

EFFECT OF CROSS-LINKING ON THE EXCESS ENTHALPY RELAXATION OF EPOXY

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ABSTRACT

A method of comparative DSC technique is proposed for excess enthalpy relaxation study. The essential of the comparative DSC technique consists of comparing the enthalpy relaxation behavior of an aged sample with a quenched sample as reference. The accuracy of comparison is improved because of simultaneous measuring of the sample and reference which makes noise of the apparatus subtractive. This technique has been applied to studying the influence of crosslinking on the enthalpy relaxation behavior of epoxy resins. The effect of crosslinking on the kinetics of enthalpy relaxation of epoxy resins is discussed.

INTRODUCTION

Significant changes have been observed in the mechanical and physical properties of glassy epoxy resin as a result of storage at temperature below its T_g (sub- T_g annealing). In general, with increasing sub- T_g annealing periods, the density increases, while the impact strength, fracture energy, ultimate elongation, creep and stress relaxation rates decrease^[1-3]. To date, it is of a general consensus that the changes in the properties of glassy polymers under sub- T_g annealing are the result of relaxation associated with the non-equilibrium nature of the glassy state^[4,5]. These phenomena are called physical aging.

In contrast to the extensive studies made on the physical aging of linear polymeric glass, crosslink polymers have not received much attention. Wilkes et al. observed the yield stress and Young's modulus increased with annealing time of the epoxy network^[6]. Mijovic studied the time-dependent changes in mechanical properties of cured epoxy resin and described them in terms of inhomogenous epoxy network morphology^[7]. Kong reported that the density of cured epoxy and its composites increased while the impact strength, fracture energy, ultimate elongation and creep rates decreased during physical aging^[8].

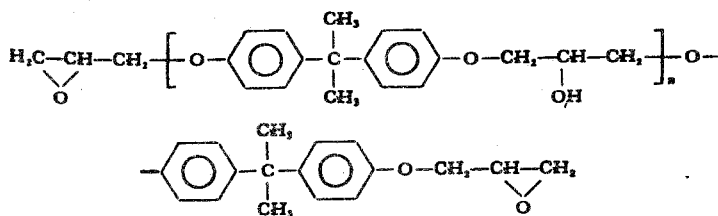
However, little has been reported about the effect of crosslinking on the excess enthalpy relaxation of epoxy networks. In the present paper some experimental results on the crosslinking effect will be reported, and the kinetics of enthalpy relaxation of epoxy network will also be discussed.

EXPERIMENTAL

Epoxy

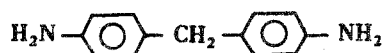
Diglycidylether of bisphenol-A (EPON) epoxies having four different epoxide equivalent values were used in this study. In other words, there were four different degrees of polymerization (*D.P.*) of DGEBA epoxide (e.g. *D.P.* = 1.09, 1.18, 1.40 and 2.94). The chemical structure of

DGEBA is



Cure agent

4,4'-diaminodiphenyl methane (DDM) was used as a cure agent. The chemical structure of DDM is



Preparation of samples

The cured epoxy samples were prepared by casting. The cure agent was mixed with the molten resin and then the mixture was poured into a preheated mold. The curing schedule was 80°C for 2 hours, 160°C for 3 hours, 180°C for post curing 8 hours, followed by slow cooling to room temperature. The samples for this experiment were disks of 4 mm in diameter, 10 mg in weight.

DSC measurements

A Mettler TA 22 Differential Thermal Analyser was used to determine the excess enthalpy behavior of cured epoxy samples. The DSC analysis was performed at a heating rate of 10°C/min. The samples were heated to $T_g + 50^\circ\text{C}$ for 10 min. and quenched to room temp., and this time was taken as time zero with respect to sub- T_g annealing time.

In the conventional DSC technique the reference is an empty sample pan or thermal stable substance such as Al_2O_3 and silicon oil. In such case, each sample was scanned again. The second scan served as a reference DSC trace of a quenched sample. Therefore, the enthalpy relaxation measurements were made by superimposing the first and second DSC scans for each sample. But the first and second DSC scans usually can not match very well, meanwhile the enthalpy relaxation peak of cured epoxy resin is rather small. So this conventional procedure is not sensitive to make an accurate quantitative analysis. Now in our laboratory, a new technique is developed with improved precision. Its principle is to measure two samples simultaneously, one is an aged sample and the other is a quenched sample as reference. The resultant DSC trace directly shows the difference of excess enthalpy of the two samples under investigation. Fig.1 schematically shows the shapes of comparative DSC (CDSC) and conventional DSC (DSC) thermograms for some probably modification of annealing endotherms. The arbitrarily assumed shape of endotherm of annealed sample (Fig.1(a) solid line) is compared with the shape of endotherm of quenched reference (Fig.1(a) dotted line) and the resultant CDSC thermogram is given by the respective plots in Fig.1(b). Four different cases are presented in Fig.1:

(a) When the DSC curve of the sample has an additional peak but without T_g shifting, the

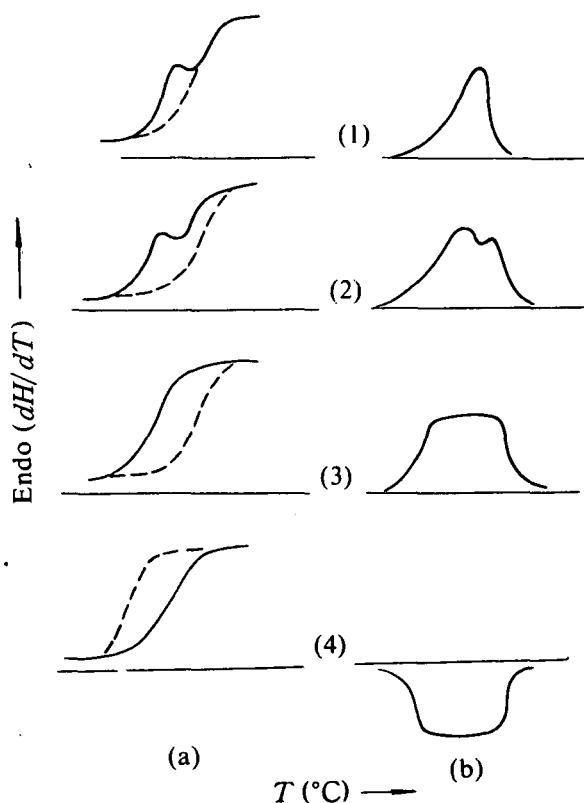


Fig. 1 Comparison of DSC and CDSC curves for excess enthalpy relaxation measurement

CDSC curve should be single peak (Fig.1(a)—(1)).

(b) When the DSC curve has an additional peak with T_g shifting, the CDSC curve should have two peaks (Fig.1(a)—(2)).

(c) When the DSC curves of the sample and the reference have T_g shift only, the CDSC curve should have a broad positive or negative peak which depends on the increase or decrease of the T_g of the annealed sample (Fig.1(a)—(3)—(4)).

RESULTS AND DISCUSSION

The excess enthalpy relaxation characters of epoxy

Fig.2 shows the comparison between DSC and CDSC curves for the sample 4 after being quenched from above T_g and then subjected to aging time of 1, 4, 16, 48 hours respectively at 80°C. The following observations were made:

(1) The DSC and CDSC curves show the enthalpy relaxation peaks appearing in the same temperature.

(2) The relaxation peak is shifting to higher temperature and growing in magnitude with increasing annealing time(see Figs. 2a and 2b).

(3) The relaxation peaks in Fig.2b are higher than their respective peak in Fig.2a, and there are two peaks appearing in each CDSC curve.

As mentioned above, Fig.2b CDSC curves are corresponding with the curve in Fig. 1b—(2),

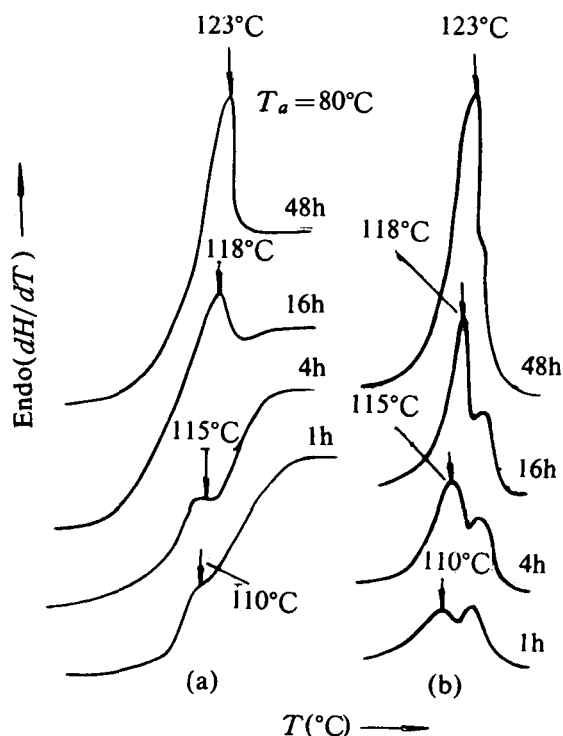


Fig.2 DSC(a) and CDSC(b) curves of sample 4 with different sub- T_g annealing time(t). $T_a = 80^\circ\text{C}$

two peaks appear in the CDSC curve, and the relaxation peak is accompanied with T_g shifting to lower temperature. This phenomenon is also observed by Mijovic by using the dynamic mechanical method when searching for the effect of the intrinsic stress on the T_g behavior of annealed epoxy. When the sample is quenched, its intrinsic stress tends to increase. This increase in intrinsic stress can be explained on the basis of increased free volume upon quenching. On the other hand, the annealing process causes the relaxation of intrinsic stress. Therefore, the physical aging of epoxy should include the enthalpy and intrinsic stress relaxation process.

Effect of crosslinking on the excess enthalpy relaxation of epoxy

Table 1 lists four samples of having different epoxide equivalent values, i.e. having different chain length between the epoxide groups. So these fully cured epoxy samples have different

Table 1 The composition of sample and their properties

Sample No.	Value of epoxy	DP (n)	Cure agent (Wt. %)	T_g ($^\circ\text{C}$)	$(\Delta H)_{\max}$ (arbt. unit)	ΔE (Kcal/mol)
1	0.54	1.09	36	166	2.2	7.6
2	0.50	1.18	30	160	3.0	7.0
3	0.42	1.40	25	145	2.4	6.7
4	0.20	2.94	12	127	3.7	6.2

degrees of crosslinking, of course.

Fig.3 shows the plots of enthalpy relaxation rate($d\Delta H/dt$) vs. log sub- T_g annealing time at different temperatures of samples 1 and 4 respectively. It is clear that a linear relationship exists between this enthalpy relaxation loss and the log of aging time. According to Arrhenius' equation, log dA/dt vs. $1/T$ is plotted in Fig.4. The apparent activation energy ΔE is calculated from the slope of Fig.4. The calculated values are listed in Table 1. Values of ΔE are rather small, about 6—7 Kcal/mol, and they seem to be independent of the degree of crosslinking of epoxy resins. This result shows that the molecular motion units of the relaxation is much smaller than the chain between the crosslinking.

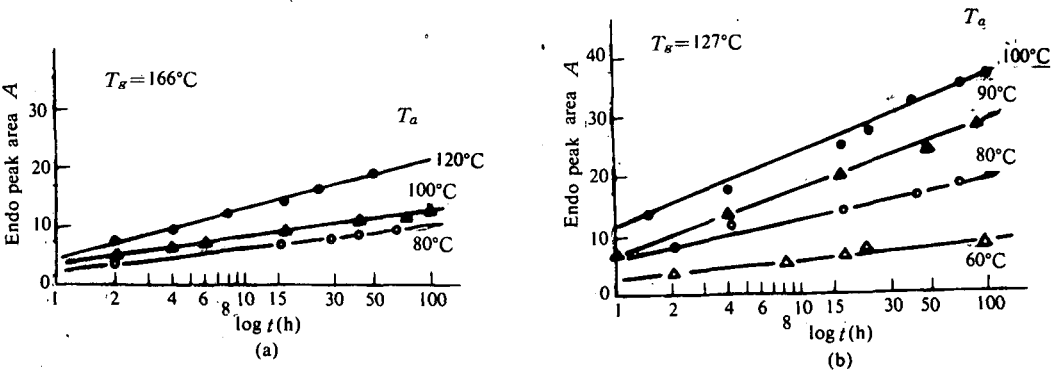


Fig. 3 Time dependence of endothermic peak of sample 1 (a) and sample 4 (b)

Fig.5 shows the correlation between the degree of polymerization of epoxy(n) and the maximum excess enthalpy $(\Delta H)_{\text{max}}$ and it is a straight line through the origin. Since the $(\Delta H)_{\text{max}}$ correlates the amount of the relaxation unit, so, the result of Fig.5 implies the molecular motion units of the excess enthalpy relaxation is much smaller than the chain between the crosslinking as mentioned above.

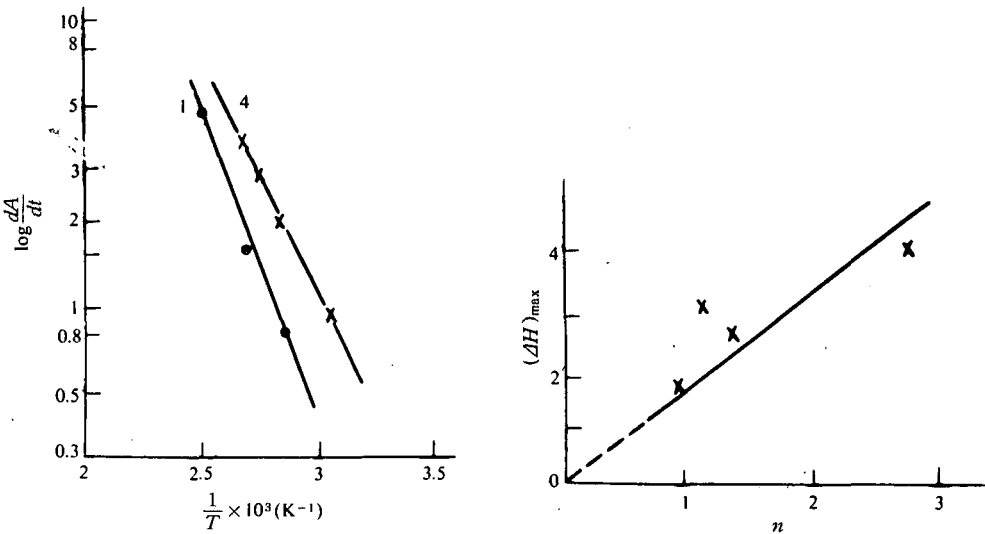


Fig.4 Arrhenius plot of sample 1 and sample 4

Fig. 5 Relationships between DP (n) and $(\Delta H)_{\text{max}}$

CONCLUSION

1. A comparative DSC technique is proposed for physical aging study.
2. The stability and accuracy of the comparative DSC technique are better than that of the conventional DSC.
3. The effect of crosslinking on kinetics of enthalpy relaxation of epoxy resins is obtained and discussed.

Keywords:

Epoxy; DSC; Physical aging; Excess enthalpy relaxation

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