

SHORT COMMUNICATION

Synthesis and Viscoelastic Properties of Thermosetting Isocyanurate–Oxazolidone Resins

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Over the past decade several studies have been carried out on the polymerization reaction in which poly-2-oxazolidones are formed from diisocyanates and diepoxides.^{1–6} A recent study⁷ on the heterocyclization reaction of phenylisocyanate and phenylglycidyl ether in a solution of dimethyl sulfoxide has shown that isocyanurate rings are formed from the isocyanates by the catalytic effects of imidazoles at temperatures below 100°C and are converted into oxazolidone rings at temperatures above 110°C.

Considering that both the isocyanurate and oxazolidone rings are heat resistant, it may be assumed

that varnishes consisting of polyfunctional isocyanates and epoxides can provide new types of heat resistant thermosetting resins. The formation reaction and the resultant chemical structure of cured resins are believed to be as shown in Figure 1. This has been confirmed by the fact that when varnishes are cured under the conditions described below, isocyanurate and oxazolidone rings are formed in the molecular structure of cured resins.

The equivalent ratio of isocyanate and epoxy groups, which can be varied at will, was tentatively selected as 2.5 in this study. As a curing agent, 0.1 phr by weight of 2-ethyl-4-methyl-imidazole was

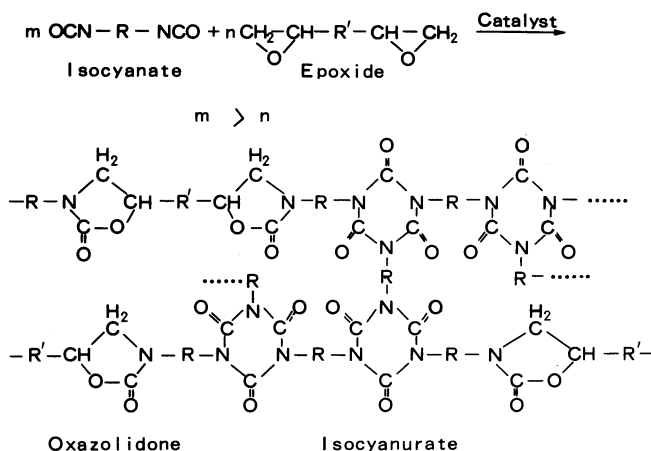


Figure 1. Chemical structure of isocyanurate–oxazolidone resins when diepoxides react with diisocyanates.

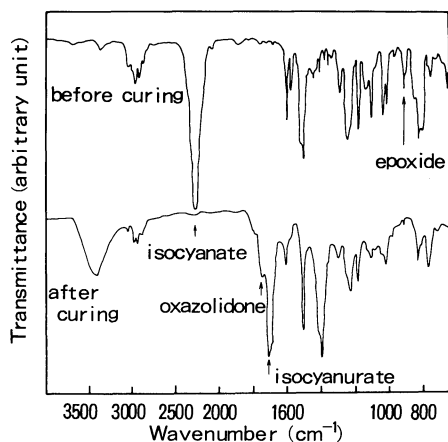


Figure 2. IR spectra before and after curing a mixture of 2,2'-bis[*p*-(2,3-epoxypropyloxy)phenyl]propane (DER332) and diphenylmethane 4,4'-diisocyanate (MDI).

employed. Curing temperatures of 80, 130, 180, and 200°C were employed in sequence.

The infrared spectra before and after curing a mixture of 2,2'-bis[*p*-(2,3-epoxypropyloxy)phenyl]propane (DER332, from DOW Chemical Co.) and diphenylmethane-4,4'-diisocyanate (MDI) are compared in Figure 2. Absorptions due to the stretching vibrations of the carbonyl groups of isocyanurate and oxazolidone rings can be observed at 1710 and 1750 cm^{-1} , respectively, while the absorptions due

to isocyanate (2275 cm^{-1}) and epoxy groups (910 cm^{-1}) cannot readily be observed. From this, it is clear that isocyanurate and oxazolidone rings are formed in cured resins. Thus, the authors designated this kind of resin "Isocyanurate-Oxazolidone Resin," and it is abbreviated "ISOX Resin."

One of the most important characteristics of ISOX resins is that their mechanical properties can be varied at will from hard to flexible. This can be done by selecting an appropriate reactant species and changing the equivalent ratio of the isocyanate and epoxy groups in the varnishes. In this study, an isocyanate species of modified diphenylmethane-4,4'-diisocyanate (L-MDI, Desmodur CD from Bayer AG) was selected and the epoxide species were varied. Of course, it is possible to change the isocyanate species too. The viscoelastic behavior of the cured ISOX resins is shown in Figure 3. The temperature dependencies of the viscoelasticity of the ISOX resins are considerably different, depending on which epoxide is used.

Three kinds of relaxations, labeled α , β , and γ , were observed in ISOX resins. α -Dispersions due to glass transitions were observed in the case of EP871 ~ L-MDI and EP4080 ~ L-MDI systems, but not in the case of the DEN431 ~ L-MDI system. The last system has a very high glass transition temperature and, therefore, α -dispersion would only be observed above 300°C. It is noteworthy that the peak temperatures of the α -dispersions of these

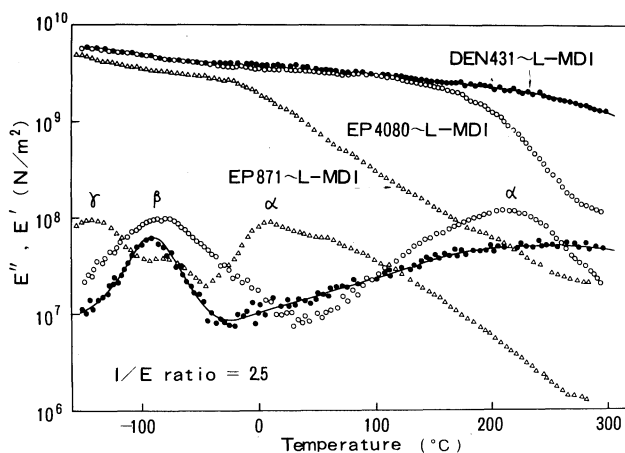


Figure 3. Viscoelastic behavior of isocyanurate-oxazolidone resins. Commercial materials used here are as follows: polyglycidyl ether of phenol-formaldehyde novolac (DEN431 from DOW Chemical Co.), 2,2'-bis[*p*-(2,3-epoxypropyloxy)cyclohexane]propane (EP4080 from Asahi Denka, Ltd.), diglycidyl ester of linoleic dimer acid (EP871 from Shell Chemical Co.), and modified diphenylmethane-4,4'-diisocyanate (L-MDI, Desmodur CD from Bayer AG).

ISOX resins are different depending on the epoxide species.

β -Dispersions were observed in the same temperature region for every ISOX resin studied here and should be assigned to the local mode motions of the backbone chains of the ISOX resins.

γ -Dispersion was observed only in the EP871 ~ L-MDI system, and not in the others. This seems to be due to the molecular motions of the alkyl chains of EP871, because the other epoxides do not have long alkyl chains in their chemical structures.

Preliminary studies show that various reactants of polyfunctional isocyanates and epoxides should be available to form a wide variety of cured ISOX resins. A detailed paper on the synthesis and viscoelastic behavior of ISOX resins is now being prepared for publication.

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