Nitrile-Containing Imidazole Cured of Novolac Epoxy Resin

INTRODUCTION

Although rheological properties of amine and imidazole cured with epoxy resin adhesives have been extensively reported,[1-5] the lack of information on 1-cyanoethyl-2-phenyl-4,5-dicyanoethoxyl methyl imidazole (CPDCMI) used as curing agent of epoxy systems prompted this work. Since CPDCMI consists of three flexible side chains with a pendent nitrile group, it stays in the liquid state at room temperature and can be mixed with novolac epoxy resin without heating. This is very desirable for some particular applications of structural adhesives, in which easy mixing and low-temperature cure (below 100°C) are wanted. The objective of the present study was to demonstrate the effect of curing condition on dynamic mechanical properties and that of nitrile side groups within CPDCMI on the curing behavior of this specific nitrile-substituted imidazole-cured epoxy system.
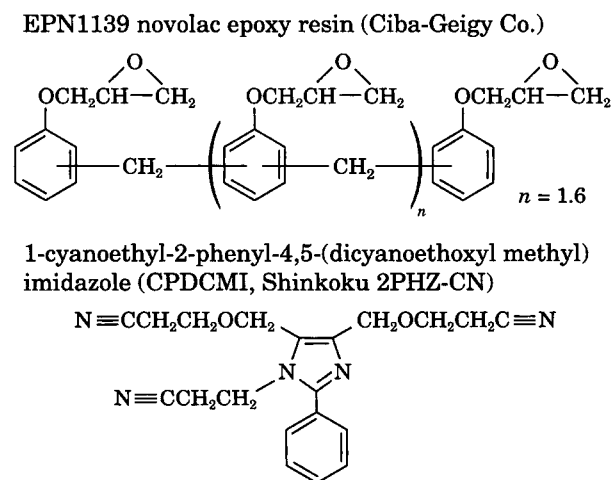
EXPERIMENTAL

Ciba-Geigy EPN1139 novolac epoxy resin was cured with 1-cyanoethyl-2-phenyl-4,5-dicyanoethoxyl methyl imidazole (CPDCMI, Sinkoku 2PHZ-CN) with Bisphenol A used as catalyst and aluminum powder as filler. The chemical structures of the resin and curing agent are shown in Table I. The composition and cure schedule of the various formulations are listed in Table II. Sample specimens of $1.25 \times 6 \times 0.3$ cm were prepared in a Teflon mold and cured according to the schedule of Table II. Prepared samples were kept at 25°C and 45% relative humidity for at least 24 h prior to testing. Dynamic mechanical measurements were performed on a rheometric mechanical spectrometer RMS-605. Testing temperature was run from 50 to 250°C. Isothermal viscosity measurement was conducted on the same instrument using the oscillating parallel plate technique. Platens of 50 mm in diameter were used. Dynamic frequency was kept at 10 rad/s for all measurements. Infrared spectroscopies of neat resins were taken from a Perkin-Elmer infrared spectrometer 580.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties

Dynamic mechanical characterizations of novolac epoxy resin cured at 90°C with different concentrations of nitrile-containing imidazole curing agent (CPDCMI) are shown in Figure 1. From these results, only one glass transition at 130°C (defined as α_1) was observed for this epoxy system with a low concentration of curing agent (4 phr CPDCMI). As the concentration of the curing agent was increased, the damping peak α_1 became lower and shifted to higher temperature while the additional separate and distinct transition at about 180°C (defined as α_2) was present. The low-temperature transition α_1 can be attributed to loose chain ends involved in the network.[6] Table III shows the infrared analyses of CR-4 (4 phr CPDCMI) and CR-16 (16 phr CPDCMI). By taking the aromatic absorption peak of 1600 cm^{-1} as an internal standard, the change of epoxide absorbance at 920 cm^{-1} is monitored with the advance of curing extent within a 4 h period under 90°C cure. The conversion of CR-4 and CR-16 obtained is 26.9% and 84.7%, respectively. This result reveals

Table I Chemical Structure of Epoxy Resin and Curing Agent

EPN1139 novolac epoxy resin (Ciba-Geigy Co.)

1-cyanoethyl-2-phenyl-4,5-(dicyanoethoxyl methyl) imidazole (CPDCMI, Shinkoku 2PHZ-CN)

Table II Various Epoxy Formulation Studied

Composition[a]
EPN1139
4–16 phr CPDCMI
5 phr Bisphenol A
10 phr Al powder

Variables
1. Curing agent concentration
2. Curing temperature

Cure Schedule
Components mixed at room temperature for 15 min and casted in Teflon mold. B-stage: 65°C, 30 min Cure: 90°C, 4 h or 120°C, 150°C, 180°C

[a] Bisphenol A: purum grade from Fluka Co. Aluminum powder: 6–9 μm in diameter, #1401 from Alcoa Co.

that, at a low concentration of CPDCMI, many unreacted epoxide groups dangling at the chain end cause more flexion on the macromolecular structure, which has been identified as transition α_1 by dynamic analysis. As CPDCMI is increased, the additional curing of the epoxide ring makes the material become harder and the higher transition temperature α_2 is exhibited. Data of storage modulus at the equilibrium rubbery state of 90°C cured resins indicate that the formulation of 10 phr CPDCMI has the best shear modulus, i.e., the highest cross-linking density, as shown in Table IV. Lower CPDCMI content generates material of low cross-linking density, while excess curing agent (over 12 phr, i.e., 0.049 mol CPDCMI/equiv epoxy) may also act as a chain end group, thus lowering the cross-linking density. This result is very consistent with Vogt's studies[1] on the imidazole-catalyzed curing of DGEBA epoxy resin in which each molecule of imidazole was proven to induce more than 20 epoxy groups to
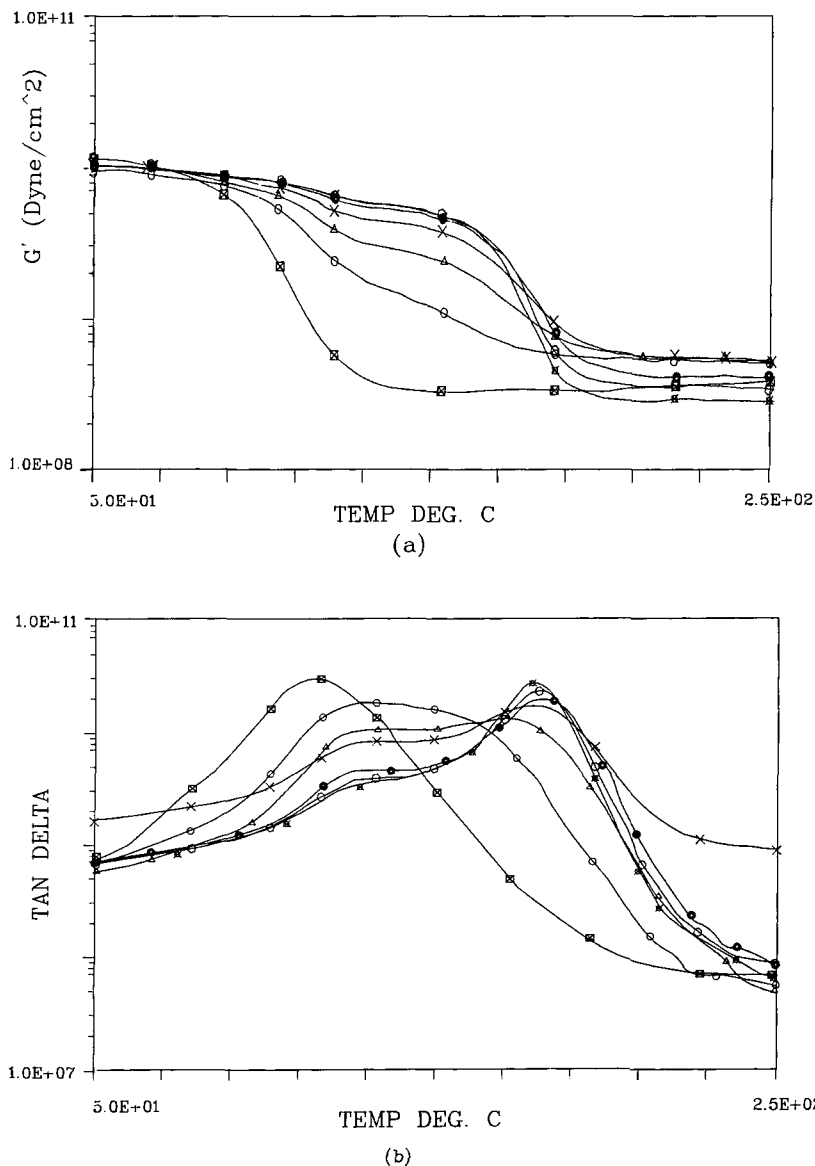
Table IV Equilibrium Storage Modulus of Resin System Cured at 90°C

| Sample | CPDCMI Content | | $G' \times 10^8$ (dyne/cm^2) |
	(phr)	(mol/equiv. epoxy)	
CR-4	4	0.106	3.295
CR-6	6	0.024	2.387
CR-8	8	0.032	5.259
CR-10	10	0.041	5.403
CR-12	12	0.049	4.179
CR-14	14	0.057	3.498
CR-16	16	0.066	2.828

undergo polyaddition. The peak height of the α_1 transition could be reduced by increasing the curing temperature from 90 to 120, 150, or 180°C for sample CR-10 (10 phr CPDCMI), as shown in Figure 2. The results show that the transition α_1 peak diminishes drastically at 120°C cure and disappears for 180°C cure. This is due to additional cross-linking by more heat energy input to overcome the barrier for further reaction. In this instance, nitrile groups of CPDCMI begin to react to form a higher degree of cross-links. Again, this has also been supported by IR data. Infrared spectra of 90°C cure indicate that the nitrile group absorbance at 2200 cm^{-1} did not change throughout the curing process [Fig. 3(a)]. However, when this resin was cured under 150°C, the absorption peak of the nitrile group disappeared at an early stage of the curing reaction [Fig. 3(b)]. Therefore, the nitrile linkage is involved in further cross-linking reaction, and, thus, it is responsible for raising T_g from 130 to 180°C. Figure 2 also shows that the α_2 peak was centered around 180°C for sample CR-10 cured between 90 and 150°C, but shifted to slightly higher temperature of 185°C due to the postcuring effect for 180°C cured resin.

Table III Infrared Spectrum Analysis of Samples CR-4 and CR-16

| Sample	Curing Time (h)	Ratio of Absorbance (960–1600 cm^{-1})	Conversion (%)
CR-4			
(4 phr CPDCMI)	0	0.89	0
	1	0.77	13.5
	2	0.76	14.6
	3	0.70	21.3
	4	0.65	26.9
CR-16			
(16 phr CPDCMI)	0	0.90	0
	1	0.33	63.0
	2	0.17	80.9
	3	0.16	82.8
	4	0.14	84.7

Figure 1 Effect of CPDCMI concentration on (a) dynamic shear modulus and (b) tan δ of cured novolac epoxy resin. (⊠) 4 phr; (○) 6 phr; (△) 8 phr; (×) 10 phr; (◉) 12 phr; (○) 14 phr; (⊗) 16 phr.
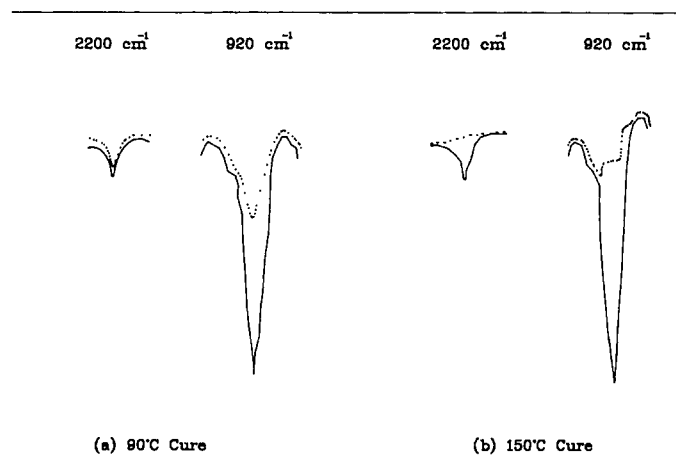
Curing Behavior

The viscosity profile of the 10 phr formulation during cure was recorded under five different curing temperatures, as shown in Figure 4. Decrease in viscosity at the early induction period may be due to the thermal property of the resin system, as observed by White.[7] Then, the viscosity increases steadily until the gelation is obtained. Thereafter, the viscosity rises abruptly until complete cure is obtained. Several empirical models[7-11] have been proposed to correlate isothermal viscosity data to reaction kinetics. The most general model has the expression

Table V   Curing Kinetics for Sample CR-10

| Reaction Temp (°C)	$k \times 10^2$ (poise/min)
75	0.724
85	1.026
90	1.556
105	2.009
120	14.740
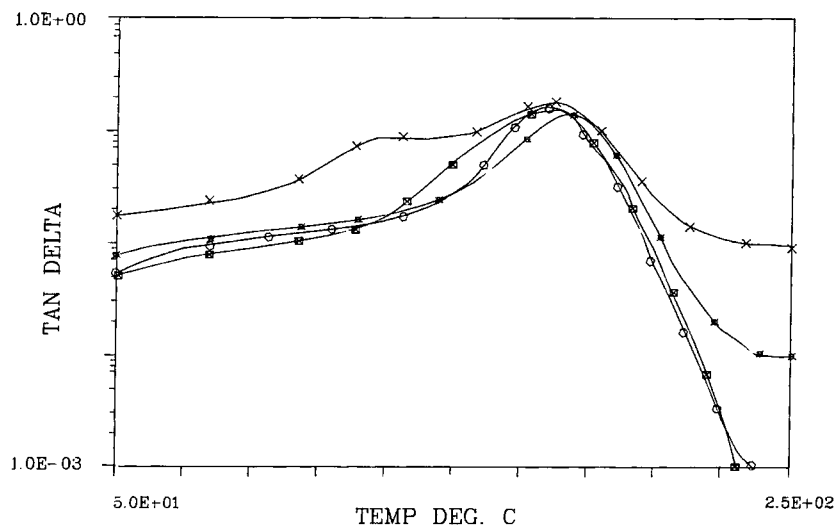
Figure 2 Effect of curing temperature on tan δ of CPDCMI cured novolac epoxy resin. (×) 90°C; (⊠) 120°C; (○) 150°C; (⊗) 180°C.

2200 cm⁻¹   920 cm⁻¹   2200 cm⁻¹   920 cm⁻¹

(a) 90°C Cure   (b) 150°C Cure

Figure 3 Infrared spectra of 10 phr CPDCMI cured novolac epoxy system at 90 and 150°C: (– – –) peak intensity before cure (———) peak intensity after 4 hr cure.
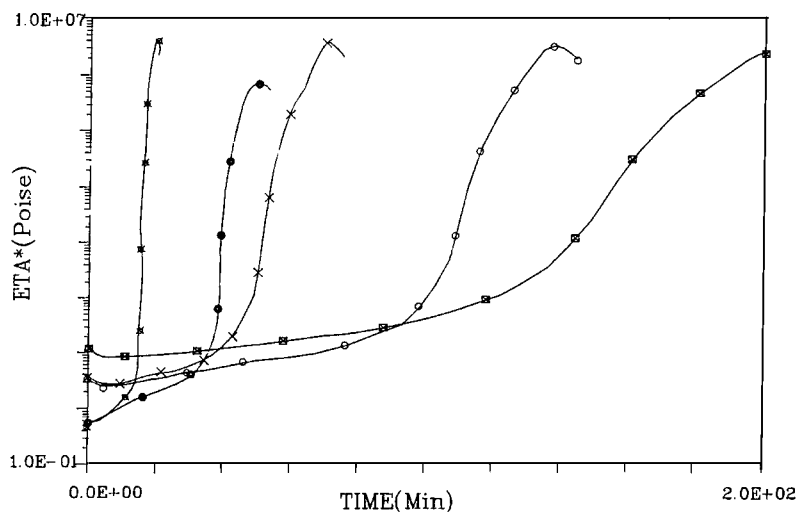
Figure 4 Dynamic viscosity profile of CPDCMI cured epoxy system. (⊠) 75°C; (○) 85°C; (×) 90°C; (●) 105°C; (⊗) 120°C
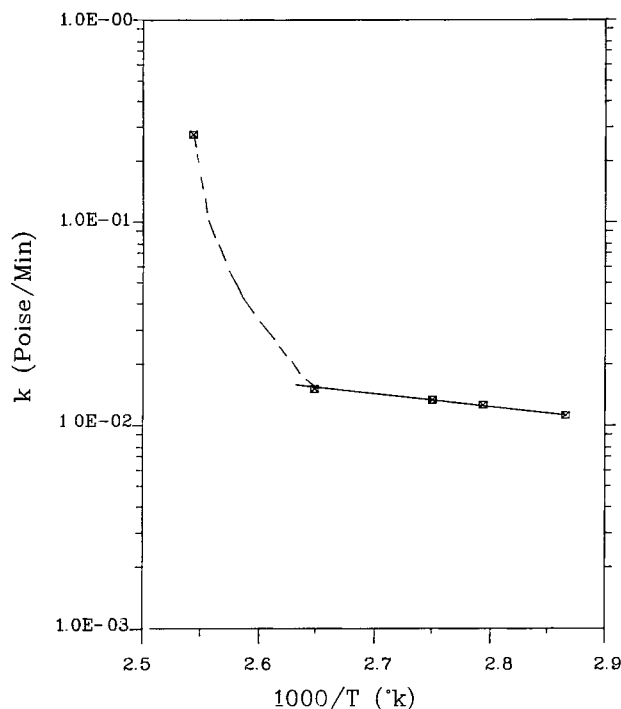
Figure 5 Arrhenius plot of the reaction kinetics for CPDCMI cured system.

$$\ln \Psi = \ln \Psi_0 + kt \tag{1}$$

where Ψ is the time-dependent viscosity, Ψ_0 is the viscosity at $t = 0$, k is an apparent kinetics constant, and t is the reaction time. In general, the abrupt change in slope of each viscosity curve is considered as the gel formation.[4] The time at the intersection of tangents to the initial and final portions of each curve is an estimate of the "gel time." Above the gel point, the structure of the curing molecule has reached a state where the viscosity approaches infinitive and the simple model [eq. (1)] no longer describes the system. Accordingly, the kinetics constant of the system at different temperatures was able to be calculated from the initial viscosity of each curve in Figure 4, and it is listed in Table V. The Arrhenius plot of Figure 5 indicates that the reactions follow the same order for the system cured between 75 and 105°C. However, when curing temperature exceeds 120°C, the reaction went very fast and deviated out of the order. This is also evidence that the nitrile groups begin an additional curing reaction to form a densely cross-linked structure.

CONCLUSIONS

The rheological properties of nitrile-containing imidazol cured with novolac epoxy resin have been studied and

reveal that this system, as cured under 90°C, gives two glass transitions centered around 130°C (α_1) and 180°C (α_2). The increase in CPDCMI concentration leads to a lower α_1 damping peak and a higher α_2 peak, and the maximum cross-linking density is at about 10 phr CPDCMI cured system. When curing temperatures exceed 120°C, the reaction kinetics show a complicated curing scheme in which nitrile groups start to react with the epoxide ring. It would be very interesting to investigate the detailed reaction mechanism for this curing system, although the reaction of simple imidazole to the epoxy model compound has been reported.[12] The reaction kinetics of the second stage involving the nitrile group and its overall effect on adhesion performance of this novolac epoxy adhesive needs to be further studied, and this will be conducted shortly.

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