

Some Mechanical Properties of an Epoxy Resin System Cured with Multiple Crosslinking Agents

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Synopsis

Arbitrary cure times and glass transition temperatures are reported for an epoxy resin cocrosslinked by various weight fractions of hexamethylenediamine (HMDA) and *m*-phenylenediamine (*m*-PLDA). The glass transition temperatures of the epoxy resin systems studied yielded an excellent fit to an empirical equation developed by Dyvik for copolymers. The cure time parameters were found to be a linear function of the weight fractions of each crosslinking agent present. The mechanical properties of the epoxy resins were measured by an *in situ* dynamic modulus technique which employed the use of a resin-coated metallic substrate.

INTRODUCTION

The glass transition temperature $T_{g(A,B)}$ of copolymers as a function of the weight fractions of each homopolymer present has been studied by a number of researchers.¹⁻³ The results of these studies led to the derivation of equations which fit the specific copolymer system under examination but are unreliable when extended to other copolymer systems. The complexity of the problem is exemplified by the recent works of Illers,⁴ Beevers,⁵ and Krause,⁶ who have shown that the dependency of $T_{g(A,B)}$ upon the weight fractions of homopolymer may be linear, have positive or negative deviations, or display a minimum or maximum. Dyvik⁷ investigated a number of copolymer systems and developed an empirical equation that satisfies some of the above deviations. The equation is:

$$T_{g(A,B)} = W_A T_{g(A)} + W_B T_{g(B)} - \psi W_A W_B \quad (1)$$

where $T_{g(A,B)}$ is the glass transition temperature of the copolymer, $T_{g(A)}$ and $T_{g(B)}$ are the glass transition temperatures of the respective homopolymers, W_A and W_B are the weight fractions of each homopolymer present. ψ is the interaction parameter which appears to be dependent upon the geometrical chain stiffness and intermolecular attraction. The value of ψ is calculated as four times the deviation of the data from a straight line connecting $T_{g(A)}$ and $T_{g(B)}$ at the 50% weight fraction composition point.

This paper presents the results of a study in which an epoxy resin was crosslinked with combinations of *m*-phenylenediamine (*m*-PLDA) and hexamethylenediamine (HMDA).

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The epoxy resin systems were analyzed as copolymers based upon the assumption that the weight fraction of each crosslinking agent present yielded identical copolymer weight fractions. By utilizing this assumption and changing the sign of Dyvik's interaction parameter, good agreement between experimental data and Dyvik's equation was obtained.

A second relationship was developed in which the time required for the epoxy systems to reach a definite viscoelastic state (arbitrarily called cure) was related to the weight fractions of each crosslinking agent present. This relationship is:

$$t_{c(A,B)} = W_A t_A + W_B t_B \quad (2)$$

Where $t_{c(A,B)}$ is the cure time for the epoxy cocrosslinked system, t_A and t_B are the cure times for the epoxy system crosslinked with 100% A or 100% B, and W_A and W_B are the weight fractions of each crosslinking agent present.

EXPERIMENTAL

General

Shell Epon 828, a diglycidyl ether of bisphenol A with a molecular weight of approximately 350–400, was used as the base resin of the epoxy systems studied. The crosslinking agents, used in this study were Eastman Kodaks' *m*-phenylenediamine (*m*-PLDA) with a molecular weight of 108.14 g./mole and functionality of four and hexamethylenediamine (HMDA) with a molecular weight of 116.21 g./mole and also a functionality of four. Two master batches of epoxy resin and the crosslinking agents were prepared with 15 parts by weight of crosslinking agent for each 100 parts of Epon 828. Each batch was thoroughly blended and aliquot portions transferred to stoppered test tubes. These test tubes were immediately transferred to a cold box maintained at -40°F . Prior to the cure and glass transition studies, one sample each of the resin-crosslinking agent systems containing 15 phr of *m*-PLDA in Epon 828 and 15 phr of HMDA in Epon 828 were removed from the cold box and allowed to rise to room temperature. Small amounts of each resin system were weighed out on an analytical balance and thoroughly blended. The weight fraction of each crosslinking agent present was computed on the basis that each resin system employed contributed equal crosslinking activity due to functionality and the sum of the crosslinking agents present represented a 100% weight fraction. Subsequent cure and transition studies were conducted on various weight fractions of crosslinking agents computed by the above procedure.

Mechanical Technique

The changes in the mechanical properties of the curing and cured crosslinked resin systems were monitored continuously *in situ* by use of a vibrating reed technique previously described.⁸ Briefly, the vibrating reed

apparatus consists of resin-coated metallic cantilever reeds which are mounted horizontally. The reeds are driven into their fundamental frequencies of vibration by use of a mechanically linked loudspeaker head driven by a low frequency oscillator. Pins mounted on the free ends of the cantilever reeds generate sinusoidal signals of variable amplitude as they move in linear variable differential transformers (LVDT). The maximum amplitude of the signals as a function of frequency were taken as the polymer-substrate resonance frequencies. The cure time and transition temperatures of the polymers were followed by plotting the change of the squared fundamental vibrational frequencies ν^2 of the composite as a function of time or temperature. The resin thickness varied between 0.040 and 0.070 in., whereas the supporting metallic reed thickness was about 0.010 in. The resin systems were brought to a cure temperature of 160°F. with two heaters controlled by a thermocouple immersed in the resin.

As the resins passed through their cure time transitions and became glassy the temperature was increased to 300°F. and held at this temperature for 72 hr. Following this heat soak period the glass transition temperatures were located by plotting the relative reed moduli as a function of temperature. The temperature was varied by 10°F. increments with 15 min. soaking periods to insure temperature equilibrium.

RESULTS AND DISCUSSION

Figure 1 depicts the normalized results obtained when the apparent mechanical conversion of the epoxy-coated substrates was plotted as a function of cure time at a constant cure temperature of 160°F. The apparent mechanical conversion is calculated from the relative modulus given by:

$$E'_{\text{DYN}} \sim A\nu^2 \quad (3)$$

where E'_{DYN} is the relative dynamic modulus of the metal-polymer laminate and ν^2 is the squared fundamental resonance frequency. It is apparent that three asymptotical lines may be drawn on the mechanical conversion curves; one curve at zero conversion, a second in the cure transition region, analogous to the glass transition region, and the third at the 100% mechanical conversion. The intersection of the zero mechanical conversion and cure transition asymptotes offers a convenient time parameter with which cure time versus composition relationships can be developed. The choice of this time parameter was based upon a previous study⁸ in which the mechanical conversion times were closely related to infrared rate studies.

Figure 2 presents the results of the cure time parameter plotted against the weight per cent fraction of *m*-PLDA present on the total weight of crosslinking agents. It is seen that this curve is a linear function of *m*-PLDA present and is adequately described by eq. (2). It is apparent that eq. (2) is analogous to equations developed which relate the changes in glass transition temperature to copolymer composition. Indeed, the

mechanical conversion curves of Figure 1 indicate that the curing resin has only one transition region which strongly suggests that the cocrosslinked resin is analogous to a compatible copolymer system. The relative slopes

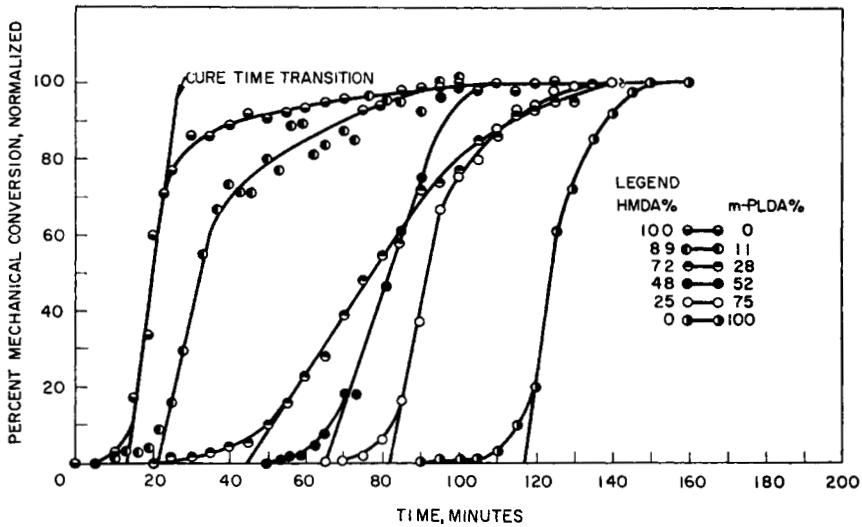


Fig. 1. Per cent mechanical conversion as a function of time and crosslinking agents. Cure temperature 160°F.

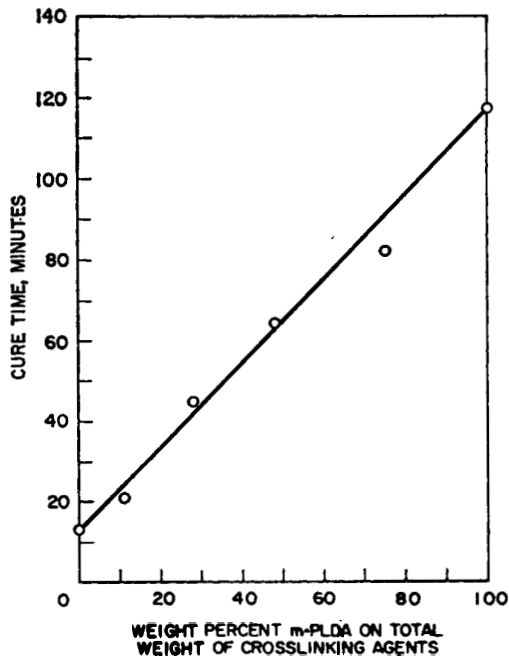


Fig. 2. Cure time as a function of weight per cent *m*-PLDA on total weight of crosslinking agents present.

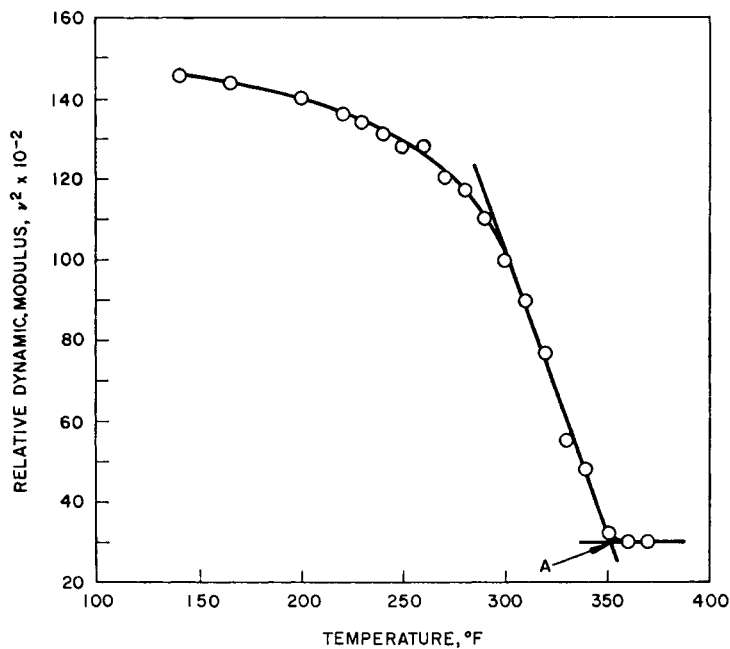


Fig. 3. Relative dynamic modulus as a function of temperature; 75% *m*-PLDA on total weight of crosslinking agents present.

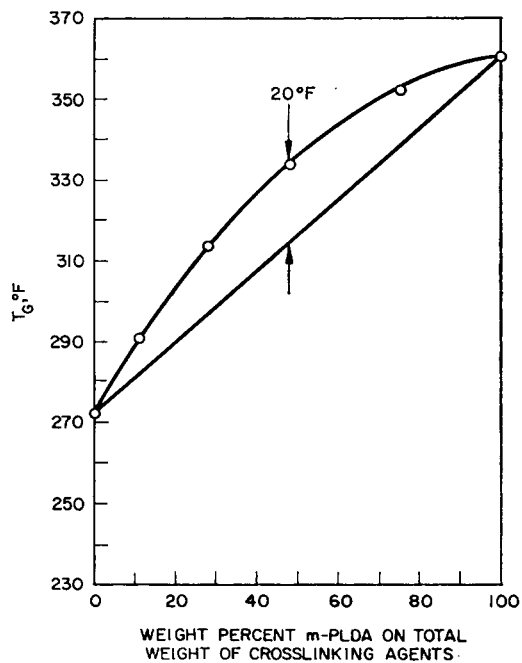


Fig. 4. Glass transition temperatures as a function of weight per cent *m*-PLDA on total weight of crosslinking agents present.

of the cure transition regions of the curves appear to be a function of the weight fractions of the crosslinking agents present. The cure transition slopes of HMDA and *m*-PLDA at 100% by weight are very sharp and distinct, whereas the cocrosslinked systems display a much broader dispersion region.

Figure 3 presents a typical curve obtained when the relative dynamic modulus of the epoxy-coated reed (75% *m*-PLDA and 25% HMDA) was monitored as a function of temperature. The intersection of the lines that are drawn asymptotically to the glass transition and rubber like regions of the curve, (point A), is considered the polymer T_g . It is recognized that this glass transition temperature is about 40–50°F. higher than generally reported, due primarily to the higher test frequency employed in this investigation and the fact that point A lies about 15–20°F. higher than where the maximum damping occurs. The location of point A, which is well defined and reproducible, is of considerable interest because its position represents the transition of the polymer from a tough leathery material to one displaying rubber elasticity. Structurally, the significance of this transition is that of various crankshaft motions which the polymer main chain can now undergo thus allowing more favorable positioning of unreacted epoxy and labile hydrogens for further reaction.

The glass transition temperature curve of Figure 3 is representative of the other systems studied and substantiates the cure time transition behavior which is illustrative of systems that are mechanically compatible. During this investigation, several heat-soak times were employed to determine the stability of the polymer T_g . When the polymer systems were held at about 300°F. for a period of 24 hr. some advancement of the T_g occurred. If the heat-soak time was increased to 48 hr. no measurable movement of the T_g was observed. Therefore, it was felt that a heat soak of 72 hr. produces a fully cured polymer if the T_g stability is taken as a criterion of cure.

Figure 4 presents the data obtained for the glass transition temperatures of the epoxy systems studied as a function of the weight fractions of each crosslinking agent present. The solid curve represents the Dyvik equation with the exception of a positive sign before the interaction factor.

$$T_{g(A,B)} = W_A T_{g(A)} + W_B T_{g(B)} + \psi W_A W_B \quad (4)$$

The increase in the polymer $T_{g(A,B)}$, as compared to a straight line connecting zero and 100% weight fraction *m*-PLDA present, is attributed to the more dense packing of the polymeric segments, which thus allows greater hydrogen bonding to arise between unreacted pendant groups of —OH, =NH, and —H.

CONCLUSIONS

An arbitrary cure time parameter was found to be directly related to the weight fraction of each crosslinking agent present and may be represented by the equation:

$$t_{c(A,B)} = t_A W_A + t_B W_B$$

An epoxy resin cured with various combination of two crosslinking agents (HMDA and *m*-PLDA) acted analogous to a compatible copolymer system.

The glass transition temperatures, $T_{g(A,B)}$, found for the systems studied obeyed the empirical equation developed by Dyvik for copolymers.

$$T_{g(A,B)} = W_A T_{g(A)} + W_B T_{g(B)} + \psi W_A W_B$$

References

1. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).
2. G. Kanig, *Kolloid-Z.*, **190**, 1 (1963).
3. M. Gordon and T. S. Taylor, *J. Appl. Chem.*, **2**, 493 (1952).
4. K. H. Illers, *Kolloid-Z.*, **190**, 16 (1963).
5. R. B. Beevers and E. F. T. White, *J. Polymer Sci. B*, **1**, 177 (1963).
6. S. Krause and N. Roman, *J. Polymer Sci. A*, **3**, 1631 (1965).
7. G. K. Dyvik, W. F. Bartoe, and N. S. Beck, *SPE Trans.*, **4**, 98 (1964).
8. R. K. Jenkins and L. E. Karre, *J. Appl. Polymer Sci.*, **10**, 303 (1966).

Résumé

Des temps de post-traitement arbitraires et les températures de transition vitreuse sont rapportées pour une résine époxy pontée avec différentes fractions en poids d'hexaméthylène diamine (HMD) et de méthaphénylène (*m*-PLDA). Les températures de transition vitreuse des systèmes résine-époxy étudiés fournissaient un accord excellent avec l'équation empirique développée par Dyvik pour les copolymères. Les paramètres post-traitement/temps étaient une fonction linéaire des fractions pondérales de chaque agent de pontage présent. Les propriétés mécaniques des résines époxy étaient mesurées par une technique de module dynamique in situ qui employait l'utilisation de la résine recouverte d'un substrat métallique.

Zusammenfassung

Nach Belieben wählbare Härtungsdauern und Glastemperaturen werden für ein mit verschiedenen Gewichtsbruchteilen an Hexamethylendiamin (HMDA) und *m*-Phenylendiamin (*m*-PLDA) co- vernetztes Epoxyharz mitgeteilt. Die Glastemperatur der untersuchten Epoxyharzsysteme liess sich sehr gut durch eine empirische von Dyvik für Copolymere entwickelte Beziehung darstellen. Der Härtungsdauer-Parameter erwies sich bei jedem Vernetzer als lineare Funktion des Gewichtsbruchteils. Die mechanischen Eigenschaften der Epoxyharze wurden mittels eines in situ-Verfahrens zur Bestimmung des dynamischen Moduls unter Verwendung eines mit Harz überzogenen Metallsubstrates gemessen.

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