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Epoxies

ΔCp, Δα and Related Quantities for Epoxy-Aromatic Amine Networks

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Summary

The parameters of glass transition in several epoxy-amine polymer networks were obtained. The changes $\Delta C_p(T_g)$ and $\Delta\alpha(T_g)$ were proved to be correlated with the concentration of crosslinks in these systems. The difference in glass transition parameters for linear and densely crosslinked polymers was analysed in terms of Simha-Boyer ($\Delta\alpha\cdot T_g$) and Boyer ($\Delta C_p\cdot T_g$) rules and Eyring's hole theory.

Introduction

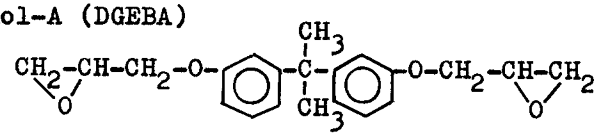
The parameters of glass transition for linear polymers are rather well measured, calculated and documented (GAUR et al. 1981). But the situation is not well established for polymers with high density of crosslinks such as epoxies, polyesters etc.

In the present paper we analyse glass transition parameters for several epoxy-amine polymer networks with different density of crosslinks and compare them with the corresponding glass transition properties of linear polymers.

Experimental

For our study we used epoxy-aromatic amine networks based on diglicidyl ethers of resorcinol (DGER)

or bisphenol-A (DGEBA)



cured with m-phenylenediamine (m-PhDA). Purification and control of components are described elsewhere (SALAMATINA et al. 1981).

The "epoxide:amine" ratio varied in the wide range $0 < R \leqslant 2$ (here $R = NH/EP$ is the molar ratio of functional groups of amine and epoxide; R=1 corresponds to stoichiometric condition). Curing conditions and thermal prehistory were:

1. curing each system at temperature 80 - 120°C up to the maximum extent of cure;
2. postcure heating of polymer to the temperature T_g+20°C;
3. slow cooling (0.5 deg/min) to the room temperature;

After the two last procedures we obtained the polymers with the standard thermal prehistory.

DSC-910 (Du Pont) equipped with APPLE-2 microcomputer and thermomechanical analyser TMS-2 (Perkin-Elmer) were employed for measurements.

Results and discussion

A. Heat capacity

It is known, that the values of heat capacity and thermal expansion coefficient exhibit a stepwise change at T_g. The experimental data on heat capacity change $\Delta C_p(T_g)$ as a function of the ratio of components R for the networks DGER+m-PhDA and DGEBA+m-PhDA is presented in Fig.1. Glass transition temperatures T_g and heat capacity changes $\Delta C_p(T_g)$ were determined by the method discussed elsewhere (MOYNIHAN et al. 1976). This dependence exhibits a minimum at stoichiometric ratio of components (R=1). It seems to be due to the highest density of crosslinks at the stoichiometric ratio, as it is seen from the figure. Indeed, the difference in values $\Delta C_p(T_g)$ of hardened and unreacted stoichiometric mixtures is quite evident.

In order to rationalize the dependence of $\Delta C_p(T_g)$ values on the density of crosslinks observed experimentally we propose that $\Delta C_p(T_g)$ is the sum of three terms

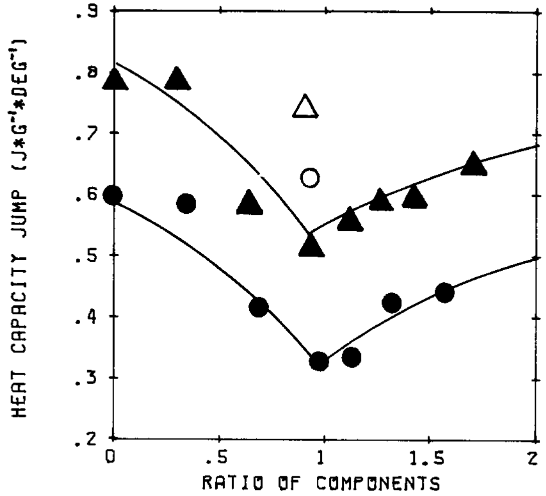


Figure 1. ΔC_p as a function of ratio of components R.
● DGER+m-PhDA completely cured and annealed
○ DGER+m-PhDA unreacted stoichiometric mixture
▲ DGEBA+m-PhDA completely cured and annealed
△ DGEBA+m-PhDA unreacted stoichiometric mixture
(Solid lines are the best fit curves)

$$\Delta C_p = N_1\cdot\Delta_1 + N_2\cdot\Delta_2 + N_3\cdot\Delta_3$$

where N_1, N_2 and N_3 are the moles of diepoxide, diamine molecules and crosslinks* per gram of mixture; $\Delta_1, \Delta_2, \Delta_3$ are the increments in heat capacity change $\Delta C_p(T_g)$ per mole of corresponding units.

Fitting of experimental points have been performed for all experimentally measured systems using standard least square procedure. Best fit parameters is presented in tab.1

Table 1. Best fit parameters of the additive scheme.

Composition	$\Delta 1$ J mole^{-1}deg^{-1}	$\Delta 2$	$\Delta 3$	Mean square root deviation of experimental and calculated points
DGER+m-PhDA	177	142	-53	4%
DGEBA+m-PhDA	204	154	-58	6%

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* "Crosslinks" mean new chemical bonds which appear in the system after chemical reaction between epoxy and amine groups.

Using these values for Δ_1, Δ_2 and Δ_3 we have reproduced curves $\Delta C_p(T_g)$ vs R, which are shown in fig.1. (Solid lines) Since $\Delta C_p(T_g)$ is a measure of change in configurational mobility at glass transition (WUNDERLICH 1960), the negative sign of Δ_3 means that each elementary step of curing decreases the configurational mobility of the networks above their T_g.

It is useful to compare our results with those of Hartmann, Lee and Long (HARTMANN et al. 1982), who performed the numerical analysis of heat capacity for different epoxy-amine (aromatic and aliphatic) networks with stoichiometric ratio of components. For analysis the authors used an additive scheme with 4 increments, each one corresponding to different fragments of the polymers. Fitting of experimental heat capacity curves appeared to be satisfactory well below and rather poor in glass transition region. The negative sign of $\Delta C_p(T_g)$ increment per benzene ring obtained by the authors seems physically meaningless. We think, that the apparent negative value is due to the strong coupling of aromatic diamine molecules with the frame of stoichiometric network. This chemical coupling strongly decreases the configurational mobility of aromatic rings of m-PhDA in the polymer. In terms of our 3-parameter scheme the increment per benzene ring of hardener may be estimated as follows:

$$\Delta(\text{ring}) = \Delta_2 + 4\cdot\Delta_3 = -70 \ (\text{J mole}^{-1}\text{deg}^{-1})$$

and is consistent with that of Hartmann et al.

B. Thermal expansion coefficient

The $\Delta C_p(T_g)$ resuls showed that heat capacity change is rather critical with respect to the density of crosslinks. In order to verify another important parameter of glass transition (change in thermal expansion coefficient at T_g) in a similar way we performed the study of linear expansion of DGER+m-PhDA networks with different R. The results are shown in fig.2. The shape of $\Delta\alpha(T_g)$ vs R curve is quite similar to that of $\Delta C_p(T_g)$ vs R curves in fig.1. This fact indicates that crosslinks influence $\Delta\alpha(T_g)$ in the same manner as ΔC_p.

C. Comparison with linear polymers

The parameters of glass transition of linear polymers

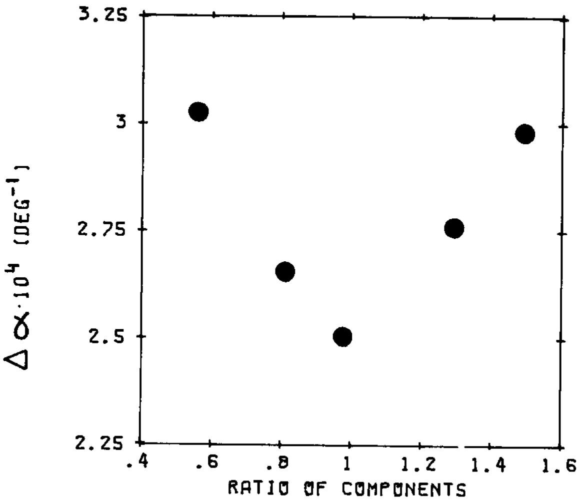

Figure 2. $\Delta\alpha(T_g)$ as a function of ratio R = NH / EP. DGER+m-PhDA completely cured and annealed.

have often been rationalized in terms of Simha- Boyer (S-B) $\Delta\alpha \cdot T_g$ rule, Boyer (B) $\Delta C_p \cdot T_g$ factor (BOYER 1973) and parameters of Eyring's hole theory (HIRAI and EYRING 1958).

Having $\Delta\alpha(T_g)$, $\Delta C_p(T_g)$, T_g and V_g (specific volume at T_g) as input parameters one can calculate S-B and B factors, as well as parameters of hole theory. Results of such calculations are presented in table 2.

The values of S-B factor for our networks are close to those of linear polymers. It confirms the validity of iso-free-volume concept of glass transition for the systems considered. On the contrary the values of B factor for our networks are twice as high as typical values for linear polymers. Accordingly values of F_g (hole fraction at T_g) for the networks are close to those of linear polymers, but hole energy E_h and concentration of holes N_h for the networks are markedly higher.

Conclusions

The above results for densely crosslinked networks gave us the possibility of drawing two conclusions.

Table 2. Parameters of hole theory, S-B and B factors.

Polymer	$\Delta\alpha \cdot T_g$	$\Delta C_p \cdot T_g$	N_h number of holes per gram at T_g ($\times 10^{21}$)	E_h hole energy (KJ/mole)	F_g hole fraction	V_g hole volume (Å^3)
Poly-isobutilene	0.091	80	1.9	6.1	0.024	20.8
Poly-styrene	0.140	126	2.6	9.5	0.047	29.3
Linear polymers*)	0.120	110	2.6	8.2	0.033	21.3
DGER+m-PhDA						
R=0.7	0.117	215	5.2	9.75	0.036	11.5
R=1.0	0.124	199	4.3	11.1	0.038	15.1
R=1.3	0.129	237	5.7	10.2	0.041	12.1

*) calculated as average over 9 typical linear polymers.

1. The high density of crosslinks does not introduce additional kinetic restrictions for approaching the iso-free-volume state at T_g.

2. As it was shown earlier while comparing linear polymers with crosslinked ones (ARTEMENKO et al. 1979), crosslinks do not change many physical and mechanical properties of glassy networks appreciably. In spite of it, the peculiarities of glass transition in epoxy-amine networks discussed above are shown to be due to high density of crosslinks in these systems. In our opinion, it is necessary to the density of crosslinks as an additional parameter for the description of glass transition in epoxy-amine networks.

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