Processing Property Relationship for Dicyandiamide-Cured Epoxy Networks

In previous works,[1,2] we have studied and demonstrated that the isothermal curing processes for a benzyldimethylamine (BDMA)-accelerated dicyandiamide (DDA) epoxy system is quite different than the reactions with usual diamine hardeners.[3,4] On the one hand, differential scanning calorimetry (DSC) and infrared spectroscopy (IR) showed that the curing temperature and the stoichiometry have a great influence on the competition between etherification and addition and on the reaction mechanism of DDA itself. Therefore, the network structure will vary with curing conditions.

On the other hand, the solubility of DDA in DGEBA prepolymers or phenyl glycidyl ether (PGE) is low, but increases with temperature. Hagnauer and Dunn[5] have shown that the concentration of DDA in PGE increases exponentially from 0.04 g DDA/100 g PGE at 30° to about 0.6 g/100 g PGE at 150°C and to 0.9 g/100 g PGE after 2 h at 150°C. Ideally, the process of gelation should be carried out at a temperature high enough to ensure a complete miscibility between the prepolymer and the curing agent, without any phase separation. But the gelation at high temperatures can often lead to exothermal problems in thick laminates, and a compromise should then be found.

The changes in network structure, as well as the existence of residual curing agent, can affect the mechanical behavior[6] and thermal performances. This note presents curing cycle effects on the network structure without and with glass beads in connection with their viscoelastic, thermal and mechanical properties.

EXPERIMENTAL

Materials

The epoxy prepolymer DGEBA (Bakelite 164), curing agent DDA (Bakelite VE 2560) and accelerator BDMA were commercial products, and used without purification.[2] Glass beads in the range 4–44 μm (Sovitec 050A0) were used as fillers without surface treatment. Table I shows the formulations and the curing cycles used in this study, where a/e indicates the amine-to-epoxy ratio of the formulation. It would be noted that a precure at 100°C for 3 h makes the difference between the curing cycles.

The materials were mixed by mechanical stirring under vacuum at 60°C for 1 h prior to the curing. Then the mixture was cast into a PTFE-coated aluminum mold (170 × 150 × 4 mm). The mold was heated in an oven, the temperature of which was controlled as indicated in Table I. The mold continuously turned at 25 rpm during heating in order to prevent the glass beads and DDA from sedimentation. However, unlike the previous work with the DSC pans which assured a good conduction of the reaction heat,[2] the big reaction volume, the poor heat conduction of the mold, and the exothermal effect did not allow us to really obtain an isothermal cure. A thermocouple set in the mold indicated that the true reaction temperature was much higher than the oven temperature due to the extreme exothermal character of the early reaction stage (Fig. 1).

After curing, the mold was taken out from the oven and cooled in the air at room temperature. The samples for various analyses were cut from the plates as prepared.

ANALYTICAL

The extractions were performed in a soxhlet apparatus, with 2 g of finely grounded samples and 180 cm³ of tetrahydrofurane (THF) as solvent. The extraction lasted 12 h for each sample; then the extracted fraction of DGEBA and DDA were determined by means of gel permeation chromatography and differential scanning calorimetry as well as IR spectral analysis.

TABLE I
Formulation and Curing Cycles for BDMA-Accelerated DDA Epoxy System

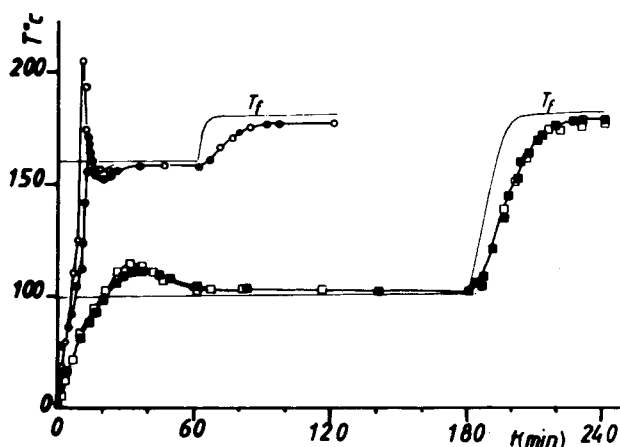| Formulation	A	A′	B	B′	C	C′	D	D′
a/e			1.0				0.6	
Accelerator	1 mL (BDMA)/100 g (DGEBA)				1 mL (BDMA)/100 g (DGEBA)			
Filler vol fraction	0	0	0.2	0.2	0	0	0.2	0.2
Curing cycle $T(°C)$–t (h)	/ 160-1	100-3 + 160-1	/ 160-1	100-3 + 160-1	/ 160-1 + 180-1	100-3 + 180-1	/ 160-1 + 180-1	100-3 + 180-1

Fig. 1.   Evolution of reaction temperature during curing, monitored by a thermocouple (—); T_f indicates the furnace temperature: (○) C; (□) C′; (●) D; (■) D′.

Gel permeation chromatography (GPC) analysis was carried out with a Waters apparatus, using THF as solvent and refractive index as detector. All infrared spectra were run on a Nicollet MX-1 FT-IR spectrometer, in KBr pellets. Differential scanning calorimetry analysis, recorded with a microcalorimeter Mettler TA-3000, was performed under argon atmosphere, with a heating rate of 10° C/min, in the temperature range 50–200° C. The viscoelastic property measurements were made on Rheovibron DDV IIB (Toyo Baldwin Co) at frequency of 11 Hz, in air current and at a heating rate of 1° C/min. The mechanical properties were measured by three-point bending test on a tensile machine (DY14 Adamel Lhomargy) with a crosshead speed of 20 mm/min, a span length of 50 mm, and specimen dimensions 60 × 10 × 4 mm.

## RESULTS AND DISCUSSION

Extraction analysis

The extracts were mixtures of unreacted DGEBA, DDA molecules, and their low molecular weight reacted compounds. The DGEBA and low molecular weight extracted fractions were determined with GPC and the results are given in Table II. In every case, the precured samples (A′, B′, C′, D′) showed a greater extracted fraction than those unprecured (A, B, C, D), and especially for the DGEBA species $n = 0$.

The extracted fraction of DDA was difficult to quantify by GPC, but its presence was determined by means of DSC. We gathered all the extract solutions of the precured samples
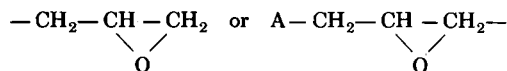
TABLE II
DGEBA-Extracted Fraction Determined by GPC

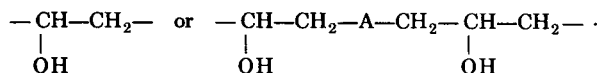| Formulation	A	A'	B	B'	C	C'	D	D'
$n = 0(\%)^a$	1.66	3.60	2.51	3.76	1.37	1.56	1.63	1.86
$n > 0(\%)^a$	0.69	0.12	0.46	0.11	0.25	0.12	0.19	0.13
Total(%)	2.35	3.72	2.97	3.87	1.62	1.68	1.83	1.99

[a] Indicates the number in the formula:
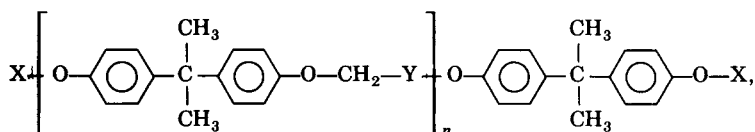
where X is

and Y is

A indicating partially reacted DDA species.

(A' + B' + C' + D'), and also those of unprecured ones (A + B + C + D). After an evaporation of solvent under vacuum, at room temperature, the extracted mixtures were analyzed by DSC from −50 to 300°C. On DSC curves, the extracted mixture from the precured samples presented an endothermic peak at 206°C due to the extracted free DDA melting and a $\Delta H = 121$ J/g. DSC run in the same conditions for pure DDA has shown its melting heat to be 273 J/g. The extracted fraction of DDA can then be estimated to be 20–30% of the quantity before curing. On the contrary, the extract mixture from unprecured samples did not show such an endothermic peak, implying the absence of the free DDA in the unprecured samples. The IR spectral analysis on the extract mixtures have also shown that the extracts from precured samples had higher contents of both amine and epoxy groups.

For the precured samples, the gelation process was carried out at 100°C, which was not high enough to ensure a complete miscibility between DDA and DGEBA, so that clusters of phase-separated residual DDA could exist. This result is in agreement with the observation of Kasturiarchchi and Pritchard.[7] But in a curing cycle without precuring, the gelation stage occurred at higher temperatures (Fig. 1), so that free residual DDA could no longer exist. As a matter of fact, the matrix of unprecured samples was transparent and the matrix of precured ones was opaque, especially those with $a/e = 1.0$.

Infrared Spectral Analysis for the Matrix

Notable differences in the IR spectra were observed for the cured samples after different curing cycles, especially in the absorbances at 2180, 1740, 1680-1650, and 1115 cm^{-1}, which correspond to the IR absorption of nitrile, carbonyl, imine, and ether groups, respectively. The phenyl group response peak height at 830 cm^{-1} was used as internal standard in order to calibrate and compare the different samples. The IR absorption of the related groups is expressed by peak height H_x or peak area A_x at x cm^{-1}. The complete results are given in Table III.

For a same formulation, the precured samples always presented higher absorbances at 2180 cm^{-1} (nitrile) and 1115 cm^{-1} (ether) and lower absorbances at 1740 cm^{-1} (carbonyl) and 1680-1650 cm^{-1} (imine) than the unprecured ones. These results are in agreement with our preceding studies for isothermal cures and we can explain them by the specificity of the present system, summarily: (i) the production of either linkages does not only depend on the initial amount of BDMA but also on the concentration and the reactivity of the amino-alcohols formed by the addition of epoxyde to primary or secondary amine[2]; (ii) the nitrile groups of DDA can be transformed into imine groups [1,8] or can react with the hydroxyl groups.[9]

Differential Scanning Calorimetry

Figure 2 gives the DSC curves of the cured samples. The absence of exothermal peak on DSC curves proves that the reactions ended for all samples. The following observations were made: (i) precure process increases the T_{g_3}, which is defined as the middle point of the transition zone on the thermogram; (ii) precure process extends the temperature range of the glass transition; (iii) the presence of glass filler increases T_{g_3} and extends the temperature range of the glass transition, especially for the precured samples. The increase in T_{g_3} and the extension of the glass transition zone related to a larger distribution of relaxation times may be due to the changes in the epoxy network and the presence of clusters of DDA. This will be discussed with viscoelastic results.

Viscoelastic Properties

The network structure can be characterized by its viscoelastic properties. In Figure 3 the elastic modulus E'_r and the loss factor $\tan \delta$ were plotted as a function of temperature. It can be seen that the behavior of the precured samples differs from that of unprecured ones. The values of three characteristic parameters, $\tan \delta$, peak temperature T_m, $\tan \delta_{max}$ peak value, and elastic modulus at the rubberlike plateau E'_r (measured at $T_{m+50°C}$) are given in Table IV, as well as DSC results.

Table IV shows that the precure at $100°C$ leads to increased T_{g_3}, T_m, E'_r and to decreased $\tan \delta_{max}$.

(i) Usually shifts in glass transition temperature are provided for three effects: the degree of crosslinking[10]; a copolymer effect[10] and the functionality of the crosslinks[11]. Higher T_{g_3} or T_m of precured samples can be related to the changes in these three effects:

—The ether crosslinks and the reactions involving nitrile groups most probably change the structure of the chains. IR analysis has shown that the amounts of both ether linkage and consumed nitrile groups vary with curing cycle; therefore, the structure of the chains will vary with curing cycles. But the effect on T_{g_3} or T_m is difficult to quantify without any model.
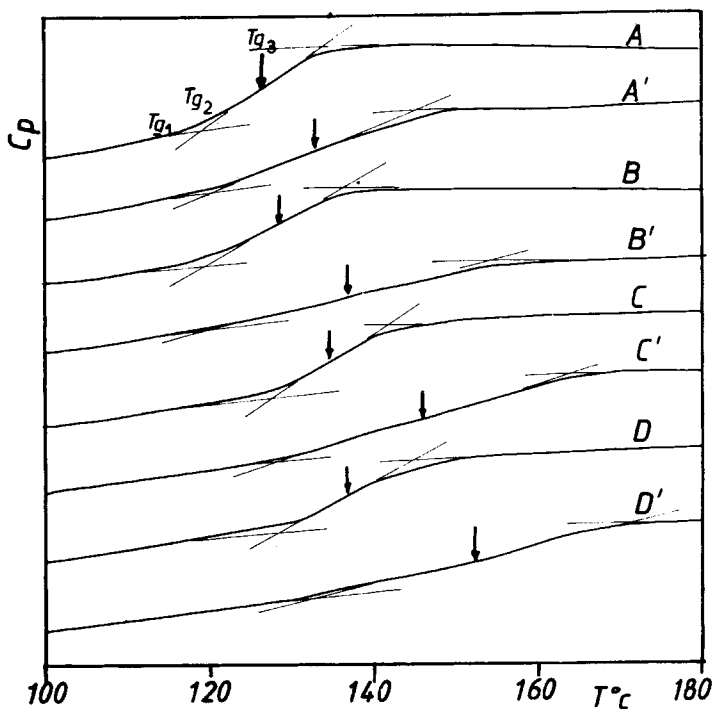

Fig. 2.   DSC traces for cured polyepoxy and composites. ↓ indicates T_{g_3}.
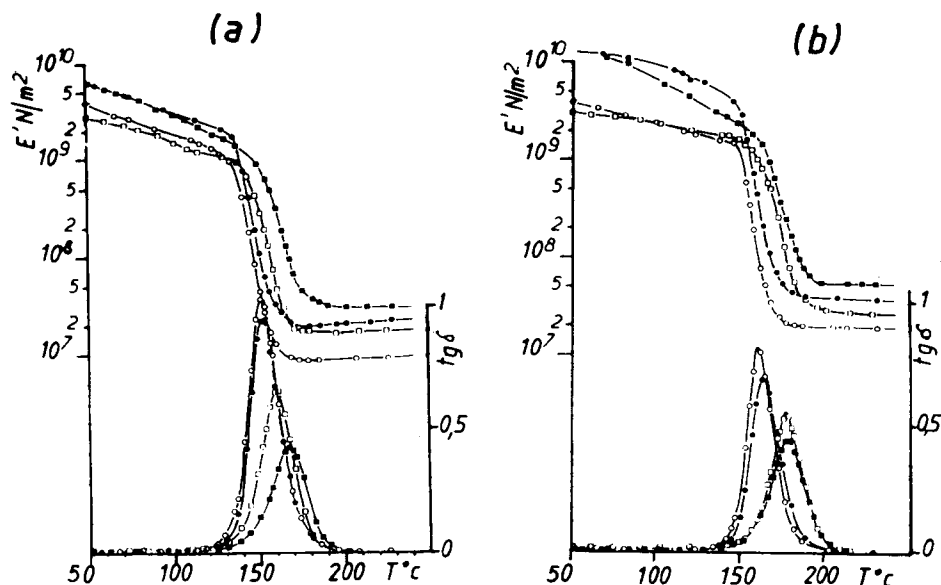
Fig. 3. Viscoelastic properties. Evolution of $E'r$ and tan δ vs. temperature for the polyepoxy: (a) (○) A; (□) A'; (●) B; (■) B'; (b) (○) C; (□) C'; (●) D; (■) D'.

—The etherification leads to effective crosslinking due to the difunctionality of the DGEBA prepolymer. Otherwise, because etherification consumes epoxy groups, the stoichiometry of the amine–epoxy addition will be disturbed. For the formulation with $a/e = 1.0$, there is a large excess of DDA, which would lead to chain extending and dangling ends formation. However, with a curing cycle including 3 h at 100°C, 20–30% of DDA remaining in crystalline clusters does not take part in the reaction, decreasing the real excess of DDA and the possibility of chain extension and dangling ends to occur. For the formulation with $a/e = 0.6$, etherification is necessary in order to balance the stoichiometric lack of curing agent, and a greater amount of ether crosslinks will be formed with the precure process (see IR results). So that a higher degree of crosslinking can be expected for the precured samples in both cases $a/e = 1.0$ and 0.6.

—An ether crosslink and an amine one are close enough to form a joint crosslink with a higher functionality. But with an excess of DDA (unprecured samples), the etherification disturbs stoechiometry and leads to residual $>$ NH groups, decreasing the real functionality of amine curing agent in cured network. Consequently, the functionality of crosslinks can also be modified by the precure process.

(ii) Parallel to these three molecular effects, clusters of crystalline DDA can also act as macroscopic crosslinks and this can also explain why the precured samples exhibited higher E'_r and lower tan δ_{max}.

(iii) The presence of glass fillers hinders the movements of epoxy network, so that the composites present always higher T_{g3}, T_m, and E'_r and lower tan δ_{max} than the pure matrix, though the effect of the precure process is not erased.

TABLE III
Results of IR Analysis for Polyepoxy Networks

Formulation	A	A'	B[a]	B'[a]	C	C'	D[a]	D'[a]
$H_{2180\,cm^{-1}}/H_{830\,cm^{-1}}$ (nitrile)	0.20	0.44	0.35	0.48	0.13	0.17	0.12	0.16
$A_{1740\,cm^{-1}}/H_{830\,cm^{-1}}$ (carbonyl)	0.71	0.11	0.33	0.11	1.02	0.30	0.82	0.18
$A_{1650-1680\,cm^{-1}}/H_{830\,cm^{-1}}$ (imine)	5.60	4.86	5.15	4.49	4.72	4.00	4.28	3.44
$H_{1115\,cm^{-1}}/H_{830\,cm^{-1}}$ (ether)	0.25	0.27	0.26	0.28	0.22	0.28	0.22	0.28
$H_{915\,cm^{-1}}/H_{830\,cm^{-1}}$ (epoxy)	0.04	0.04	0.06	0.06	0.04	0.03	0.05	0.04

[a] For 20% glass-bead-filled composite. The value of H_{830} is decreased by a factor $0.82 \cong 0.85$ so that the results in these columns have been corrected

TABLE IV
Viscoelastic and DSC Characteristic Parameters of Polyepoxy Networks

Formulation	A	A'	B	B'	C	C'	D	D'
$T_{g3}(°C)$	126	132	128	137	134	146	135	152
$T_m(°C)$	151	161	153	166	161	177	163	178
$\tan \delta_{max}$	1.03	0.66	0.84	0.43	0.81	0.55	0.71	0.45
$E_r' \times 10^7 (N/m^2)$	1.0	1.7	2.1	3.1	1.8	2.6	3.9	5.2

Mechanical Properties

Figure 4 shows the load–deflection curves for three-point bending tests. The precured samples exhibit lower ultimate stresses and deflections at failure. As indicated by the previous results, precured samples are inhomogeneous (clusters of DDA, large distribution of relaxation times). Under deformation, these inhomogeneities will lead to the formation of localized stresses, which can be considerably higher than the applied stress, and hence the rupture of the samples occurs at smaller deflections. So the lower strength properties of the precured samples can be related to their worse homogeneity.

The formulation with $a/e = 0.6$ exhibits smaller deflection at failure than that with $a/e = 1.0$ (compare C to A), which may be due to their higher degree of crosslinking and lower mobility (E_r', $\tan \delta_{max}$).

However, the different curing cycles did not appreciably change the flexural modulus.

CONCLUSION

The extraction analysis has shown that a low precure temperature for the present system will lead to the presence of inhomogeneities in cured products. The DDA extracted fraction (20–30%) indicates the presence of phase-separated residual DDA. However, carrying out the gelation at higher temperature can overcome this problem.

Because the reaction temperature can affect the curing mechanism of the present system therefore the network structure formed and hence its intrinsic properties, such as thermodynamic, mechanical, and viscoelastic properties, vary with processing conditions. Unlike other systems,[12] these effects cannot be erased by a subsequent post-cure treatment. This should be taken into account in the choice of formulations and processing conditions.
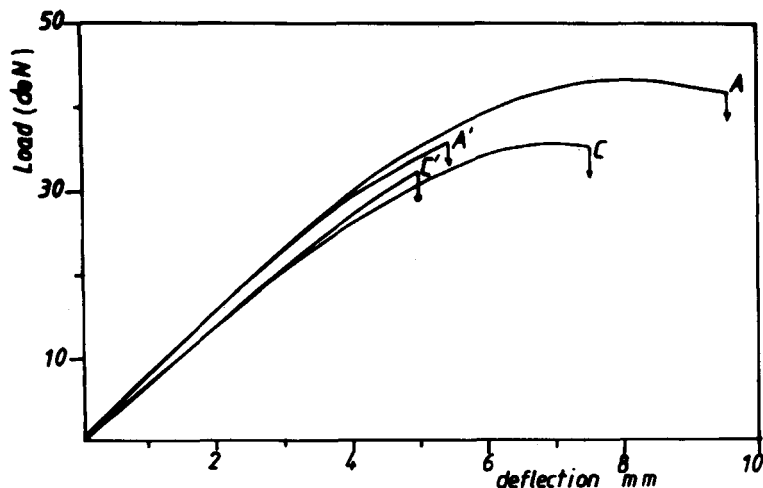

Fig. 4.   Load–deflection curves for three point bending tests at room temperature.

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