer derived from the rearrangement of urea groups.

In Fig. 4 the absorption band of the IC group is seen to diminish with increasing heating temperature. The absorption band at about 1700 cm^{-1} as a shoulder of 1665 cm^{-1} was not observed at 290°C. The bands at about 1661 and 2100 cm^{-1} were missing in the temperature range 325°C–360°C. Therefore degradation of the main chain of IC resin polymer would take place in this temperature range.

Based on the above results, the dynamic mechanical behavior of cured IC resin in Fig. 2 was analyzed. From room temperature to about 200°C the chemical structure of cured IC resin was rather stable, except for some dissociation in

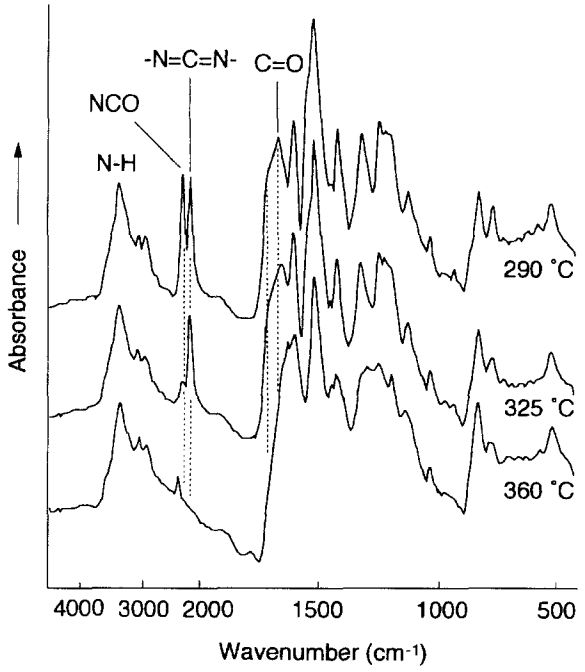

Fig. 4. Infrared spectra changes of cured IC resin during DMA measurement from 290° to 360°C

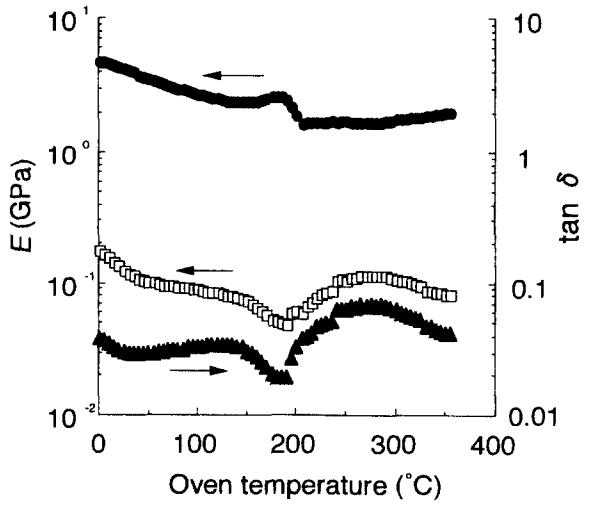

Fig. 5. Dynamic mechanical properties of cured PF resin. *Filled circles*, E'; *open squares*, E''; *filled triangles*, tan δ

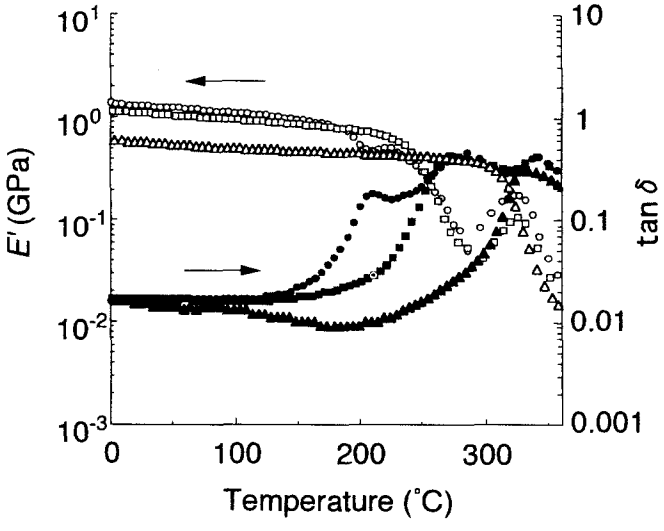

Fig. 6. Effect of heat treatment of the mechanical properties of cured IC resin; *Circles*, 160°C for 10 min; *squares* 200°C 10 min; *triangles*; 300°C for 10 min

hydrogen bonding. Urea groups are considered to contribute to hydrogen bonding in two different directions simultaneously, as each C=O group is balanced by two NH groups in the urea configuration.[25] When the IC resin was heated to 200°C, segmental motion of the IC resin polymer took place. The temporary recovery of E' at about 220°C was thought to form a more stable structure because of rearrangement of urea groups. Thereafter the rapid decrease of E' with increasing temperature can be accounted for by the onset of a degradation reaction, such as formation of carbodiimide. Using torsional braid analysis (TBA), Furusho et al.[26–28] observed that the relative shear modulus of several thermoplastic polymers increased temporally at a higher temperature. This behavior was attributable to the formation of the cross-linked structure, the cyclic compound, and the C—C double bond during the decomposition reaction. These formations were confirmed in polyureas.[29] Therefore the temporary increase of E' at 325°C was thought to be due to the occurrence of the above chemical reactions.

Thermal properties of cured PF resin

The thermal properties of cured PF resin were studied for comparison with those of cured IC resin. The result is shown in Fig. 5. The cured PF resin at room temperature had high rigidity. The E' value decreased gradually when the temperature was increased to about 160°C because of thermal softening. It fell sharply from 2.6 to 1.6 GPa at about 180°C, probably caused by the recommencement of segmental motion. Thereafter the E' increased slightly with increasing temperature. The tan δ had a broad peak from 190°C to 360°C, whereas the cured PF resin appeared to take place after curing in this temperature range. Generally, when the heating temperature is increased above the curing temperature, the reaction of the cross-linked polymer continues to take place. When measuring the modulus as a function of temperature, the modulus decreases when the curing temperature is approached. If further reaction takes place, the modulus soon starts to increase, rather than decrease, as the temperature is raised.[30,31] Consequently, it can be deduced that the cured PF resin has better thermal stability than the cured IC resin.

Effect of heat treatment

To improve the thermal stability, the cured IC resin was further treated by heating. Fig. 6 shows the dynamic me-

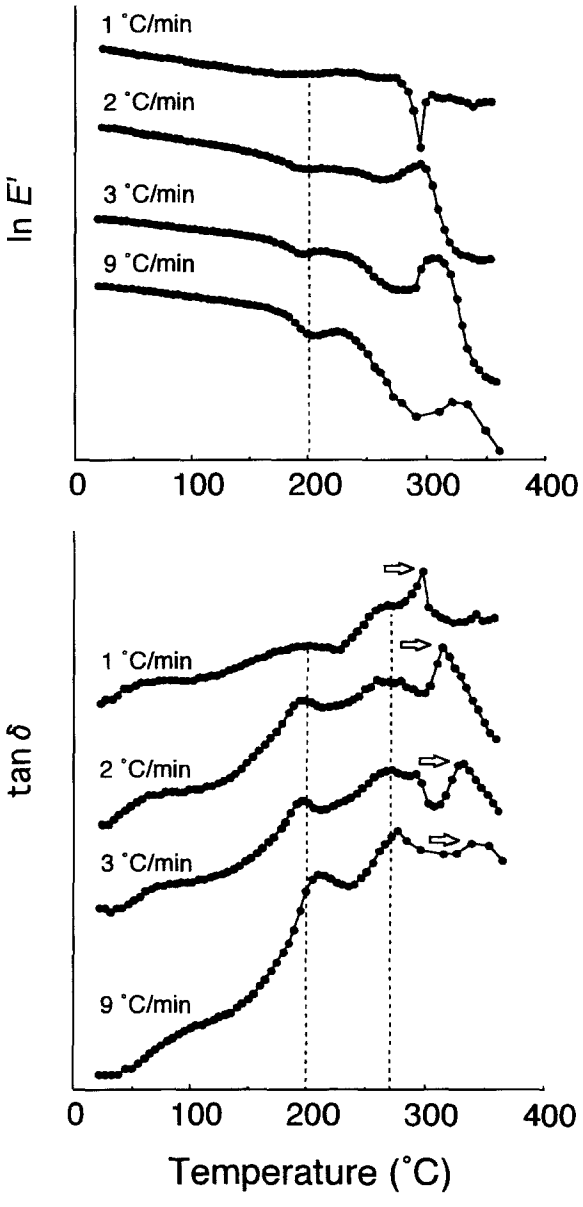

Fig. 7. Heating-rate dependence for the mechanical properties of IC resin

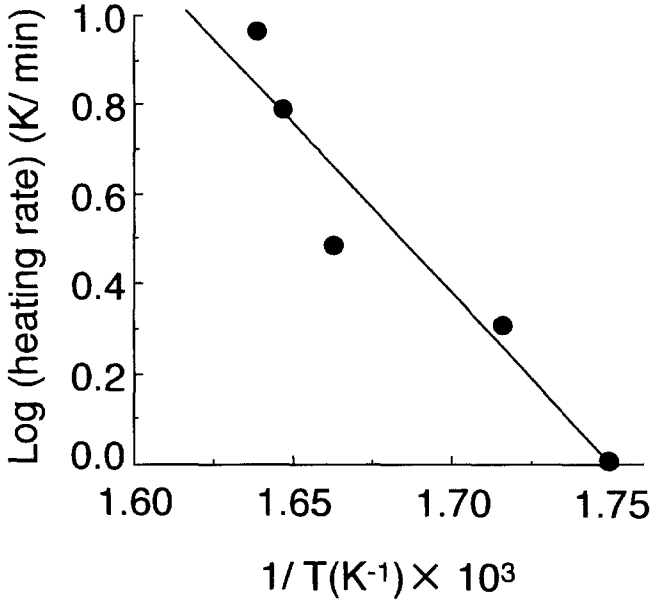

Fig. 8. Plots of the logarithmic heating rate versus the reciprocal temperatures of the maximum tan δ of IC resin

chanical properties of cured IC resins treated at 160°, 200°, and 300°C for 10 min. For the resin treated at 160°C for 10 min, the behaviors of E' and tan δ exhibited a trend similar to that of the untreated cured IC resin, as shown in Fig. 2. Because the hydrogen-bonded urea structure has good thermal stability[22] this heat treatment seemed insufficient to allow the segmental motion. In the case of treatment at 200°C for 10 min, the decrease in E' was not observed at about 200°C, and tan δ also did not register a peak at this temperature. The heat treatment at 200°C probably provided enough thermal energy to allow the improved ordering of the molecular structure.[16,24] The behavior of E' and tan δ at temperatures >200°C was similar to that of the untreated IC resin. When the resin was treated at 300°C for 10 min, the E' at room temperature indicated a low value. To investigate the chemical structure of the treated IC resin the IR spectra were obtained, based on which the disappearance of the isocyanate group and appearance of the carbodiimide were observed. Consequently, the low E' value could be attributed to considerable decomposition during the treatment. When the treated resin was heated to >300°C, the E' value decreased rapidly owing to further decomposition. Based on the above results, improvement of the thermal stability by heat treatment was considered less effective. Further study is necessary to identify a more effective method for improving the thermal stability of cured IC resin.

Dependence of mechanical properties on heating rate

Figure 7 shows the dependence of the mechanical properties of cured IC resin on the heating rate. When the temperature was raised at a rate of 1°C/min, the E' value decreased slightly until about 280°C; It then dipped sharply at about 300°C. The tan δ recorded a broad peak at around 200°C, followed by two peaks at about 270°C and 300°C. When heated at 2°C/min, a slight decrease in E' was observed at about 200°C, with a temporary increase at about 300°C. Three tan δ peaks were clearly observed at about 200°C, 270°C, and 310°C. The behaviors of E' and tan δ at the 3° and 9°C/min rates were similar to those seen at 2°C/min.

Furusho et al.[27] reported that mechanical behavior due to physical processes such as melting and glass transition was scarcely affected by the heating rate, whereas the chemorheological behavior due to chemical processes such as decomposition was shifted to a higher-temperature re-

gion with increasing heating rate. Based on the logarithmic decrement curves measured at several heating rates, the apparent activation energy during thermal degradation of polymers was calculated.[28]

In the present study it was observed that the tan δ peaks at about 200°C, indicating that segmental motion and 270°C were scarcely affected by the heating rate. Within this region, the degradation reaction, such as formation of carbodiimide, was observed, as discussed above. From the above discussion, it can be concluded that this mechanical change was affected significantly by the physical process rather than by the chemical process. On the other hand, the tan δ peak at >300°C was shifted to higher temperatures with the increasing heating rate. In this region considerable degradation reactions are considered to have taken place, as mentioned above. The apparent activation energy of the thermal degradation of cured IC resin was calculated based on the above report.[28] Figure 8 shows the relation between the logarithm of the heating rate and the reciprocal of the temperature of the maximum tan δ peak. The apparent activation energy obtained from the slope of the line was 62.7 kJ/mol, a value similar to that for polyurea, reported in a previous paper.[29]

Conclusions

The thermal properties of IC resin cured with water were studied using DMA and FT-IR. When the cured IC resin was heated to 200°C, a sudden decrease in E' derived from the segmental motion was observed. The temporary recovery of E' at about 220°C could be caused by formation of the more stable structure. Thereafter E' rapidly decreased with increasing temperature. Cured IC resin exhibited lower thermal stability than cured PF resin. The improvement in thermal stability by heat treatment was thus considered to be less effective for IC resin. The effect of the heating rate on the mechanical properties was also investigated. Based on the results obtained, when the heating temperature was >300°C significant degradation reactions could have taken place. The apparent activation energy at >300°C was 62.7 kJ/mol.

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References

1. Johns WE (1982) Isocyanates as wood binders: a review. J Adhesion 15:59–67
2. Steiner PR, Chow S, Vadja S (1980) Interaction of polyisocyanate adhesive with wood. Forest Prod J 30(7):21–27
3. Weaver FW, Owen NL (1995) Isocyanate-wood adhesive bond. Appl Spectrosc 49:171–176
4. Taki K, Tomita B, Mizumzchi H (1983) Studies on aqueous vinyl polymer solution isocyanate adhesives. III. (in Japanese). Mokuzai Gakkaishi 29:145–152
5. Lay DG, Cranley P (1994) Applications and developments of polyurethane adhesives. Adhesives Age 31(6):6–9
6. Juliá J, Salvatella D, Lope J (1994) Aqueous polyurethane dispersions for adhesive applications. Adhesives Age 31(5):26–31
7. Dieterich D (1981) Aqueous emulsions dispersions and solutions of polyurethanes; synthesis and properties. Prog Organic Coatings 9:281–340
8. Christenson CP, Harthcock MA, Meadows MD, Spell HL, Howard WL, Creswick MW, Guerra RE, Turner RB (1986) Model MDI/butanediol polyurethanes: molecular structure, morphology, physical and mechanical properties. J Polym Sci (B) Polym Phys 24:1401–1439
9. Grassie N, Zulfiqar M (1978) Thermal degradation of the polyurethane from 1,4-butanediol and methylene bis(4-phenyl isocyanate). J Polym Sci Polym Chem Educ 16:1563–1574
10. Nakayama N, Ino T, Matsubara I (1969) Infrared spectra and structure of polyurethane elastomers from polytetrahydrofuran, diphenylmethane-4,4′-diisocyanate, and ethylenediamine. J Macromol Sci Chem A3:1005–1020
11. Luo N, Wang D-N, Ying S-K (1996) Crystallinity and hydrogen bonding of hard segments in segmented poly(urethane urea) copolymers. Polymer 37:3577–3583
12. Camargo RE, Macosko CW, Tirrell M, Wellinghoff ST (1983) Hydrogen bonding in segmented polyurethanes: band assignment for the carbonyl region. Polymer Commun 24:314–315
13. Luo N, Wang D-N, Ying S-K (1996) Hydrogen bonding between urethane and urea: band assignment for the carbonyl region of FTIR spectrum. Polymer 37:3045–3047
14. Coleman MM, Lee KH, Skrovanek DJ, Painter PC (1986) Macromolecules 19:2149–2157
15. Elwell MJ, Ryan AJ, Grünbauer HJM, Van Lieshout HC (1996) FTIR study of reaction kinetics and structure development in model flexible polyurethane foam systems. Polymer 37:1353–1361
16. Coleman MM, Sobkowiak M, Pehlert GJ, Painter PC (1997) Infrared temperature studies of a simple polyurea. Macromol Chem Phys 198:117–136
17. Bailey FE Jr, Critchfield FE (1981) Chemical reaction sequence in the formation of water-blown, urethane foam. J Cell Plast 17: 333–339
18. Born L, Hespe H (1985) On the physical crosslinking of amine-extended polyurethane urea elastomers: a crystallographic analysis of bis-urea from diphenyl methane-4-isocyanate and 1,4-butane diamine. Coll Polym Sci 263:335–341
19. Beachell HC, Ngoc Son CP (1963) Color formation in polyurethanes. J Appl Polym Sci 7:2217–2237
20. Merten R, Lauerer D, Dahm M (1968) IR spectroscopic studies of urethane foam formation. J Cell Plast 4:262–275
21. Prister RD, Mcclusky JV, O'Neill RE, Turner RB (1990) FTIR: a probe into the reaction kinetics and morphology development of urethane foams. J Cell Plast 26:346–367
22. Teo L-S, Cem C-Y, Kuo J-F (1997) Fourier transform infrared spectroscopy study on effect of temperature on hydrogen bonding in amine-containing polyurethanes and poly(urethane-urea)s. Macromolecules 30:1793–1799
23. Brunette CM, Hsu SL, MacKnight WJ (1982) Hydrogen-bonding properties of hard-segment model compounds in polyurethane block copolymers. Macromolecules 15:71–77
24. Luo N, Wang D-N, Ying S-K (1997) Hydrogen-bonding properties of segmented polyester poly(urethane urea) copolymer. Macromolecules 30:4405–4409
25. Bonart R (1979) Thermoplastic elastomers. Polymer 20:1389–1403
26. Furusho N, Komatsu T, Nakagawa T (1973) Study of thermal degradation of several polymers by torsional braid analysis. Nippon Kagaku Kaishi 94:1166–1174
27. Furusho N, Komatsu T, Nakagawa T (1975) A torsional braid analysis of polymethacrylates, polyacrylate, poly(vinyl alcohol), and their related polymers during the thermal degradation. Bull Chem Soc Jpn 48:396–402
28. Furusho N, Komatsu T, Nakagawa T (1975) The heating-rate dependence of the mechanical properties of several polymers at higher temperatures. Bull Chem Soc Jpn 48:1404–1410

29. Belyakov VK, Bukin II, Tarakanov OG, Berlin AA (1971) Several features of the thermal and thermaloxidative degradation of polyureas. Polymer USSR 13:1779–1798
30. Nielsen LE (1969) Cross-linking: effect on physical properties of polymers. J Macromol Sci Rev Macromol Chem C3(1):69–103
31. Hirai Y, Kubota Y, Matsumoto A (1993) Relationship between structure and physical properties of cured phenolic resins (in Japanese). Netsukokasei Jushi 14:196–201