Synthesis and Viscoelastic Properties of New Thermosetting Resins Having Isocyanurate and Oxazolidone Rings in Their Molecular Structures

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Synopsis

A new type of thermosetting resin can be obtained from solventless varnishes composed of polyfunctional isocyanates and epoxides. The IR spectra show that the cured resins have isocyanurate and oxazolidone rings in their chemical structure, hence their name, isocyanurate–oxazolidone resins. The viscoelastic behavior of the cured resins can be varied considerably by selecting an appropriate reactant species and changing the equivalent ratio of the isocyanate and epoxy groups in the varnishes. Three relaxations, labeled α, β, and γ, characterize their dynamic mechanical spectra. The α-dispersion is due to the glass transition, the β-dispersion, to local mode motions of the backbone chains of resins, and the γ-dispersion, to the molecular motions of long alkyl chains. If certain additives are mixed into the varnishes before curing, microphase separation takes place during the reactions. The resins finally obtained have a peculiar physical structure in which rubber particles are dispersed throughout a matrix phase as confirmed by scanning electron-microscopic analysis and viscoelastic behavior.

INTRODUCTION

Over the past decade an increasing number of investigations have been made to develop and analyze thermosetting resins and their properties. Solventless varnishes have received considerable attention because of their practical applications; for example, epoxy resins are now widely used.[1–5]

Generally speaking, the structure of thermosetting resins can be very complex. Their chemical and physical structures depend not only on the monomer species used for curing, but also on specific curing conditions, because more than one reaction can take place and the kinetics of each reaction exhibit different temperature dependencies. As a result, mechanical properties differ variously depending on the combination of these factors. In the same way, the dynamic mechanical properties of various polymers over wide ranges of temperature and frequency have been studied by a number of investigators, since they are very sensitive to changes of chemical and physical structures of polymer molecules.[6,7] As for the thermosetting resins, they are significantly influenced by the degree of cross linking, network structure, chemical species, morphology, etc.

The purpose of this paper is, first of all, to present new thermosetting resins which are composed of polyfunctional isocyanates and epoxides and then to show how the chemical and physical structures of the cured resins reveal themselves in their viscoelastic behavior.

TABLE I
Commercially Available Monomers for Isocyanurate–
Oxazolidone Resins

| Monomer | | Viscosity (Pa·s) | Equivalent weight | Maker |
sign	name			
L–MDI	modified diphenyl – methane diisocyanate	0.1 at 25℃	138	Bayer AG
DER332	diglycidylether of bisphenol A	4~5 at 25℃	172~179	Dow Chem. Co.
DEN431	polyglycidylether of phenolnovolac	1.4~2.0 at 50℃	172~179	Dow Chem. Co.
EP 830	diglycidylether of bisphenol F	3.0~4.0 at 25℃	170~190	Dainihon Ink Ltd.
EP4080	diglycidylether of biscyclohexanolpropane	3.0~4.5 at 25℃	235~255	Asahi Denka Ltd.
CY192	diglycidylester of tetrahydrophthalic acid	0.45~0.55 at 25℃	151~167	Ciba Geiay
CY183	diglycidylester of hexahydrophthalic acid	0.32~0.38 at 25℃	147~161	Ciba Geigy
EP871	diglycidylester of linoleic dimer acid	0.4~0.9 at 25℃	390~470	Shell Chem. Co.

EXPERIMENTAL

Materials

All the materials used were commercially available. The mechanical properties of isocyanurate–oxazolidone resins can be systematically varied from hard to flexible. This can be done by changing the species and quantity of epoxides and/or isocyanates in the mixture before curing, as discussed later in detail. In this report, modified diphenylmethane-4,4-diisocyanate (L-MDI, Desmodur CD from Bayer AG) was selected as the isocyanate component for various epoxide components, since it was possible to obtain solventless varnishes having low viscosity. The viscosity of L-MDI was 0.1 Pa·s at 25°C. The epoxides used here are presented in Table I, together with their physical and chemical properties. The viscosities of the epoxide components were rather low. Therefore, all the mixtures of L-MDI and epoxides were low viscosity liquids without solvent. Although the respective viscosities differed depending on the compositions, they were in the range of 0.1–5.0 Pa·s at 25°C.

Liquid copolymer of carboxyl-terminated butadiene–acrylonitrile (CTBN) containing 17 wt % bound acrylonitorile was studied as an additive. This compound is manufactured by B. F. Goodrich Co. under the trade name Hycar CTBN. As a curing agent, 0.1 wt % of 1-cyanoethyl-2-ethyl-4-methylimidazole was employed. The equivalent ratio of isocyanate and epoxy groups, one of the dominant factors determining the mechanical properties, was varied from 1.0 to 10.0. Curing temperatures of 80, 130, 180, and 200°C were employed sequentially.

Measurements

The infrared spectra were obtained for the cured isocyanurate–oxazolidone resins by using a Hitachi 260-50 Spectrometer.

Dynamic mechanical spectra were obtained using a fully automated viscoelastic spectrometer VES-S (Iwamoto Co., Ltd.) at a frequency of 10 Hz over the temperature range of −160–300°C.

RESULTS AND DISCUSSION

Chemistry of the New Thermosetting Resins

Several studies have been carried out on the polymerization reaction in which poly(2-oxazolidones) are formed from diisocyanates and diepoxides.[8–14] In order to obtain information on the reaction mechanism and process leading to poly(2-oxazolidones), studies on the formation of a model compound 3-phenyl-5-phenoxymethyl-2-oxazolidone have also been made.[8–11] Research on the heterocyclization reaction of phenylisocyanate and phenylglycidyl ether in a solution of dimethyl sulfoxide has shown that the isocyanurate rings are formed from the isocyanates by the catalytic effects of imidazoles at temperatures below 100°C and converted into oxazolidone rings at temperatures above 110°C.[15] The reactions are as follows:
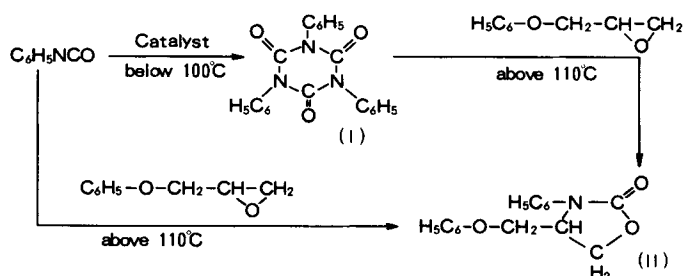
The formation kinetics of (I) and (II) have already been investigated. The reaction mechanism producing the trimer of phenylisocyanate was reported in detail by Sanders and Frish.[9] Koyama and Narahara[15] considered the rate process in investigating the reaction of the trimer of phenylisocyanate with phenylglycidyl ether to produce 3-phenyl-5-phenoxymethyl-2-oxazolidone.

Since both the isocyanurate and oxazolidone rings were easily formed by the reaction of isocyanate and epoxy groups, it may be assumed that varnishes consisting of polyfunctional isocyanates and epoxides can provide new types of heat resistant thermosetting resins.[16,17] The formation reaction and the resultant chemical structure of cured resins are believed to be as shown in Figure 1. Comparison of the infrared spectra before and after curing a mixture of diepoxides and diisocyanates showed that when the mixture was thermally cured under certain conditions, isocyanurate and oxazolidone rings were formed in the molecular structure of cured resins, while isocyanate and epoxy groups of monomers disappeared.[17]

Resins cured from the varnishes composed of polyfunctional isocyanates and epoxides were hard and rather brittle. Taking their most noticeable structural feature into account, the authors designated this kind of resin "isocyanurate–
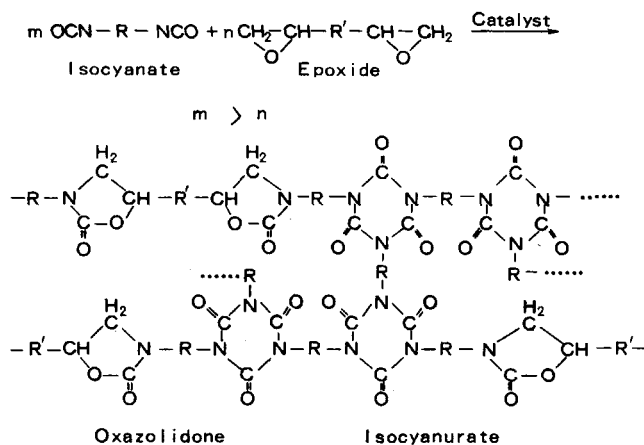
Fig. 1. Chemical structure of isocyanurate–oxazolidone resins when diisocyanates react with diepoxides.

oxazolidone resin," abbreviated as ISOX resin. Before curing, most of the varnishes obtained by mixing L-MDI and epoxides shown in Table I were low viscosity liquids without solvent, one of the most important characteristics of ISOX resins.

Infrared spectra of various ISOX resins are shown in Figures 2–4. Absorptions due to the stretching vibrations of the carbonyl groups of isocyanurate and oxazolidone rings could be observed at 1710 and 1750 cm^{-1}, respectively, while the
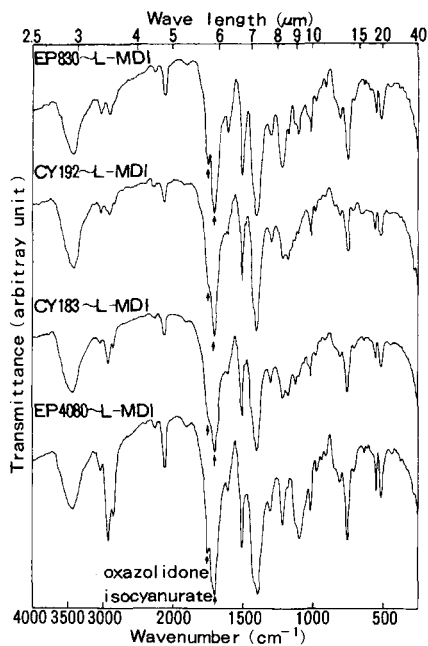

Fig. 2. IR spectra of isocyanurate–oxazolidone resins in which epoxide components were changed for the selected isocyanate component of L-MDI with I/E ratio of 2.5.
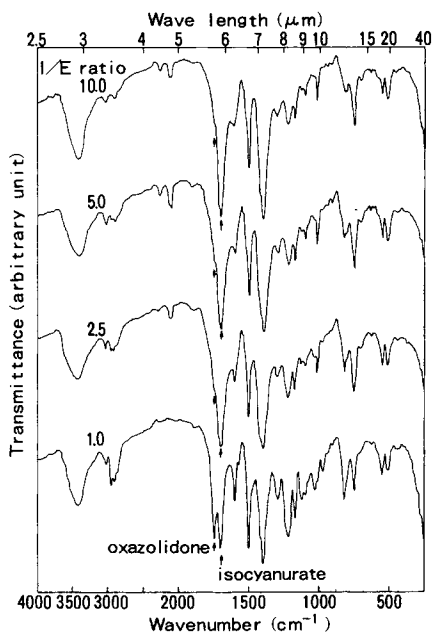
Fig. 3. IR spectra of isocyanurate–oxazolidone resins. The I/E ratio in the varnishes composed of L-MDI and DER322 was changed.

absorptions due to isocyanate (2275 cm^{-1}) were very small. Epoxy groups (910 cm^{-1}) could not be readily observed.

The absorption at 2100–2150 cm^{-1} should be due to the carbodiimide group of the isocyanate monomers used here, because this absorption was not observed
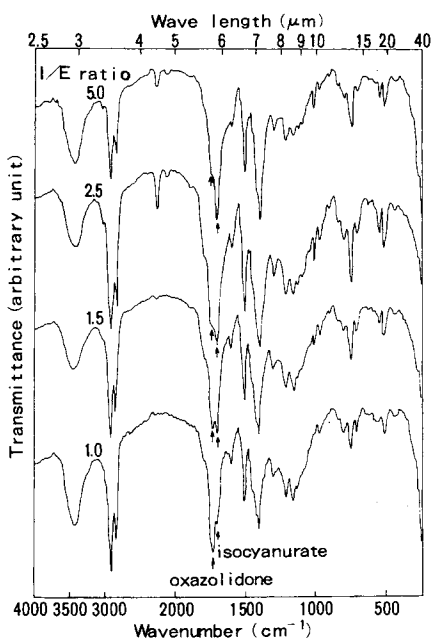

Fig. 4. IR spectra of isocyanurate–oxazolidone resins. The I/E ratio in the varnishes composed of L-MDI and EP871 was changed.

in the case of ISOX resins cured by using purified isocyanate monomers (diphenylmethane-4,4'-diisocyanate) as reported previously.[17]

It was assumed that the molar ratio of isocyanurate and oxazolidone rings in the cured ISOX resins was governed not only by the equivalent ratio of isocyanate and epoxy groups (I/E ratio) in the varnishes before curing, but also by the chemical nature of the reactant species themselves. In Figure 2, IR spectra of ISOX resins are compared, in which epoxide components were different for the selected isocyanate component and the selected I/E ratio of 2.5. In every case, the intensity of absorption due to isocyanurate rings was much larger than that due to oxazolidone rings.

Figures 3 and 4 show how the IR spectra change with increasing I/E ratio of the varnishes. There was a tendency for the intensity of absorption due to isocyanurate groups to become smaller, while that due to oxazolidone groups to become larger with decreasing I/E ratio. This tendency differed considerably depending on the epoxy species used for the resins. When ISOX resins using aromatic epoxides such as DER332 were prepared, the intensity of absorption due to isocyanurate rings was larger than that due to oxazolidone rings even for the I/E ratio of 1.0. However, in the case of ISOX resins (I/E ratio of 1.0) prepared using aliphatic epoxides such as EP871, the absorption due to oxazolidone was very large and that due to isocyanurate, very small. Thus this polymer was similar to poly(2-oxazolidone) having only slight amounts of isocyanurate rings in their chemical structure.

Taking into account the results of model reactions reported by Koyama and Narahara,[15] it was felt that isocyanurate rings which were formed in the first curing process of varnishes at 80°C and unreacted isocyanate groups might react with epoxides and convert to oxazolidone rings in the second and third curing processes at temperatures higher than 130°C. This seemed to occur easily in the systems which have low glass transition temperatures, but not in those which have high glass transition temperatures. That is, the conversion to oxazolidone rings from isocyanurate rings would occur more easily in EP871–L-MDI ISOX resins than in DER332–L-MDI ISOX resins. This should reflect on the viscoelastic properties of the various ISOX resins in which the molar ratio of isocyanurate rings and oxazolidone rings in the structure of the cured resins differed depending on the I/E ratio and epoxy groups of the varnishes and reactant species.

Viscoelastic Properties of Homogeneous ISOX Resins

Viscoelastic behavior of the resins which were cured from the varnishes consisting of L-MDI and various epoxides with the I/E ratio of 2.5 is shown in Figures 5 and 6. Figures 7–9 also show the temperature dependence of viscoelasticity of the various ISOX resins cured from the varnishes having I/E ratios from 1.0 to 5.0.

Three kinds of dispersions were observed for the homogeneous ISOX resins. The peak temperatures of each dispersion are summarized in Table II, together with the results observed for the rubber-modified ISOX resins which are discussed in the following section. The peak temperature of the α-dispersions which is due to the glass transition were considerably different depending on the epoxide species and I/E ratio. The decreasing effect of epoxides on the α-peak temperature was in the following order:

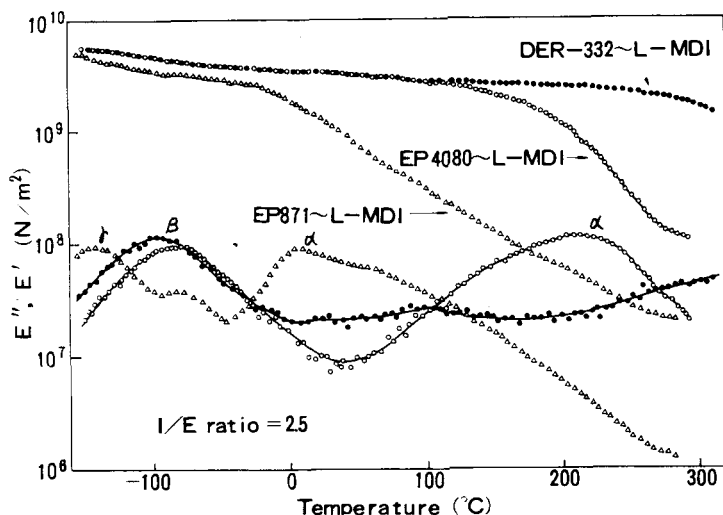DEN431 = DER332 > EP830 > CY192 > EP4080 > EP871.
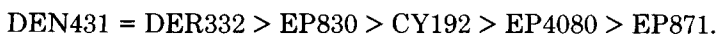
Fig. 5. Viscoelastic behavior of isocyanurate–oxazolidone resins. Epoxide components were changed for the selected isocyanate components of L-MDI with I/E ratio of 2.5.

This suggested that the aromatic epoxides were much more effective in increasing the α-peak temperature of the ISOX resins than the aliphatic and/or alicyclic epoxides. The I/E ratio was also effective in changing the α-peak temperature, because the molar ratio of isocyanurate and oxazolidone rings in the ISOX resins should be a function of the I/E ratio. The α-peak temperature increased with increasing I/E ratio in every case. However, this tendency was more noticeable in the ISOX resins prepared with aromatic epoxides such as DEN431 and DER332 than in those obtained from aliphatic epoxides such as EP871. For example, the α-peak temperature of the DER332–L-MDI ISOX resin at an I/E ratio of 1.0 was 210°C, but when the I/E ratio was above 2.5, the
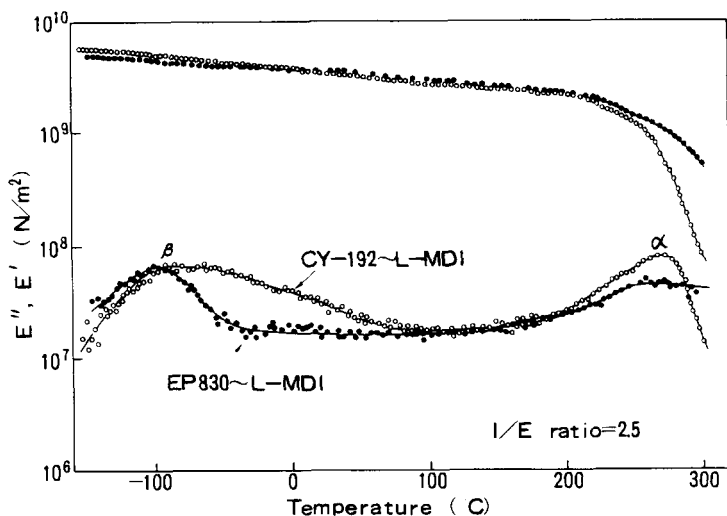

Fig. 6. Viscoelastic behavior of isocyanurate–oxazolidone resins. Epoxide components were changed for the selected isocyanate components of L-MDI with I/E ratio of 2.5.
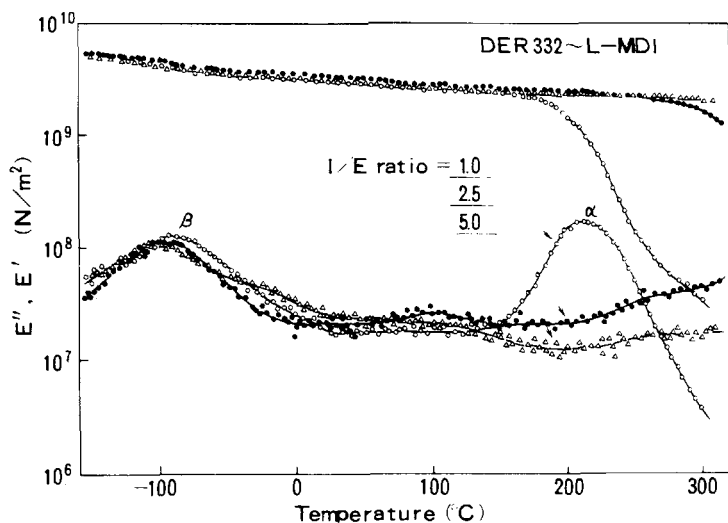
Fig. 7. Viscoelastic behavior of isocyanurate–oxazolidone resins prepared from the varnishes composed of L-MDI and DER332 with various I/E ratios.

α-peak temperature was higher than 300°C. In the case of EP871–L-MDI ISOX resin, the α-peak temperature became a little bit higher with increasing I/E ratio; however, the shift amount of the α-peak temperature toward higher temperatures was not so large. Broadening of the α-dispersion was more prominent. This suggested that the increase of the I/E ratio brought about diversity in the relaxation mechanisms.

Increasing the I/E ratio had two effects on the chemical nature of the ISOX resins, which should directly reflect the mechanical properties. One was an increase in the cohesive energy density, and the other was an increase in the
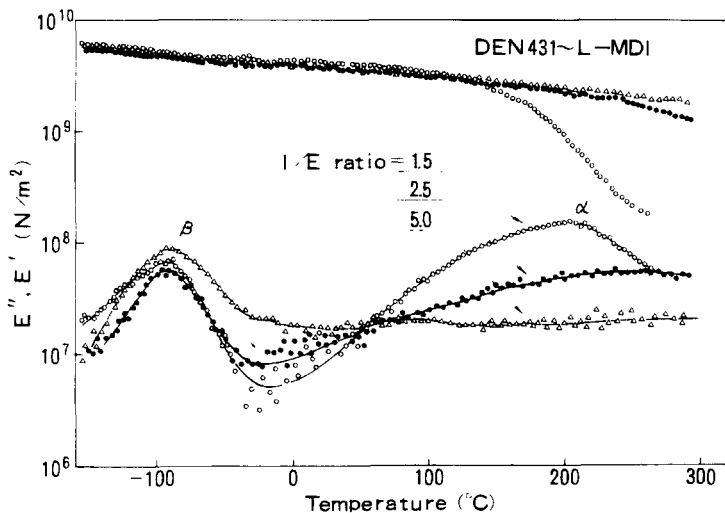

Fig. 8. Viscoelastic behavior of isocyanurate–oxazolidone resins prepared from the varnishes composed of L-MDI and DEN431 with various I/E ratios.
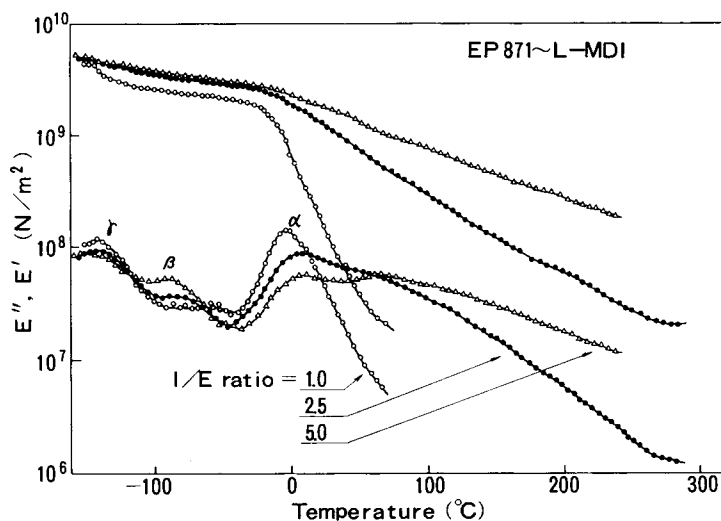
Fig. 9. Viscoelastic behavior of isocyanurate–oxazolidone resins prepared from the varnishes composed of L-MDI and EP871 with various I/E ratios.

crosslinking density. Both effects resulted from the difference in the bonding modes between the isocyanurate and oxazolidone rings. That is, the isocyanurate ring has three bonding sites and the oxazolidone ring has two. This difference in the bonding modes is probably responsible for the shift of the α-peak toward higher temperatures with increases in the I/E ratio.

As for the β-dispersion, the β-peak temperatures of ISOX resins were quite close to each other. In other words, the β-dispersion is not affected by changes in epoxide species used or in the I/E ratio. This indicated that the β-dispersion was assigned to molecular motions which were not influenced by the crosslinking

TABLE II
Peak Temperatures of Dispersions Observed for
Isocyanurate–Oxazolidone Resins

Isocyanate	Epoxide	$\frac{I}{E}$ ratio	dispersion (°C)		
			α	β	γ
L–MDI	DER 332	2.5	>300	− 95	—
	EP 4080		215	− 85	—
	EP 871		6	− 80	−140
	EP 830		260~290	− 100	—
	CY 192		270	−90~−60	—
L–MDI	DER 332	1.0	210	− 90	—
		2.5	>300	− 95	—
		5.0	>300	− 100	—
	DEN 431	1.5	200	− 90	—
		2.5	>300	− 90	—
		5.0	>300	− 90	—
	EP 871	1.0	− 2	—	−140
		2.5	6	− 80	−140
		5.0	10	− 90	−140

— : no dispersion

density and cohesive energy density. The behavior of β-dispersions observed in Figure 9 is also noteworthy. The β-dispersion almost disappeared in a resin with an I/E ratio of 1.0, because the chemical structure of such a resin was very similar to that of poly(2-oxazolidone). Considering that most ISOX resins have no side chains, the β-dispersion should be due to the local mode motions[18] of the ISOX resin backbone chains including isocyanurate rings.

The γ-dispersion was observed only in the cured resins obtained from varnishes including EP871. Its intensity was found to correlate with the EP871 content in the varnishes before curing. This could be assigned to the molecular motions of the long alkyl chains of EP871, for which the characteristics resembled those observed for various polymers such as aliphatic nylon, polyurethane, and polymethacrylates at low temperatures (about $-150°C$ to $-160°C$, 1 Hz).

Viscoelastic Properties of Microphase Separated ISOX Resins

It is well known that the dispersion of rubber particles into matrix polymer phases improves the toughness of a hard and brittle polymer matrix.[19–22] Carboxyl-terminated copolymers of butadiene and acrylonitrile (CTBN) are increasingly being used in many epoxy applications as a means of improving the fracture toughness of epoxy resins.[23–26] Recent studies have shown that this improvement is brought about by the partially miscible nature of components such as epoxides and CTBN.[27,28] This miscibility allows the morphology of a mixture to be manipulated by controlling the composition and curing conditions.

The authors found that ISOX resins could also be modified by additives to develop a physical structure in which particles are dispersed throughout a matrix phase. Epoxide and isocyanate additives were considered in the present study.

DEN431 and EP871 are immiscible, however, L-MDI makes the two compounds miscible, allowing for transparent one-phase varnishes to be produced. When such varnishes were heated after adding 0.1 phr by weight of 1-cyanoethyl-2-ethyl-4-methylimidazole as a curing agent, phase separation was observed before gelation during the cross-linking reaction under an isothermal condition of 80°C. The final cured products were opaque hard resins. Scanning electron-microscope analysis showed that the particle phases were randomly scattered in the continuous matrix phases as shown in Figure 10.

The viscoelastic behavior of the cured resins of DEN431–EP871–L-MDI ternary systems are shown in Figure 11. The I/E ratio was 2.5. The relaxation behavior of these resins showed the typical pattern which is usually observed for rubber-modified plastics such as ABS, HIPS, and rubber-modified epoxies. Three dispersions, labeled α_S, β, and γ, could be observed in the temperature range from $-160°C$ to 300°C. The peak height of the α_S-dispersion increased with increasing EP871 content in the varnishes. The results suggested that the α_S-dispersion was due to the glass transition of the rubber phase which was probably a product of the reaction of L-MDI with EP871. The α-dispersion due to glass transition of the matrix phase was not observed in this study, since the measurement temperature range was below 300°C. The β-dispersion of rubber-modified ISOX resins should be assigned to the local mode motions of the backbone chains of ISOX resins forming the matrix phase. The γ-dispersion

├────────────────┤ 10 μm

Fig. 10. SEM micrograph of rubber-modified ISOX resins prepared from the trinary varnishes composed of L-MDI, DEN431, and EP871. The I/E ratio was 2.5, and the contents of EP871 and DEN431 were the same weight.

was also observed in the rubber-modified ISOX resins and should be due to the molecular motions of long alkyl chains of EP871.

It is well known that isocyanates easily react with carboxylic acids to produce amides. CTBN undergoes a similar reaction with excess L-MDI to produce CTBN capped with L-MDI. This reaction is as follows:

$$2 \text{ OCN—R—NCO} + \text{HOOC—R'—COOH}$$
$$\text{(L-MDI)} \qquad \text{(CTBN)}$$

$$\rightarrow \text{OCN—R—NHCO—R'—CONH—R—NCO}$$
$$\text{(CTBN capped with L-MDI)}$$

Varnishes composed of L-MDI, CTBN capped with L-MDI, and DEN431 were transparent before curing. However, phase separation occurred during curing

Fig. 11. Viscoelastic behavior of rubber-modified ISOX resins which were prepared from the varnishes composed of L-MDI, EP871, and DEN431. The I/E ratio was 2.5.
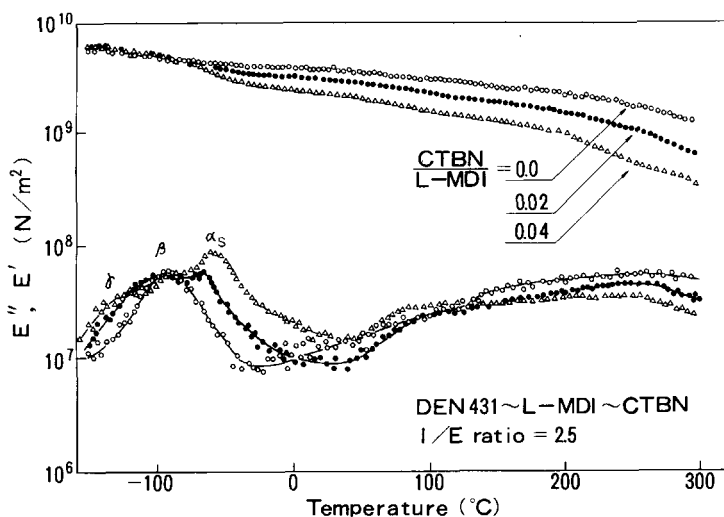
Fig. 12. Viscoelastic behavior of rubber-modified ISOX resins which were prepared from the varnishes composed of L-MDI, DEN431, and CTBN capped with L-MDI. The I/E ratio was 2.5.

after the addition of a catalyst. The resultant cured products were opaque, hard plastics. The viscoelastic behavior of these resins is shown in Figure 12, which also shows the typical behavior pattern observed for rubber-modified plastics. In this case, α_S- and β-dispersion could be readily observed, while γ-dispersion was not so readily evident. The relaxation strength of the α_S-dispersion increased with increasing CTBN content. The α_S-dispersion was probably due to the glass transition of the rubber phase, which included CTBN.

The α_S-dispersion in Figure 11 was observed at $-42°C$, which was lower than the temperatures of $-3°C$ and $-20°C$ observed for cured EP871–L-MDI and EP871,[29] respectively. On the other hand, the α_S-dispersion in Figure 12 was observed at $-60°C$, which was lower than the temperature of $-45°C$ obtained for unreacted CTBN.[27] That is, the glass transition of the rubber domains scattered in the hard matrix apparently always occurs below the T_g of bulk state rubber. The occurrence of a relaxation at such temperatures is probably caused by thermal shrinkage stresses, which are produced by the difference in the thermal expansion coefficients of the rubber particles and the glassy matrix. A similar phenomenon was observed in CTBN-modified epoxies.[27]

Results of additional studies on other properties of rubber-modified ISOX resins will be published separately in the near future.[29]

CONCLUSION

(1) The mixtures composed of polyfunctional isocyanates and epoxides can be thermally cured by the catalytic effects of imidazoles to form plastics which have isocyanurate and oxazolidone rings in their molecular structures. These kinds of new thermosets have been named isocyanurate–oxazolidone resins.

(2) The mechanical properties of cured resins can be changed systematically from hard to soft or from brittle to toughened by selecting the type and quantity of isocyanates and epoxides in the varnishes.

References

1. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967.

2. H. Kakiuchi, *Epoxy Resin*, Shoko-do, Tokyo, 1970 (in Japanese).

3. S. A. Paipetis, P. S. Theocaris, and A. Marcbese, *Colloid Polym. Sci.*, **257**, 478 (1979).

4. M. Ochi and M. Shimbo, *Nippon Kagaku Kaishi* **1981**, 1306 (1981).

5. T. Murayama and J. P. Bell, *J. Polym. Sci.*, A-2, **8**, 437 (1970).

6. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967.

7. J. D. Ferry, *Viscoelastic Properties of Polymers*, 2nd ed., Wiley, New York, 1970.

8. G. F. Speranza and W. J. Peppel, *J. Org. Chem.*, **23**, 1922 (1958).

9. S. R. Sandler, F. Berg, and G. Kitagawa, *J. Appl. Polym. Sci.*, **9**, 1994 (1965).

10. R. R. Dileone, *J. Polym. Sci.*, A-1, **8**, 609 (1970).

11. J. E. Herweh and W. Y. Whitmore, *J. Polym. Sci.*, A-1, **8**, 2759 (1970).

12. G. Bald, K. Kretzchmar, H. Markert, and M. Wimmer, *Angew. Makromol. Chem.*, **44**, 151 (1975).

13. D. Braun and J. Weinert, *Liebigs Ann. Chem.*, **1979**, 200, 210 (1979).

14. D. Braun and J. Weinert, *Angew. Makromol. Chem.*, **78**, 1 (1979).

15. T. Koyama and T. Narahara, ACS/CSJ Chemical Congress, Honolulu, Hawaii, April 1–6, 1979, Abstract ORGN, p. 304.

16. N. Kinjo, T. Koyama, T. Narahara, and J. Mukai, Proceedings of the 14th Electrical/Electronics Insulation Conference, 1979, p. 129.

17. N. Kinjo, S. Numata, T. Koyama, and Y. Katsuya, *Polym. J.*, **14**, 505 (1982).

18. N. Saito, K. Okano, S. Iwayanagi, and T. Hideshima, *Solid State Physics*, Vol. 14, F. Seits and D. Turnbull, Eds., Academic, New York, 1963, p. 387.

19. E. H. Merz, G. C. Claver, and M. J. Baer, *J. Polym. Sci.*, **22**, 325 (1956).

20. S. Newman and S. Strella, *J. Appl. Polym. Sci.*, **9**, 2297 (1965).

21. R. P. Kambour, *Macromol. Rev.*, **7**, 134 (1971).

22. C. B. Bucknall and R. R. Smith, *Polymer*, **6**, 437 (1965).

23. E. H. Rowe, A. R. Siebert, and R. S. Drake, *Mod. Plast.*, **47**, 110 (1970).

24. J. N. Sultan and F. J. McGarry, *Polym. Eng. Sci.*, **13**, 29 (1973).

25. N. Kalfoglou and L. Williams, *J. Appl. Polym. Sci.*, **17**, 1377 (1973).

26. S. Kunz-Douglass, P. W. R. Beaumont, and M. F. Ashby, *J. Mater. Sci.*, **15**, 1109 (1980).

27. L. T. Manzione, J. K. Gillham, and C. A. McPherson, *J. Appl. Polym. Sci.*, **26**, 889, 907 (1981).

28. T. T. Wang and H. M. Zupko, *J. Appl. Polym. Sci.*, **26**, 2391 (1981).

29. S. Numata and N. Kinjo, *Kobunshi Ronbun-shu*, **39**, 563 (1982).