

SHORT COMMUNICATION

Rubber-Modified Isocyanurate-Oxazolidone Resins

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It is well known that the dispersion of rubber particles into matrix polymer phases improves the toughness of a hard and brittle polymer matrix. Much research¹⁻⁴ has been carried out in this area and many ideas have been proposed to explain this rubber-toughening phenomenon. Thermoplastic resins, such as acrylonitrile-butadiene-styrene copolymer (ABS), styrene-butadiene-styrene copolymer (SBS), and high impact polystyrene (HIPS), are outstanding examples of rubber-modified plastics that have been found to have practical utility, because of their ability to improve polymer toughness.

A similar method has also been used to produce toughened thermosetting resins. 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.⁵⁻⁸ Recent studies^{9,10} have shown that this improvement is brought about by the partially miscible nature of components such as epoxides and CTBN. This miscibility allows the morphology of a mixture to be manipulated by controlling the composition and curing conditions. New rubber-modified thermosetting resins will be described in this study.

The authors have previously reported that varnishes composed of polyfunctional isocyanates and epoxides can readily form isocyanurate and oxazolidone rings in the molecular structure of the cured resins. These resins are called "Isocyanurate-Oxazolidone Resins" or "ISOX Resins."^{11,12} The objective of this study is to show that ISOX resins can also be modified by additives to develop a

physical structure in which particles are dispersed throughout a matrix phase. Epoxide and isocyanate additives will be considered in this paper.

Polyglycidyl ether of phenol-formaldehyde novolac (DEN431 from DOW Chemical Co.) and diglycidyl ester of linoleic dimer acid (EP871 from Shell Chemical Co.) are immiscible with each other. However, commercially available diphenylmethane-4,4'-diisocyanate (L-MDI, Desmodur CD from Bayer AG) makes the binary systems of EP871 and DEN431 miscible with each other,¹⁵ so that transparent one-phase varnishes can be produced. When such varnishes were heated after adding 0.1% by weight of 2-ethyl-4-methylimidazole as a curing agent, a visible micro-phase separation was observed during the cross-linking reaction under an isothermal condition of 80°C, before gelation. The final cured products were opaque hard resins. SEM analysis has shown that particle phases are randomly scattered in continuous matrix phases. These results will be reported elsewhere.

The viscoelastic behavior of the cured resins of DEN431 ~ EP871 ~ L-MDI ternary systems are shown in Figure 1. The equivalent ratio of isocyanate and epoxy groups was 2.5. As can be seen from the figure, the relaxation behavior of these resins shows the typical pattern which is usually observed for rubber-modified plastics. Three dispersions, labeled α_s , β , and γ , can be observed in the temperature range from -196°C to 300°C. The peak height of the α_s -dispersion increases with increasing EP871 content in the varnishes. This suggests that the α_s -dispersion is due to a glass transition in the rubber phase which is probably

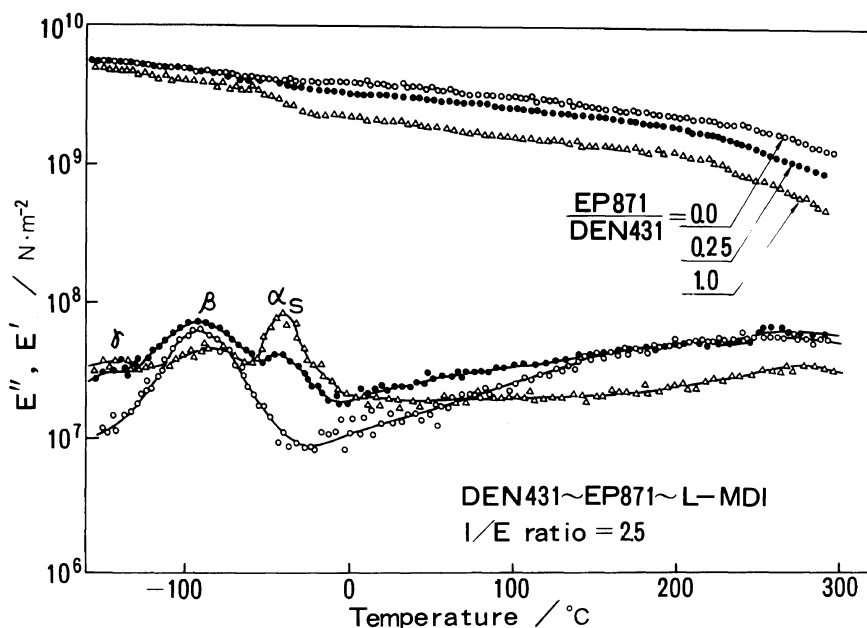
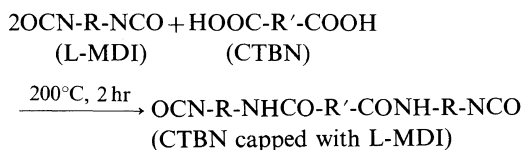


Figure 1. Viscoelastic behavior of rubber-modified Isocyanurate-Oxazolidone resins. The following commercial materials were used: polyglycidyl ether of phenol-formaldehyde novolac (DEN431 from DOW Chemical Co.), diglycidyl ester of linoleic dimer acid (EP871 from Shell Chemical Co.) and modified diphenylmethane-4,4'-diisocyanate (L-MDI, Desmodur CD from Bayer AG).

resulting from the reaction of L-MDI with EP871. The α -dispersion due to this glass transition in the matrix phase was not observed below 300°C in this study. The β -dispersion was assigned to the local mode motion of the backbone chains of ISOX resins. The γ -dispersion was 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.¹³ CTBN undergoes a similar reaction with excess L-MDI to produce CTBN capped with L-MDI. The reaction for this is as follows:



The CTBN used in this study was Hycar CTBN (1300×8), manufactured by B. F. Goodrich Co. The acrylonitrile content of the CTBN is 17 wt% and the T_g measured by TBA (< 1 Hz) is reported to be -45°C.⁹

Varnishes composed of L-MDI, CTBN capped

with L-MDI and DEN 431 are transparent before curing. However, phase separation occurred during curing after the addition of a catalyst. The resultant cured products were opaque hard plastics. The viscoelastic behavior of these resins is shown in Figure 2, which also shows the typical behavior pattern observed for rubber-modified plastics. In this case, the α_s -dispersion and β -dispersion can be readily observed, but the γ -dispersion is not so readily evident. The relaxation strength of the α_s -dispersion increases with increasing the CTBN content. The α_s -dispersion is probably due to the glass transition in the rubber phase, which includes CTBN.

The α_s -dispersion in Figure 1 was observed at -42°C, which is lower than the temperatures of 10°C and -25°C observed for cured EP871~L-MDI¹² and EP871,¹⁴ respectively. The α_s -dispersion in Figure 2 was observed at -60°C, which is lower than the temperature (-45°C) obtained for unreacted CTBN. 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 glass transition at such

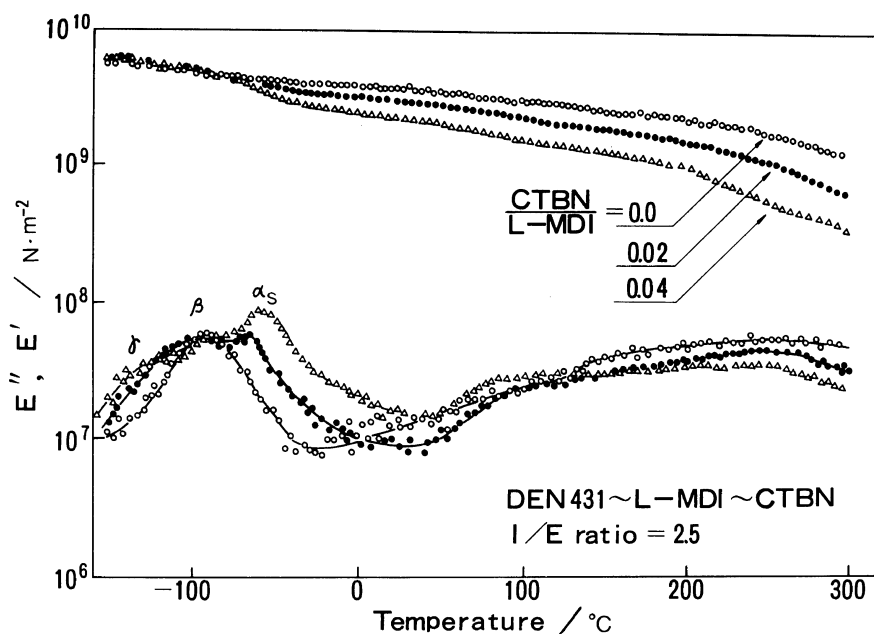


Figure 2. Viscoelastic behavior of rubber-modified Isocyanurate-Oxazolidone resins cured from vanishes consisting of L-MDI, CTBN capped with L-MDI and DEN431.

temperatures is apparently caused by thermal shrinkage stress produced by the difference in the thermal expansion coefficients of the rubber particles and glassy matrix. A similar phenomenon was observed in CTBN modified epoxides.⁹

The results of additional studies on other properties of rubber-modified ISOX resins now under way will be published in the near future.

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