Correlations between dynamic mechanical properties and nodular morphology of cured epoxy resins

Jovan Mijović and Leelan Tsay
Polytechnic Institute of New York, Department of Chemical Engineering, 333 *Jay St., Brooklyn, NY* 11201, *USA*

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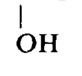
Various epoxy resin formulations, based on the diglycidyl ether of bisphenol A (DGEBA) and cured with diethylene triamine (DETA) were studied. Dynamic mechanical measurements were used to characterize changes in mechanical properties as a function of temperature. The morphology of the cured resins was investigated by transmission electron microscopy. Correlations between dynamic mechanical properties and morphology were described and discussed by applying the concept of inhomogeneous (nodular) thermoset morphology. The elastic storage modulus in the glassy state was determined primarily by the internodular matrix, whereas the glass transition of cured resins depended upon the intranodular crosslink density.

INTRODUCTION

Numerous attempts have been made to correlate the dynamic mechanical properties of epoxy resins with their structure. Most investigators focused their attention upon changes in the low temperature relaxation as a function of curing conditions and/or chemistry and concentration of resin and curing agent. This low temperature relaxation, commonly referred to as the β transition, occurs between approximately $-40°$ and $-60°$C in dynamic mechanical spectra, depending on the frequency of mechanical oscillation which typically lies between 0.1 and 100 Hz. β relaxation was first reported by Kaelble in 1959[1]. Studies of the dynamic mechanical properties of various epoxies during the 1960s have been summarized by Delaticky[2]. Several subsequent research efforts are listed in ref 3–7. Recently, however, interest in structure–property correlations in epoxy resins has intensified due to their widespread use as the matrix material in composite structures. This is clearly witnessed by a number of current dynamic mechanical investigations of various structural epoxies[8–11]. Briefly to summarize the past work: the low temperature β relaxation is believed to represent the onset of the crankshaft motion of the glyceryl group,



$$\text{—O—CH}_2\text{—}\underset{\text{OH}}{\text{CH}}\text{—CH}_2\text{—}$$

Considerable interest in the β relaxation stems primarily from the fact that its magnitude and location can be directly correlated with changes in the degree of cure and the structure of various epoxy formulations.

Nevertheless, a conspicuous absence of any meaningful correlation between dynamic mechanical properties and thermoset morphology has existed, primarily because of the lack of understanding of morphology of highly crosslinked thermosets. The concept of homogeneous infinite networks represented by one giant molecule has long been erroneously applied to describe the morphology of all thermosetting polymers. However, a growing demand for better understanding of thermoset structures resulted in research efforts which, within the last two decades, have produced ample experimental evidence for the existence of inhomogeneities in the morphology of highly crosslinked polymers, such as epoxy resins. A chronological development of this concept has recently been reviewed[12]. It is now generally agreed that the more highly crosslinked nodules are immersed in an internodular matrix of lower crosslink density.

The objective of this paper is to describe the changes in dynamic mechanical properties of epoxy resins, caused by variations in curing conditions and curing agent concentration, in terms of the nodular morphology model.

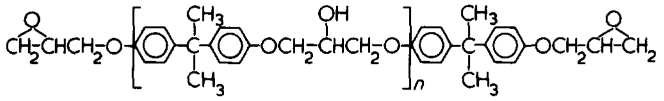
EXPERIMENTAL

Chemical systems

Epon 825, Shell's liquid diglycidyl ether of bisphenol A (DGEBA) resin was cured with diethylene triamine (DETA). The chemical structure of resin and curing agent is shown in *Table 1*. The composition and cure schedule of the various formulations are listed in *Table 2*.

Table 1 Chemical structure of epoxy resin and curing agent

Typical diglycidyl ether of bisphenol A (DGEBA) resin



Diethylene triamine (DETA) curing agent

$H_2N—CH_2—CH_2—NH—CH_2—CH_2—NH_2$

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Table 2 Various epoxy formulations studied

Formulation or cure schedule no.	Composition	Variable	Cure schedule
1	Epon 825* + 6–20 phr DETA	Curing agent concentration	Components mixed at room temperature for 5 min and cured in silicone moulds; 24 h at room temperature + 20 h at 120°C
2	Epon 825 + 8 phr DETA	Postcure time	Components mixed at room temperature for 5 min and cured in silicone moulds; 24 h at room temperature + postcure at 120°C

* Epon 825, Shell's liquid DGEBA resin, is a purified form of commercially available Epon 826

Techniques

A Silastic E RTV rubber (Dow Corning) cured with 10 phr* of Silastic E curing agent was used for the preparation of the moulds. Specimens were cast in the moulds and cured according to the schedule of *Table 2.* All samples were kept at 20°C and 45% r.h. for at least 24 h prior to testing. Dynamic mechanical measurements were performed in DuPont's DMA 981 instrument. Tests were run at the oscillation amplitude of 0.2 mm peak-to-peak, and heating rate of 5°C min^{-1}. One stage carbon–platinum (C–Pt) replicas of fracture surfaces were prepared as previously described[13]. A JEOL 100B model transmission electron microscope was used to investigate the surface morphology.

RESULTS AND DISCUSSION

We first consider the effect of curing agent concentration on changes in the room temperature elastic storage modulus. Assuming that each epoxy group reacts with an amine hydrogen on the curing agent, the stoichiometric ratio was calculated to be 12.2 phr. As seen from *Figure 1*, the room temperature value of elastic modulus decreases as the curing agent concentration is increased up to and slightly beyond the stoichiometric ratio. This phenomenon has been observed in several other thermosetting systems, although no rationalization has been offered by these authors[6,14,15]. Kenyon and Nielsen[16], however, measured dynamic mechanical properties of an epoxy formulation (DGEBA/TETA) and found that lower room temperature shear moduli were obtained at higher curing agent concentration. They accounted for the lower modulus of the curing agent-rich formulation by suggesting a two-phase epoxy system, with modulus being determined by the weaker matrix phase. Nevertheless, they studied only two different curing agent concentrations and showed no evidence for the assumed homogeneous morphology of the lower curing agent concentration resin.

In order to clarify the concept of nodular morphology, the onset of formation of an inhomogeneous thermoset network will first be considered. Although not explicitly studied in this work, it is believed that the formation of nodules commences at random spots in the resin-curing agent mixture (shown schematically in *Figure 2*). The incipient formation of nodules takes place prior to gelation, as suggested by several authors[17,18]. If vitrification occurs during the course of formation of a thermoset network, it becomes necessary to raise the curing temperature above the glass transition of the fully-cured resin — $T_{g,\infty}$[19]. This will ensure completion of chemical reactions and eliminate artifacts in dynamic mechanical spectra, caused by continuation of crosslinking during testing. Transmission electron microscopy[12,13] showed that the size and shape of nodular structures of samples cured below $T_{g,\infty}$ do not change with postcure above $T_{g,\infty}$. Although simultaneous changes in mechanical properties take place, indicating further crosslinking, the constancy of noduali size points to their formation during early stages of cure.

We further believe that higher curing agent concentrations lead to more excessive *intra*nodular reactions, at the expense of the *inter*nodular matrix. The room temperature elastic modulus is determined by the weakest of the two phases, i.e. the internodular matrix. Therefore, the relative lowering of the crosslink density of internodular matrix, as the curing agent concentration is increased, accounts for the decrease in modulus observed in *Figure 1.* A simplified schematic presentation of a relative variation in moduli of nodules and matrix as a function of curing agent concentration is shown in *Figure 3.* This schematic presentation is further corroborated by electron microscopy. *Figure 4* shows transmission elec-

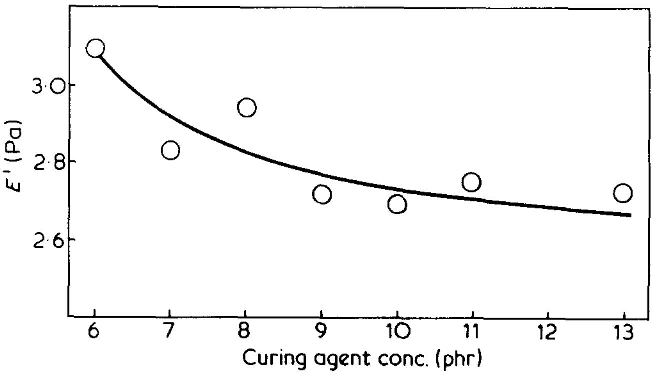

Figure 1 Room temperature elastic storage modulus as a function of curing agent concentration for formulation 1 (*Table 2*)

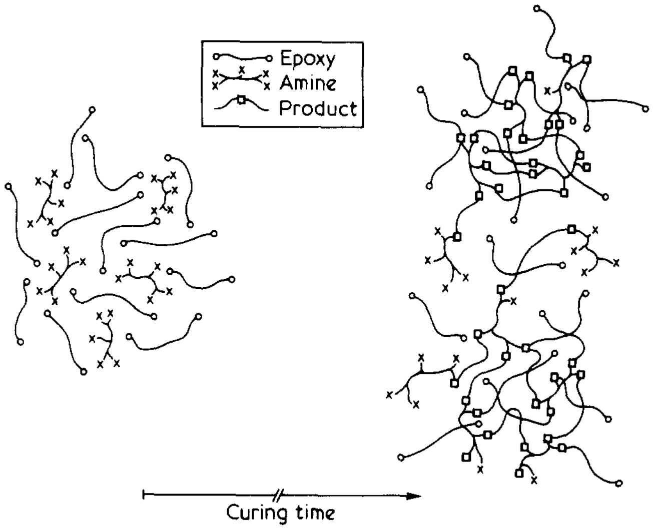

Figure 2 Schematic presentation of initial formation of nodules in the resin curing agent mixture

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* phr = parts per hundred parts of resin, by wt.

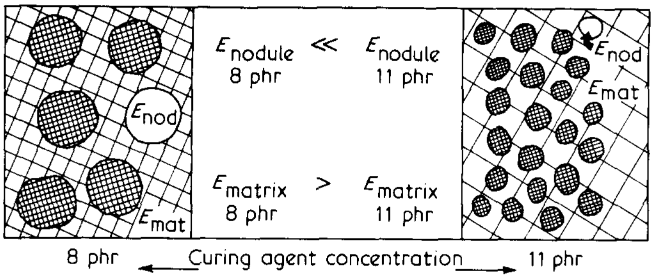

Figure 3 Schematic presentation of variations in moduli of nodules and matrix as a function of curing agent concentration

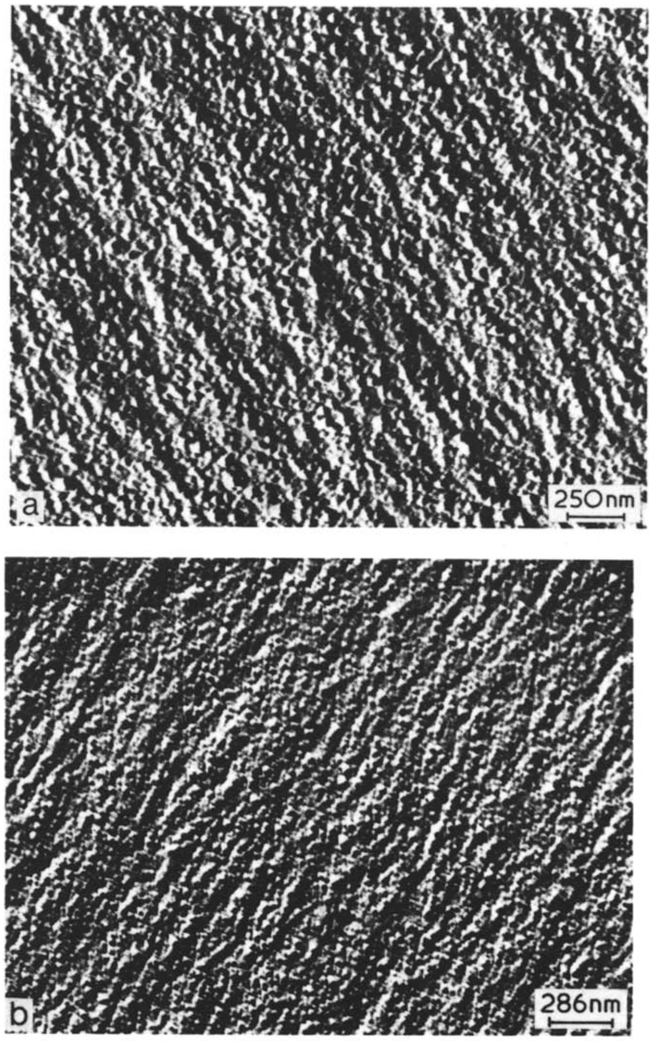

Figure 4 (a) Transmission electron micrograph of a one-stage C–Pt replica of fracture surface of an Epon 825/8 phr DETA resin. Sample was subjected to cure schedule 1 (*Table 2*). Magnification 40 000X. Average nodule diameter was 30 nm. (b) Transmission electron micrograph of a one-stage C–Pt replica of fracture surface of an Epon 825/11 phr DETA resin. Sample was subjected to cure schedule 1 (*Table 2*). Magnification X 35 000. Average nodule diameter was 200 nm

tron micrographs (*TEM*) of fracture surface replicas of samples cured with 8 phr (*4a*) and 11 phr (*4b*) of curing agent. Although no direct information about the relative values of moduli of nodules and matrix can be deduced from *Figure 4*, it is apparent that fracture occurs *through* the matrix and around nodules, indicating that the latter are indeed sites of higher crosslink density. The average diameter of nodules in *Figures 4a* and *4b* was found to be 30 and 20 nm, respectively. This result agrees, at least qualitatively, with the suggested schematic model of *Figure 3*. Had we been able, however, to direct fracture *through the nodules*, higher values of elastic moduli would be expected at higher curing agent concentrations.

A direct consequence of this morphological mechanism is an increase in free volume of the internodular matrix at higher curing agent concentration. A similar argument has been used to explain the decrease in room temperature elastic modulus with increased postcure time[19].

Statistical arguments have also been advanced to support the concept of favourable intranodular reactions. For instance, Labana *et al.*[20] showed that the probability of intramolecular reactions within 'gel balls' (nodules) exceeds that of the internodular reactions, leading to the formation of a lower crosslink density matrix. Chompff[21] has proposed that extensive intranodular crosslinking is a consequence of conformational barriers to the diffusion of reactive groups.

The effect of varying curing agent concentration upon the height, breadth and location of the β relaxation peak is shown in *Figures 5* and *6*. The magnitude of tan δ and the breadth of the damping peak increase up to the stoichiometric ratio and then drop with increased curing agent concentration. An explanation of this behaviour is again offered in terms of the nodular morphology model. The breadth of the damping peak becomes larger with increasing curing agent concentration indicating (1) an increase in the total number of glyceryl groups in both phases and (2) the formation of a broader spectrum of glyceryl groups with respect to their capability to commence molecular motion. The more hindered groups within highly crosslinked nodules will display more difficulty in initiating the crankshaft motion and will do so only at a relatively higher temperature. Consequently, both the β relaxation peak temperature and the high temperature end of the damping curve will be shifted to higher temperature, as seen in *Figures 5* and *6*. According to the nodular morphology model, the difference between the crosslink density of the nodules and the matrix is most pronounced in curing agent-rich formulations. Indeed, careful examination of the broad damping peak of resin cured with the stoichiometric amount of curing agent

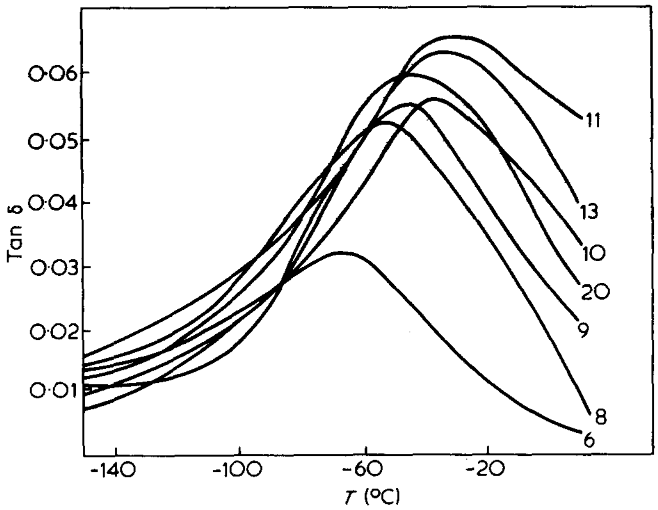

Figure 5 Variation of low temperature damping peak as a function of temperature with curing agent concentration as a parameter, for formulation 1 (*Table 2*)

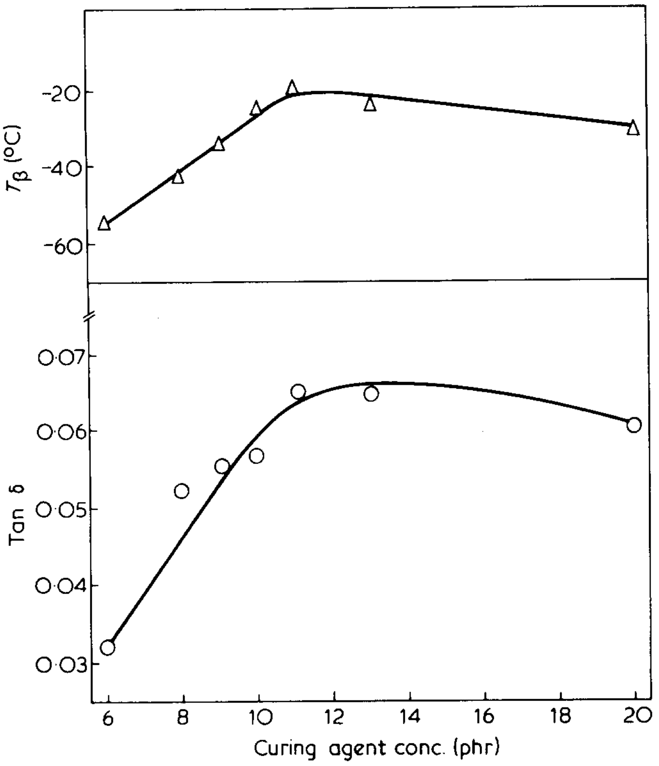

Figure 6 Changes in temperature and height of the maximum in the low temperature damping peak as a function of curing agent concentration for formulation 1 (*Table 2*)

seems to indicate the presence of two overlapping individual peaks, corresponding to relaxation in the matrix and nodules, respectively.

While the value of the room temperature elastic storage modulus is determined by the internodular matrix, the glass transition of a cured formulation depends primarily upon the crosslink density within nodules. Changes in elastic modulus in the vicinity of glass transition for formulations of various curing agent concentrations are shown in *Figure 7*. The glass transition of cured formulations was observed to increase with increased curing agent concentration. A large excess of curing agent caused a plasticization effect and reduced T_g considerably. On the molecular level, these experimental findings can also be explained by the nodular morphology model.

Referring back to the proposed model in *Figure 3*, resin morphology is most clearly understood by envisioning nodules as supporting elements of a rigid framework which hold the entire network together. Although polymeric chains in the matrix are capable of crankshaft-type motion (secondary β transition), they are tightly held by the nodular framework and will not initiate the transition into the rubbery state. Instead, the onset of molecular motion, corresponding to the glass transition, will be determined by the onset of motion within nodules. The nodular crosslink density is higher in curing agent-rich formulations, and therefore, a higher temperature will be needed to induce the molecular motion in these systems. Indeed, an increase in T_g as a function of increased curing agent concentration has been experimentally observed as shown in *Figure 7*.

Changes in size and location of the low temperature damping peak of samples postcured for various times are shown in *Figure 8*. Simultaneous increases in damping (tan δ) and shifts to higher peak temperatures (T_β) have been observed within the first 20 h of postcure as shown in *Figure 9*. Beyond that point T_β remains constant whereas tan δ shows a slight decrease, probably caused by some degradation due to prolonged exposure to high temperature. The maximum value of the low temperature damping apparently serves as an indicator of the attainment of fully-cured state for a particular formulation.

At this point, it is instructive to emphasize a similarity between dependence of non-destructive (dynamic mechanical) and destructive (fracture) properties of this resin formulation on the postcure time. In a previous study[12], it was shown that the fracture energy (strain energy release rate) reached an asymptotic value as a function of postcure time after approximately 20 h. This result parallels dynamic mechanical data on β relaxation, suggesting that the information obtained from non-destructive tests may possibly be used to specify the ultimate mechanical properties of fully cured resins.

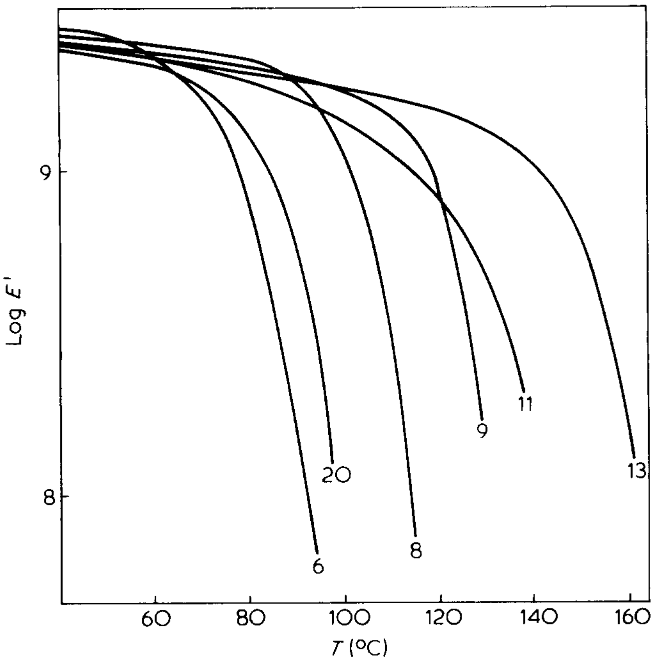

Figure 7 Elastic storage modulus in the vicinity of glass transition as a function of curing agent concentration for formulation 1 (*Table 2*)

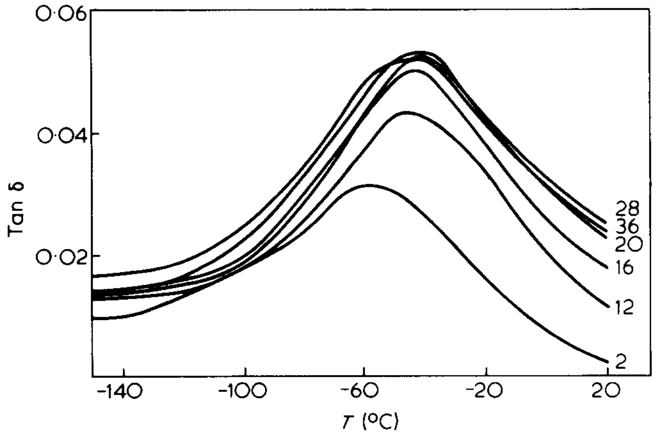

Figure 8 Variation of low temperature damping peak as a function of temperature with postcure time as a parameter, for formulation 2 (*Table 2*)

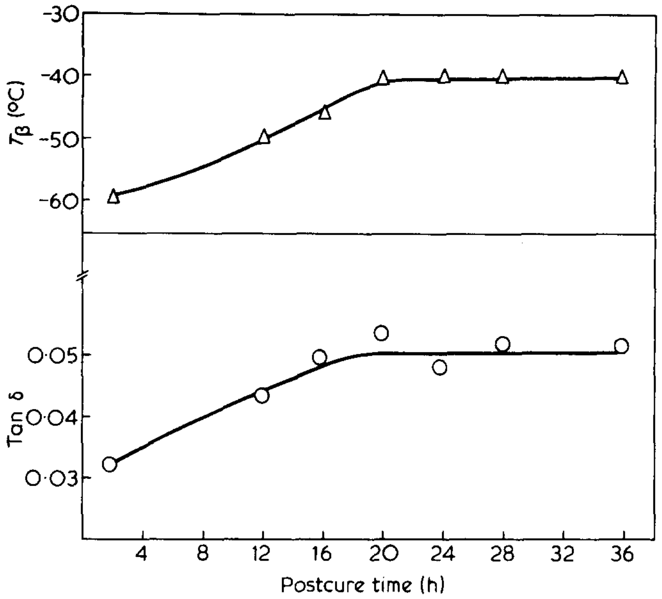

Figure 9 Changes in temperature and height of the maximum in low temperature damping peak as a function of postcure time for formulation 2 (*Table 2*)

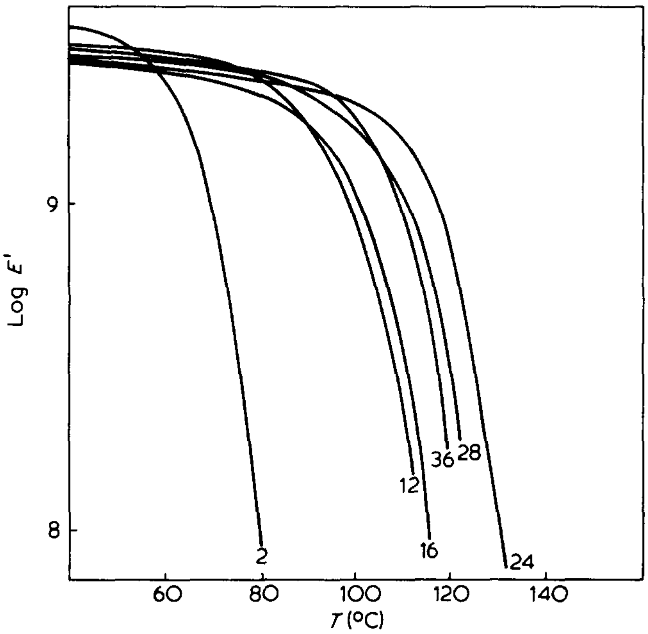

Figure 10 Elastic storage modulus in the vicinity of the glass transition as a function of temperature with postcure time as a parameter, for formulation 2 (*Table 2*)

Dynamic mechanical tests provide information about stored and dissipated energy during application of non-destructive stress. Linear elastic fracture mechanics tests, however, describe energy stored in the system before and after a finite amount of crack motion. Therefore, a proposal to correlate dynamic mechanical and fracture properties is based upon an underlying conceptual similarity in physical significance between the dynamic mechanical parameters and the critical strain energy release rate (G_{1c}). Further research on these lines is presently being conducted in our laboratories.

The glass transition of samples postcured for various times initially shifts to higher temperatures and then drops slightly beyond the 20 h mark. This behaviour, shown in *Figure 10*, can readily be explained by the concept of nodular morphology. High crosslink density nodules act as supporting sites of a framework which hold the thermosetting network together. As the postcure time is increased, additional crosslinking takes place, both in the nodules and in the internodular matrix. However, of utmost importance to the change in T_g is the further increase of nodular crosslink density which leads to the formation of more rigid framework. Higher curing agent concentrations will produce nodules of increased crosslink density and, consequently, higher temperatures will be needed to cause the onset of molecular motion, corresponding to T_g, in such a network. Prolonged exposure (above 24 h) to high postcuring temperature probably causes some degradation of the polymeric network, resulting in a decrease in elastic storage modulus and T_g.

CONCLUSIONS

Experimental evidence obtained from dynamic mechanical analysis and electron microscipy has been used to advance further the concept of inhomogeneous morphology of thermosetting polymers. The model of higher crosslink density nodules immersed in a lower crosslink density matrix was supported by the experimental data. An increase in curing agent concentration, up to the stoichiometric ratio, led to the formation of smaller nodules of higher crosslink density at the expense of the relatively weaker matrix. The elastic storage modulus in the glassy state is determined primarily by the internodular matrix, whereas the onset of molecular motion, corresponding to the glass transition, depends directly upon the intranodular crosslink density.

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REFERENCES

1 Kaelble, D. H. *SPE J.* 1959, **15**, 1071
2 Delaticky, O., Shaw, J. C. and Williams, J. G. *J. Polym. Sci. (A-2)* 1969, **7**, 753
3 Cuddihy, E. F. and Moacanin, J. *J. Polym. Sci. (A-2)* 1970, **8**, 1627
4 Pogany, G. A. *Polymer* 1970, **11**, 66
5 Arridge, R. G. C. and Speake, J. H. *Polymer* 1972, **13**, 443
6 Hirai, T. and Kline, D. E. *J. Appl. Polym. Sci.* 1972, **16**, 3145
7 Hirai, T. and Kline, D. E. 1973, **17**, 31
8 Williams, J. G. *J. Appl. Polym. Sci.* 1979, **23**, 3433
9 Lewis, A. F., Doyle, M. J. and Gillham, J. K. *ACS Div. Org. Coat. Plast. Chem. Prepr.* 1979, **40**, 860
10 Von Kuzenko, M. and Browning, C. E. *Ibid.* 1979, **40**, 694
11 Keenan, J. D., Seferis, J. C. and Quinlivan, J. T. *Ibid.* 1979, **40**, 700
12 Mijovic, J. *Polymer* 1979, **20**, 1095
13 Mijović, J. and Koutsky, J. A. *J. Appl. Polym. Sci.* 1979, **23**, 1037
14 Mostovoy, S. and Ripling, E. J. *J. Appl. Polym. Sci.* 1966, **10**, 1351
15 Lee, H. and Neville, K., 'Handbook of Epoxy Resins', McGraw-Hill, NY 1967, Ch 7, p 8
16 Kenyon, A. S. and Nielsen, L. E. *J. Macromol. Sci. (A)* 1969, **3**, 275
17 Bobalek, E. G., Moore, E. R., Levy, S. S. and Lee, C. D. *J. Appl. Polym. Sci.* 1964, **8**, 625
18 Solomon, D. H. and Hopwood, J. J. *Ibid.* 1966, **10**, 1893
19 Gillham, J. K. *SPE 38th Annual Tech. Conf. Preprints, NY*, May 1980, pp 268–271 and ref therein
20 Labana, S. S., Newman, S. and Chompff, A. J. in 'Polymer Networks' (Eds. A. J. Chompff and S. Newman) Plenum Press, NY, 1971, p 453
21 Chompff, A. J. *ACS Div. Org. Coat. Plast. Chem. Prepr.* 1976, **36**, 529