

Chemorheology of epoxy resin

Part II Polyurethane-cross-linked epoxy resin cured with a tertiary amine

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A secondary hydroxyl group containing epoxy resin was reacted and cross-linked with polyurethane (PU). This PU-cross-linked epoxy resin was cured with a tertiary amine and the viscosity and dynamic mechanical properties were determined by a cone-and-plate rheometer. A dual Arrhenius viscosity model was modified to predict the viscosity profile with time before gelation during non-isothermal curing, and the calculated values coincided with the experimental data. The activation energy of this system (NCO/OH ratio = 30 mol%) calculated by the modified model was 13 kcal mol⁻¹ for the initial region, and 16.8 kcal mol⁻¹ for the final region. After gelation, the dynamic complex modulus was correlated to the reaction kinetics according to the rubber elasticity theory, and the activation energy calculated was 5.2 kcal mol⁻¹. These activation energies are all lower than those of the unmodified epoxy resin system. Consequently, the reaction rate of the PU-cross-linked epoxide system was less affected by temperature than that of the unmodified epoxide system. It was also found that the rate of increase of viscosity and dynamic moduli decreased with increasing PU content. The gelling point was estimated by rheological measurements.

1. Introduction

Epoxy resin is used in many industrial applications, owing to its great versatility, low shrinkage, good chemical resistance, and outstanding adhesion [1]. However, owing to its rather high glass-transition temperature, it is quite hard and brittle. Therefore, many attempts have been made to improve the toughness of the epoxy resins. The incorporation of reactive liquid polymer (RLP) was first adopted to enhance the toughness of epoxy resins [2–4]. The carboxyl-terminated butadiene acrylonitrile copolymer (CTBN)/epoxy systems were also widely studied [5–7]. Recently, it was found that the epoxy resin cross-linked with PU shows an improvement in impact properties [8–10]. The performance of cured thermosets is closely related to the composition of the reactants and the processing conditions.

In a previous study, a change in slope in the semi-log plot of viscosity profiles with time for the unmodified epoxide system was observed [11]. The viscosity model for isothermal condition may be written as

$$\ln \eta = \ln \eta_0 + k_1 t \quad \text{for } t \leq t_c \quad (1)$$

$$\ln \eta = \ln \eta_c + k_2(t - t_c) \quad \text{for } t > t_c \quad (2)$$

where η is viscosity, η_0 is the zero time viscosity, t_c is the curing time at the inflexion point, η_c is the viscosity at t_c , and k_1 and k_2 are the apparent kinetic factors for a curing time less than t_c and larger than t_c ,

respectively. k_1 and k_2 can be expressed in Arrhenius form, and a modified dual Arrhenius viscosity model for non-isothermal cure was obtained as follows

$$\begin{aligned} \ln \eta(t, T) = & \ln \eta_\infty + \Delta E_\eta / RT \\ & + \int_0^t k_{1\infty} e^{-\Delta E_{k_1} / RT} dt \quad \text{for } t \leq t_c \end{aligned} \quad (3)$$

$$\begin{aligned} \ln \eta(t, T) = & \ln \eta_\infty + \Delta E_\eta / RT \\ & + \int_0^{t_c} k_{1\infty} e^{-\Delta E_{k_1} / RT} dt \\ & + \int_{t_c}^t k_{2\infty} e^{-\Delta E_{k_2} / RT} dt \quad \text{for } t > t_c \end{aligned}$$

where T , the cure temperature, is a function of reaction time, R is the gas constant, ΔE_η is the activation energy for viscosity, η_∞ is the Arrhenius pre-exponential viscosity, ΔE_{k_1} and ΔE_{k_2} are the corresponding reaction activation energies for k_1 and k_2 , respectively, and $k_{1\infty}$ and $k_{2\infty}$ are the pre-exponential factors.

After gelation, the dynamic complex modulus was related to the reaction kinetics according to the rubber elasticity theory [11, 12]. The gelling time can be estimated as the time, t_0 , at which the tangent to the rapidly rising portion of the complex modulus curve intersects the time axis [13]. Assuming this reaction to be first order, and $|G^*|$ to be zero at t_0 , a dynamic

modulus model is postulated as follows

$$|G^*| = |G_\infty^*| - |G_\infty^*| \exp[-k_x(t - t_0)] \quad (4)$$

where $|G^*|$ is the complex dynamic modulus, $|G_\infty^*|$ the complex modulus near infinite time, k_x is the kinetic factor of the cross-link reaction, and t is the reaction time. The value of k_x is a function of temperature and can be expressed in Arrhenius form

$$k_x = k_{x\infty} \exp(-\Delta E_x/RT) \quad (5)$$

where ΔE_x is the apparent activation energy for the cross-link reaction, and $k_{x\infty}$ is the pre-exponential kinetic factor to k_x .

In this study, a cone-and-plate rheometer was utilized to monitor the rheological properties of the PU-cross-linked epoxy resin during cure. The viscosity and dynamic modulus profiles were investigated with the viscosity and modulus models. These rheological properties of PU-cross-linked epoxy resin were compared with the results of the unmodified epoxy resin [11], and the gelation times were determined from the rheological measurements.

2. Experimental procedure

2.1. Materials

2.1.1. Preparation of polyurethane prepolymer

Polyurethane prepolymers were prepared by the reaction of 4,4'-diphenylmethane diisocyanate (MDI) (Bayer Chemical Co.) with poly(oxypropylene) glycol (PPG-1000) (mol. wt = 1000, Chiun Glong Co.). MDI was first put into a reaction kettle and heated to the melting state, and then PPG-1000 was poured into the kettle and mixed with MDI by stirring. The reaction took place for about 5 h under dry nitrogen purge at 68 °C until the isocyanate content, determined by the di-*n*-butyl amine titration method [14], reached a theoretical value.

2.1.2. Preparation of polyurethane-cross-linked DGEBA

The diglycidyl ether of bisphenol A (DGEBA) type epoxy resin (DER 331, EEW = 186–192, Dow Chemical Co.) and PU prepolymer were mixed at different ratios. A few drops of dibutyltin dilaurate (DBTDL) were added to accelerate the reaction of PU cross-linking epoxy resin, which was carried out under nitrogen purge at 68 °C until the –NCO groups were reacted with the –OH groups of epoxy resin, as determined by detecting the absorption peak of the –NCO groups (2270 cm⁻¹) in infrared spectra (IR).

2.1.3. Curing agent

The curing agent used in this study was a tertiary amine, 2,4,6-tris (dimethylaminomethyl) phenol (TDAP) (Merck Chemical Co.).

2.2. Measurements

Rheological measurements were the same as those described in Part I [11] except that the unmodified

epoxy resin was replaced by the PU-cross-linked epoxy resin.

3. Results and discussion

3.1. Shear viscosity before the gelling point

Fig. 1 shows the dependency of viscosity profiles on shear rate for PU-cross-linked epoxy resin cured with TDAP at constant temperature. As seen in Fig. 1, the viscosity increases with increasing time due to the curing reactions, and near the gelling point, the viscosity rises sharply and tends toward an infinite value. Measurements of viscosity profile with time at various cure temperatures are shown in Fig. 2. As the cure temperature increases, the rate of rising in viscosity increases, and the time at which the viscosity approaches infinity, i.e. t_{η_∞} , decreases. Fig. 3 shows that the higher the content of curing agent, the higher is the rate of increase of viscosity.

The viscosity profiles versus curing time for PU-cross-linked epoxide system with various NCO/OH ratios, i.e., the number of –NCO groups of PU to –OH groups of epoxy resin, are shown in Fig. 4: the higher the PU content of modified epoxy resin, the higher is the molecular weight of reactants. The initial viscosity increases with NCO/OH ratio. The rate of increase of viscosity decreases as the NCO/OH ratio increases, because the mobility of the molecule decreases with increasing NCO/OH ratio.

It was observed that there is a change in slope in the semi-log plot of the viscosity profiles with time for the PU-cross-linked epoxide system, as seen for the unmodified epoxide system [11]. Fig. 5 shows the Arrhenius plot of k_1 , k_2 , and η_0 , and the parameters of the modified viscosity model are indicated in Table I. For non-isothermal curing, the viscosity profile can be obtained as a function of cure time according to Equation 3. Fig. 6 shows a comparison between

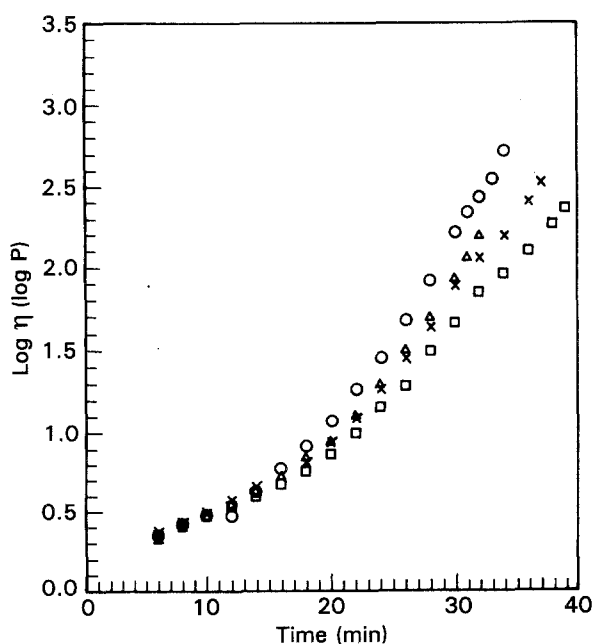


Figure 1 Viscosity versus cure time at various shear rates (at $T = 70^\circ\text{C}$, NCO/OH = 30 mol %, TDAP = 3 p.h.r.). (Δ) 1 s^{-1} , (\circ) 2 s^{-1} , (\times) 4 s^{-1} , (\square) 6 s^{-1} .

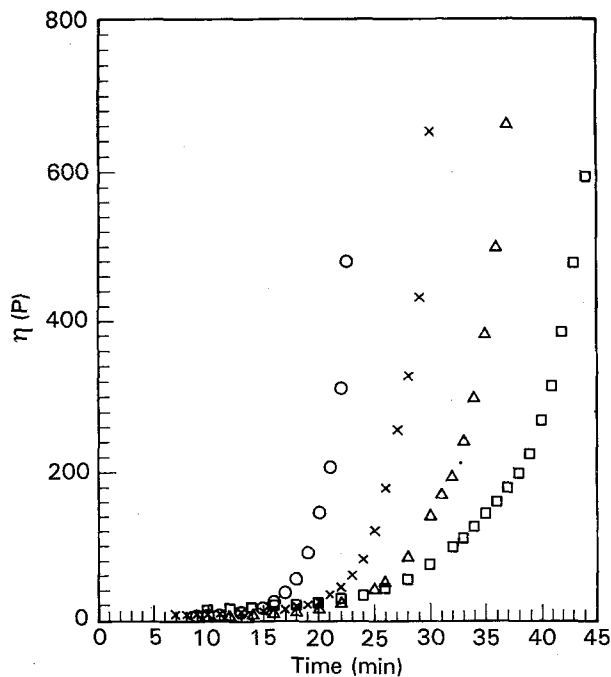


Figure 2 Viscosity versus cure time at various temperatures (at shear rate = 2 s^{-1} , TDAP = 3 p.h.r., NCO/OH = 30 mol %). (○) 80°C , (×) 75°C , (△) 70°C , (□) 65°C .

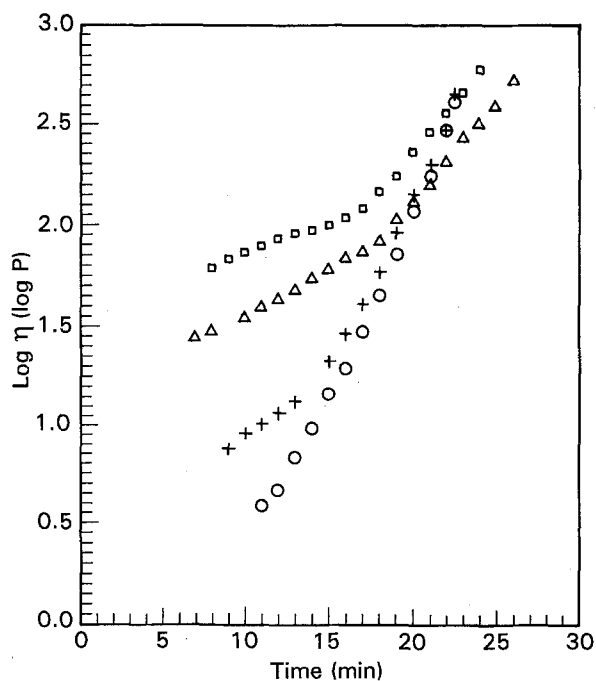


Figure 4 Viscosity versus cure time for PU-cross-linked epoxy resin with various NCO/OH mole ratios (at $T = 80^\circ\text{C}$, TDAP = 3 p.h.r., shear rate = 2 s^{-1}). (□) 100 mol %, (△) 80 mol %, (+) 30 mol %, (○) 0 mol %

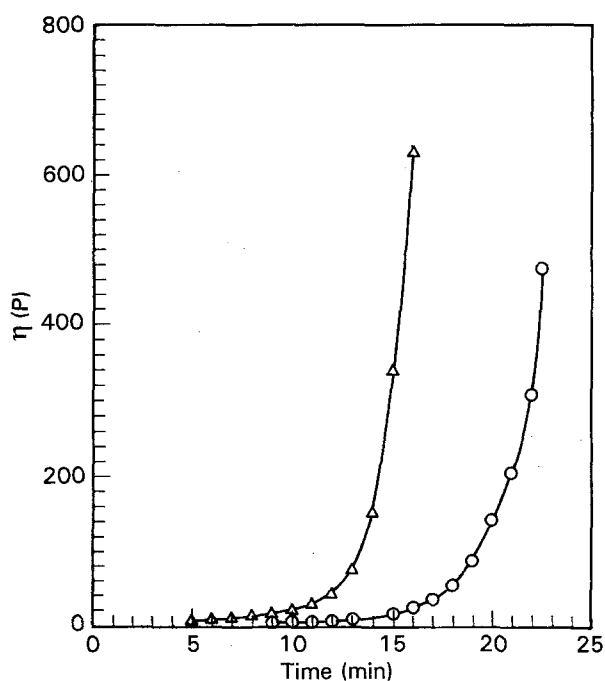


Figure 3 Viscosity versus cure time with various amounts of TDAP (at $T = 80^\circ\text{C}$, shear rate = 2 s^{-1} , NCO/OH = 30 mol %). (○) 3 p.h.r., (△) 4 p.h.r.

experimental and calculated temperature-viscosity profiles from 20– 80°C . The predicted cure time and the minimum viscosity value conform well with the experimental data, except that the predicted viscosity near the gelling point is a little lower.

3.2. Dynamic mechanical properties

The dynamic moduli, G' and G'' , and loss tangent, $\tan \delta$, during the isothermal cure at 70°C are shown in Fig. 7. In the early stage of cure, the material is still in the liquid state and the molecular weight is low.

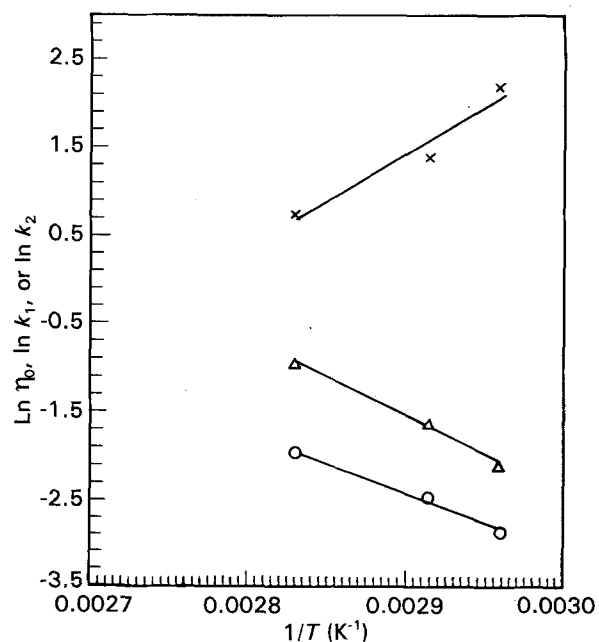


Figure 5 (○) $\text{Ln } k_1$, (△) $\text{Ln } k_2$ or (×) $\text{Ln } \eta_0$ versus $1/T$ (at TDAP = 3 p.h.r., shear rate = 2 s^{-1} , NCO/OH = 30 mol %).

Hence, the loss modulus is greater than the storage modulus, consequently, both moduli are very small. Because the elastic property of the resultants increases as the curing reaction progresses, the storage modulus first rises gradually, then rapidly, and eventually exceeds the loss modulus.

Figs 8 and 9 show the dependency of G' and G'' on frequency, respectively. As the frequency decreases, the curves of G' and G'' tend to shift horizontally from left to right. The dynamic mechanical properties during the cure at various temperatures are shown in Figs 10 and 11. The higher curing temperature results in

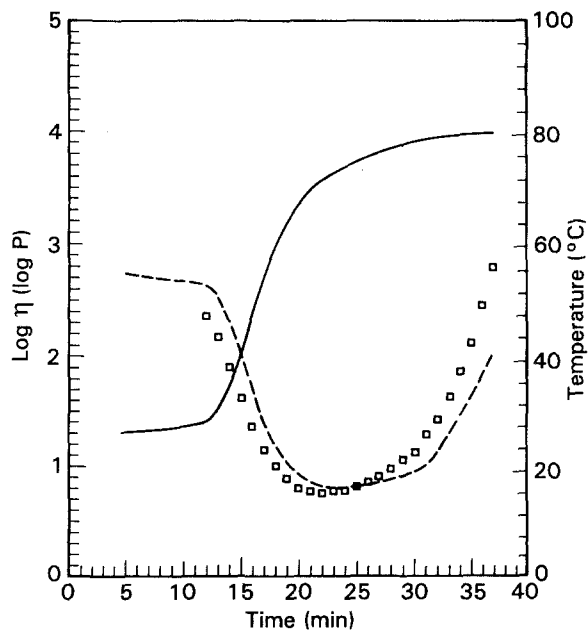


Figure 6 Comparison of (---) the curve of Equation 3 with (□) the measured viscosity (at TDAP = 3 p.h.r., shear rate = 2 s^{-1} , $\log \eta_c = 1.2$, NCO/OH = 30 mol %) under non-isothermal conditions. (—) Temperature.

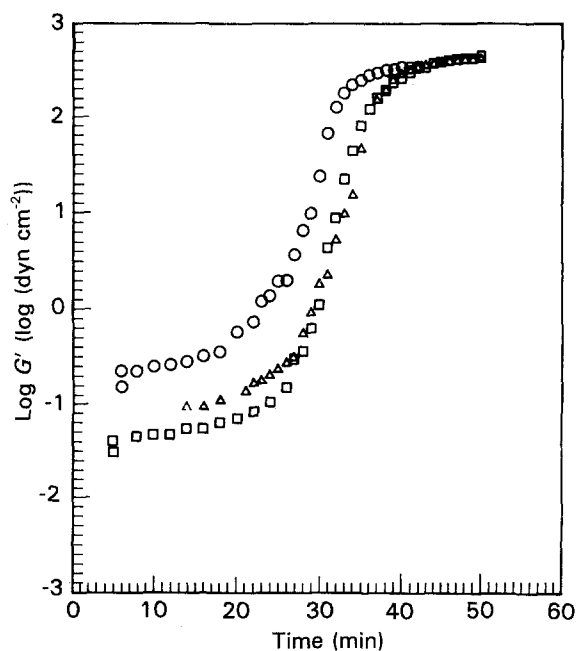


Figure 8 Storage modulus versus cure time at various frequencies (at $T = 75^\circ\text{C}$, TDAP = 3 p.h.r., NCO/OH = 30 mol %). (○) 0.5 Hz, (△) 0.2 Hz, (□) 0.1 Hz.

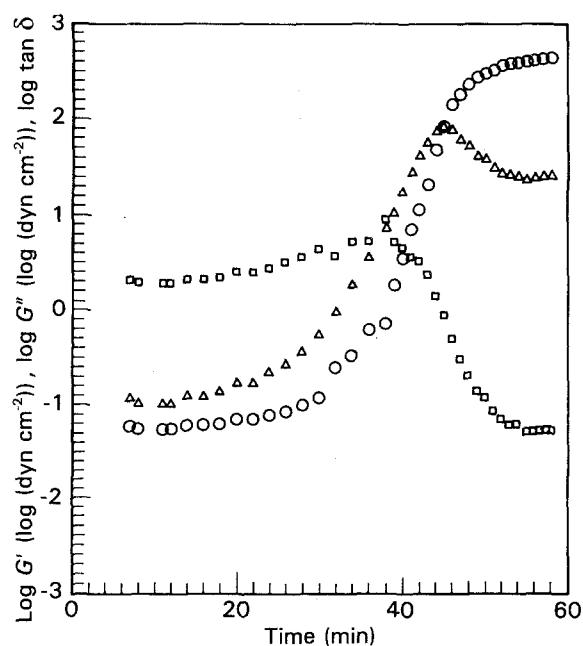


Figure 7 Dynamic mechanical properties versus cure time (at $T = 70^\circ\text{C}$, TDAP = 3 p.h.r., $f = 0.1\text{ Hz}$, NCO/OH = 30 mol %). (○) G' , (△) G'' , (□) $\tan \delta$.

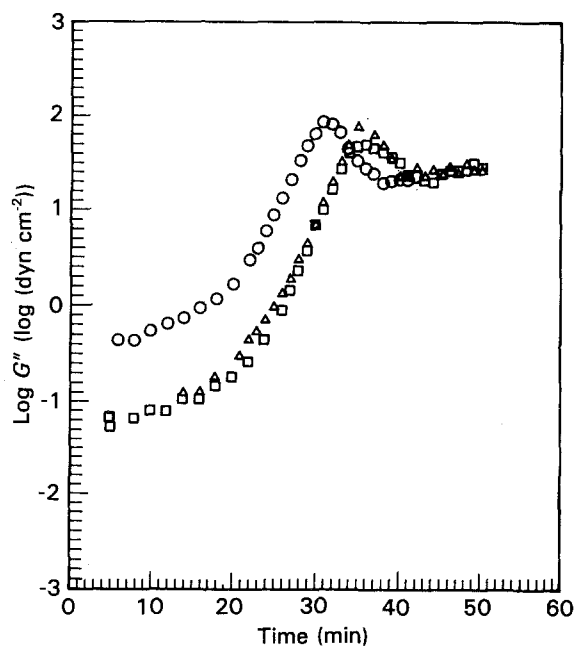


Figure 9 Loss modulus versus cure time at various frequencies (at $T = 75^\circ\text{C}$, TDAP = 3 p.h.r., NCO/OH = 30 mol %). (○) 0.5 Hz, (△) 0.2 Hz, (□) 0.1 Hz.

TABLE I The parameters of Equations 1 and 2 of the modified viscosity model

$T(^{\circ}\text{C})$	k_1	k_2	$\ln \eta_0$	$\log \eta_c$	t_c (min)
80	0.144	0.402	0.77	1.2	14.5
70	0.090	0.207	1.43	1.5	23.0
65	0.060	0.132	2.24	1.6	25.0

$\ln \eta_{\infty} = -30.0$	$\Delta E_{\eta} = 21.6\text{ kcal mol}^{-1}$
$\ln k_{1\infty} = 16.6$	$\Delta E_{k_1} = 16.6\text{ kcal mol}^{-1}$
$\ln k_{2\infty} = 23.0$	$\Delta E_{k_2} = 16.8\text{ kcal mol}^{-1}$

the faster curing reactions, so the time at which G' rises sharply or $\tan \delta$ reaches a maximum value, is earlier.

The dynamic storage moduli and loss moduli versus curing time for PU-cross-linked epoxide system with various NCO/OH ratios, are shown in Figs 12 and 13. The rate of increase of G' and G'' profiles decreases with increasing PU content of the modified epoxide; hence, the mobility of the molecule decreases with increasing NCO/OH ratio. These phenomena are consistent with those described for the viscosity profiles in Fig. 4.

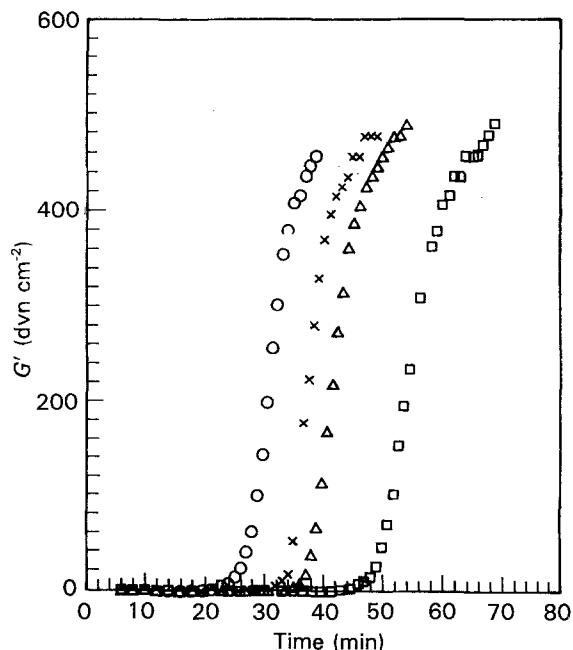


Figure 10 Storage modulus versus cure time at various temperatures (at $f = 0.2$ Hz, TDAP = 3 p.h.r., NCO/OH = 30 mol %). (○) 80°C, (×) 75°C, (△) 70°C, (□) 65°C.

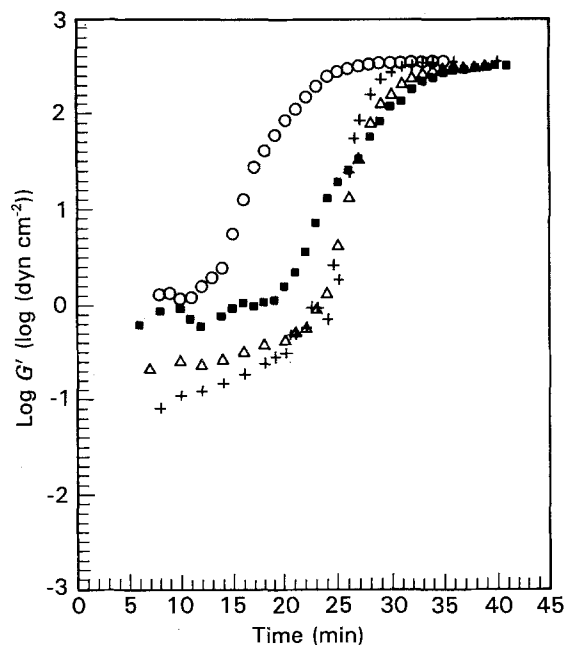


Figure 12 Storage modulus versus cure time for PU-cross-linked epoxy resin with various NCO/OH mole ratios (at $T = 80^\circ\text{C}$, $f = 0.5$ Hz, TDAP = 3 p.h.r.). (○) 100 mol %, (■) 80 mol %, (△) 30 mol %, (+) 0 mol %.

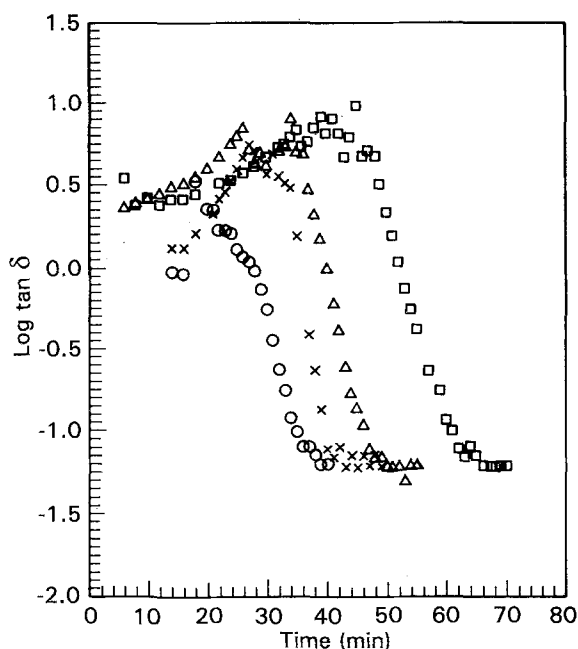


Figure 11 Loss tangent versus cure time at various temperatures (at $f = 0.2$ Hz, TDAP = 3 p.h.r., NCO/OH = 30 mol %). (○) 80°C, (×) 75°C, (△) 70°C, (□) 65°C.

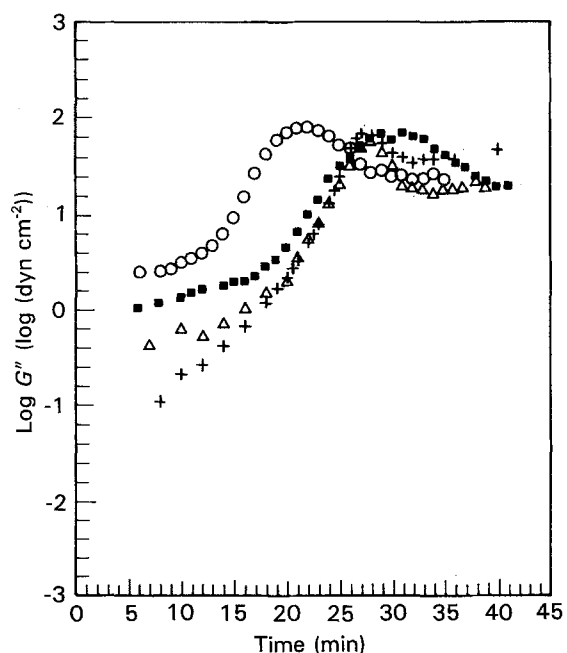


Figure 13 Loss modulus versus cure time for PU-cross-linked epoxy resin with various NCO/OH mole ratios (at $T = 80^\circ\text{C}$, $f = 0.5$ Hz, TDAP = 3 p.h.r.). (○) 100 mol %, (■) 80 mol %, (△) 30 mol %, (+) 0 mol %.

TABLE II The parameters of dynamic modulus model

$T(^{\circ}\text{C})$	t_0 (min)	$ G_{\infty}^* $ (dyn cm $^{-2}$)	$\ln k_x$
80	28	511	-1.61
75	34	504	-1.72
70	37	497	-1.77
65	49	490	-1.97

The values of t_0 , $|G_{\infty}^*|$ and k_x , according to Equation 4, were calculated and are listed in Table II. The values of k_x are shown by the Arrhenius plot in Fig. 14. The activation energy, ΔE_x , is 5.2 kcal mol $^{-1}$, and the

value of $\ln k_{x\infty}$ is 5.7. Fig. 15 shows the calculated and measured complex modulus curves with time at various temperatures. It is seen that the calculated values agree fairly well with the measurements in the rapidly rising portions.

3.3. Determination of the gelling time from rheological measurements

There are many different suggestions of how to determine the gelling time during isothermal cure from

TABLE III The gelling times determined from rheological measurements

T (°C)	Frequency (Hz)	$t(\tan \delta = 1)$ (min)	$t(G''_{max})$ (min)	$t(G')$ (min)	$t(\tan \delta_{max})$ (min)	$t_{\eta_{\infty}}$ (min)	$\dot{\gamma}^a$ (s ⁻¹)
80	0.5	27	27	26	23	21	1
80	0.2	27	29	27	18	21	2
80	0.1	28	28	28	24	21.5	4
75	0.5	31	31	30	26	27	2
75	0.2	35	34	34	28	27	4
75	0.1	34	36	33	28	26.5	6
70	0.2	40	40	38	36	34	2
70	0.1	44	44	43	38	—	—
65	0.2	53	53	50	44	41	2
65	0.1	54	54	51	46	—	—

^a $\dot{\gamma}$, shear rate.

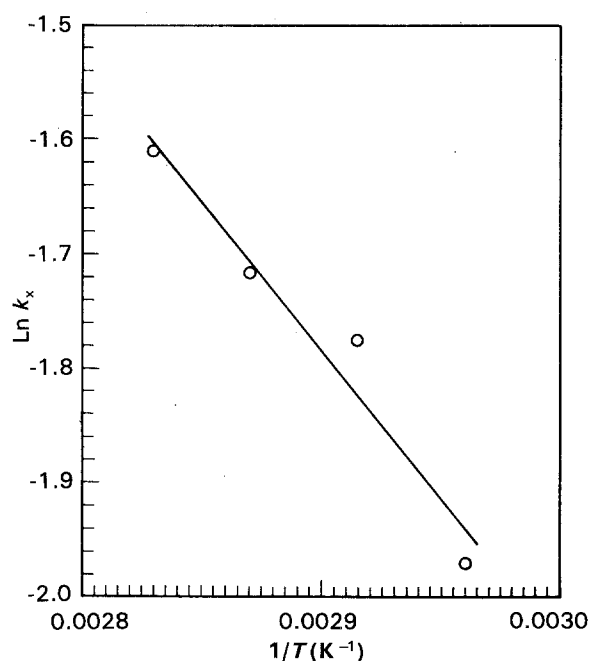


Figure 14 $\ln k_x$ versus $1/T$ for the epoxy reaction (at $f = 0.2$ Hz, TDAP = 3 p.h.r., NCO/OH = 30 mol %).

TABLE IV The dependency of $t(\tan \delta = 1)$ on the NCO/OH ratio

NCO/OH (mol %)	0	30	80	100
$t(\tan \delta = 1)$	27	27	30	18

rheological measurements [11, 15–20]. As shown in Table III, the gelling times determined from dynamic tests are affected by frequency for the PU-cross-linked epoxide system. However, at high cure temperature (say, 80 °C), the effect on frequency is not apparent, because of the rapid reactions. Furthermore, both $t(G')$ and $t_{\eta_{\infty}}$ are smaller than $t(\tan \delta = 1)$, and $t(\tan \delta = 1)$ is almost the same as $t(G''_{max})$. It was also found that $t(\tan \delta_{max})$ is closer to $t_{\eta_{\infty}}$ than the other values. Table IV shows the dependency of $t(\tan \delta = 1)$ on the NCO/OH ratio for PU-cross-linked epoxy resin cured with TDAP at 80 °C. The gelling time varies with the NCO/OH ratio.

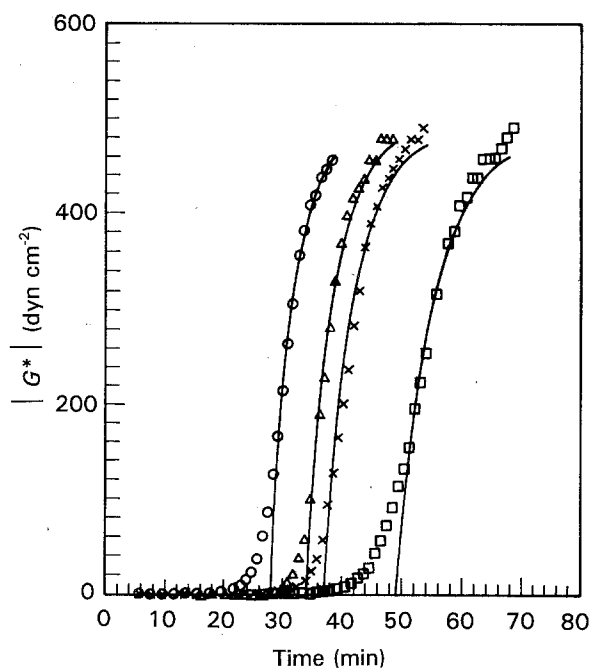


Figure 15 Comparison of (—) calculated Equation 4 with measured complex modulus (at TDAP = 3 p.h.r., $f = 0.2$ Hz, NCO/OH = 30 mol %). (○) 80 °C, (△) 75 °C, (×) 70 °C, (□) 65 °C.

4. Conclusion

The viscosity and complex dynamic modulus of the system PU-cross-linked epoxy resin cured with TDAP under isothermal and non-isothermal conditions, were studied in this work. A modified dual Arrhenius viscosity model was proposed to predict the viscosity profile before gelation. For isothermal cure, the calculated complex modulus on the basis of the rubber elasticity model agrees fairly well with the experimental measurements after the gelling point.

The activation energies of the different stages of the PU-cross-linked epoxide system are all lower than those of the unmodified epoxide system. Hence, the reaction rate of the PU-cross-linked epoxide system is less affected by temperature than that of the unmodified epoxide system. It was also found that the rates of increasing of viscosity and dynamic moduli decrease with increasing PU content. Furthermore, the time at which $\tan \delta$ reaches a maximum value almost

coincides with the time at which shear viscosity approaches an infinite value.

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