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Physical ageing studies of polysiloxane-modified epoxy resin

Jinsong Shen, Zhengzhong Shao and Shanjun Li*
Department of Macromolecular Science, Fudan University, Shanghai 200433, China
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Epoxy network systems were prepared based on diglycidyl ether of bisphenol A with two kinds of low molecular weight polysiloxane, aminopropyldimethyl-terminated polysiloxane and phenyl-terminated polysiloxane. Their physical ageing phenomena were studied by differential scanning calorimetry. The calorimetric data obtained after annealing the neat and the modified cured epoxy resins at 175°C show that two kinds of relaxation – internal stress relaxation and enthalpy relaxation – take place simultaneously during annealing. Furthermore, the extent and the rate of relaxation are closely related to the kind of modifiers and their ratio.

(Keywords: epoxy resin; physical ageing; polysiloxane)

INTRODUCTION

The physical ageing of linear polymers has been widely studied; however, in recent years more interest has been paid to physical ageing in network polymers. The molecular basis for this non-equilibrium behaviour has been discussed elsewhere. In brief, one of the characteristics of the quenched glassy state is an excess of trapped free volume which is manifested as a lowering of the bulk polymer density. Thermodynamic state functions, such as enthalpy and volume of a newly quenched glass, are in excess of their equilibrium values. During annealing, the molecular system does approach the true equilibrium state function variables with time. The so-called physical ageing phenomenon is the time-dependent approach towards equilibrium and it is typically viewed as a recovery phenomenon. Basically, volume relaxation and enthalpy relaxation take place in physical ageing. The two parameters are nearly identical in their time-dependent behaviours. Much work[1,2] has been done to investigate the relation between free volume relaxation and enthalpy relaxation.

Owing to the ease with which enthalpy changes are monitored by differential scanning calorimetry (d.s.c.), enthalpy is one of the parameters most frequently used to follow the degree of non-equilibrium character of a thermally quenched polymeric glass. For the d.s.c. study, any difference in area under the d.s.c. traces represents an enthalpy difference between the sub-glass transition temperature (sub-T_g) states. According to the free volume model, Matsuoka and Bair[3] have derived the equation:

$$H_1 - H_2 \approx T_g(S_1 - S_2) = T_g\Phi R(f_1 \ln f_1 - f_2 \ln f_2)/M_w \qquad (1)$$

where the subscripts refer to samples at two different annealing times, S is the entropy, M_w is the segmental molecular weight and f is the fractional free volume. The factor Φ is the ratio of the total entropy increase to that part of the entropy corresponding to volume increase. Using Kovas' equation for the relaxation time:

$$\tau = ko^{-1}\exp(1/f) \qquad (2)$$

and equation (1), Matsuoka and Bair calculated the excess enthalpy in the way suggested by Richardson and Savill[4], i.e. by subtracting the area of aged from that of unaged sample on the d.s.c. scan. It is noted that the excess enthalpy values calculated by this method tally with the theory values quite well.

It is noted that the peak of enthalpy relaxation of the aged samples shifts to higher temperature with the ageing time and accordingly the area of the enthalpy relaxation peak increases as well. Johnson *et al.*[5] observed that the dielectric relaxation rate decreased with sub-T_g annealing time. Other researchers[6–8] have also demonstrated the correlation of time-dependent mechanical properties of polymeric glasses with enthalpy relaxation.

Epoxy resins are used extensively in the aerospace and electronics industries, often at temperatures high enough for physical ageing to occur. Physical ageing is associated with conformational rearrangement, increased molecular packing and densification, which is always accompanied by embrittlement of the polymer. The change of properties may lead to premature and catastrophic failure. The large amount of work on the physical ageing of epoxy resins is hardly surprising in view of their widespread applications, and particularly with the growing importance of long-term durability to design considerations. Recently, many elastomers, especially some polysiloxane elastomers, have been widely used to modify the epoxy resin system in order to improve the toughness and reduce the internal stress of the epoxy resin without compromising the modulus and the T_g[9,10].

The physical ageing of linear glassy polymers has been

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* To whom correspondence should be addressed

well documented, and research[11–15] has shown that physical ageing also exists in network epoxy glasses. In this paper, we report results of an investigation on the enthalpy relaxation process for a selected group of network glasses. Epoxy resin networks containing two different polysiloxanes were prepared in our research. From the results we expect to learn something about the formation of chemical bonding and non-chemical bonding between matrix resin and the modifiers, and how this affects resin physical ageing behaviour. It is believed that this research will be helpful in looking into the internal nature of physical ageing phenomena and the relationship between physical ageing and internal stress.

EXPERIMENTAL

A difunctional epoxy resin of diglycidyl ether of bisphenol-A (DGEBA; E51, Shanghai Resin Factory, epoxy equivalent weight = 190) was employed. Two different modifiers were used: a reactive elastomer, aminopropyldimethyl-terminated polydimethylsiloxane (ATPS; PS510, Huls America Inc.), and a phenyl-terminated phenylsiloxane oligomer (PTPS; no. 275, Shanghai Resin Factory). Their number-average molecular weights were 2500 and 600 g mol^{-1}, respectively.

A certain amount of ATPS was dissolved with the solvent methyl ethyl ketone (MEK) homogeneously, then the prereaction was performed by DGEBA and ATPS in a nitrogen atmosphere for 8 h at 120°C. A large proportion of the solvent was distilled, and further solvent was removed by degassing at 120°C for 1 h. A large amount of PTPS was then added and the mixture was stirred for 30 min at 160°C; an appropriate amount of 4,4′-diaminodiphenylsulfone (DDS) was added as curing agent at the same temperature while the mixture was stirred. The system was maintained at 160°C and degassed under vacuum for 30 min. All the mixture was poured into polished steel moulds in a period of 5 min, then the mixture was cured at 150°C for 2 h, 180°C for 3 h, then 200°C for 2 h. Specimens were cut from the cured mouldings and scanned at 10°C min^{-1} on a SETARAM DSC92 to ensure that the materials were fully cured.

Several different systems were prepared by varying the ATPS or PTPS content in the materials. In the material designation the letter is the matrix resin, the first number is percentage PTPS, and the second number is percentage ATPS, e.g. E-5-10 represents epoxy E51–5% PTPS–10% ATPS. The different compositions used in the study are reported in *Table 1*.

The fracture surfaces of the modified epoxy resins were examined by scanning electron microscopy (SEM). SEM specimens were coated with a thin film of Au by sputtering.

Table 1 Formulation and the glass transition of the quenched samples

Material	E51 (wt%)	PTPS (wt%)	ATPS (wt%)	T_g^{a} (°C)
E-0-0	100	0	0	214
E-0-10	90	0	10	211
E-5-5	90	5	5	209
E-10-0	90	10	0	209
E-20-0	80	20	0	197
E-2.5-2.5	95	2.5	2.5	206
E-7.5-7.5	85	7.5	7.5	201

^{a} Defined as the inflection temperature in the d.s.c. scan

A SETARAM DSC92 instrument was used for the d.s.c. studies, with a heating rate of 10°C min^{-1}. Specimens were cut from the mouldings; their weight was about 15 mg and their size was about 3 mm × 3 mm × 1 mm. These samples were placed into sample pans, equilibrated at 30°C above the calorimetric T_g and then quenched with liquid nitrogen. They were at once annealed at 175°C for various times, and quenched with liquid nitrogen at the end of annealing. Specimens were scanned on the differential scanning calorimeter and thermograms of aged and unaged samples were subtracted after dividing by the sample weight. The enthalpy relaxation was measured as the area of the peak of the subtracted curves.

RESULTS AND DISCUSSION

Characteristics of stress relaxation and free volume relaxation

The relaxation characteristics as determined by d.s.c. techniques for the unmodified epoxy are shown in the d.s.c. scans in *Figure 1*. Their differential curves are shown in *Figure 2* as a function of annealing time at constant sub-T_g temperature of 175°C. The polysiloxane-modified epoxies show similar behaviour. It is seen in the d.s.c. scan that a new heat-flow transition appears well below the original glass transition and the original glass transition of the annealed sample is somewhat higher than in the quenched state. It is also observed that during the annealing the relaxation peak (according to the subtracted curve of aged and unaged samples) shifts to higher temperature while growing in magnitude. The effects of these phenomena have been explained by Kreibich and Schmid[16] as phase separation and orientation processes that take place upon annealing well below T_g. But the proposed explanation is open to question; owing to the high viscosity, the crosslinking network is frozen so that it is unlikely that phase separation takes place by the large-scale motion of the molecular chains, though inhomogeneity does exist in these materials.

Stress relaxation and free volume relaxation[12] occur simultaneously during annealing. Matsuoka *et al.*[17] have

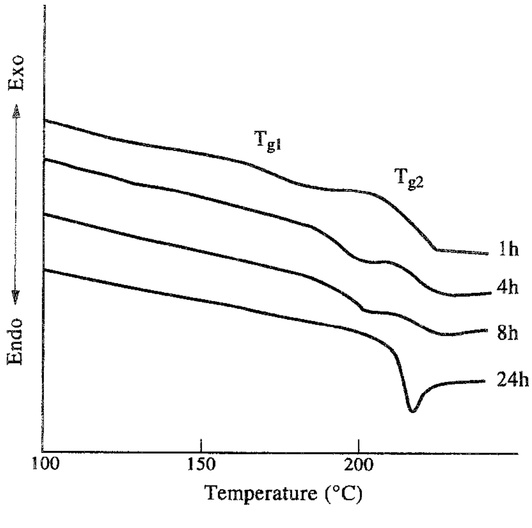

Figure 1 Typical effects of annealing time on the d.s.c. trace of E-0-0

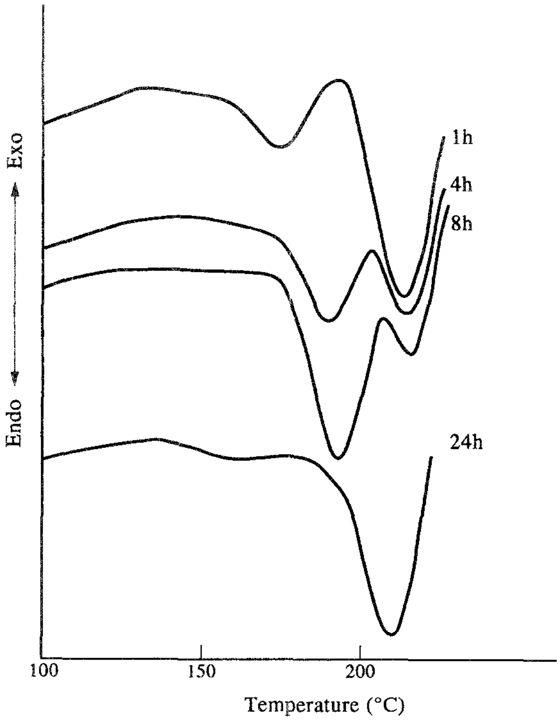

Figure 2 Typical effects of annealing time on the d.s.c. differential curve of E-0-0

shown that stress relaxation rates and creep to failure are also strongly coupled to the enthalpy relaxation process and to the loss of free volume. Mijovic[14] observed that T_g decreased with the annealing time, and this was attributed to the existence of internal stress relaxation. It was also observed by Brahatheeswaran and Gupta[18] that internal stresses relaxed on sub-T_g ageing due to free volume collapse, and the rate of stress relaxation is related to T_g.

It is known that when the epoxy resin is quenched from above T_g, especially with liquid nitrogen, the quenched molecular network of the sample is in the non-equilibrium state, with large internal stress and large extra free volume. With annealing, the motions of local molecular chain segments rearrange the local network and lead to stress relaxation at the same time, approaching the relative equilibrium state. Therefore, at the early period of annealing, it is observed that a new heat-flow transition (T_{g1}) appears at a much lower temperature and coexists with the original glass transition (T_{g2}). It is believed that the former represents the state of the stress-relaxed chains (also termed relaxation transition later in this paper) and the latter corresponds to the state with stress. At the same time, the network releases extra free volume for the equilibrium state. The volume relaxation, characterized by the decrease of free volume and the increase of density, also leads to a shift of both T_{g1} and T_{g2} to higher temperature, as shown in *Table 2*. With the relaxation of internal stress, the relaxation transition (T_{g1}, which later develops into a peak) becomes more evident, while the original glass transition (T_{g2}) gradually disappears. As a result, the original glass transition is substituted by the relaxation peak (T_{g1}) in the d.s.c. scan.

The present research also shows that a new heat-flow transition does not appear in all the d.s.c. scans of the samples cooled from above T_g to various temperatures below T_g at the cooling rate of 0.1°C min^{-1}. It is known that the consequence of annealing at a constant temperature below T_g is equivalent to that of cooling from above T_g at a constant cooling rate. Then the reason for the absence of the new heat-flow transition is that the internal stress of the sample is negligible and can be ignored due to the very slow cooling rate. This further proves that the appearance of the new heat-flow transition is related to stress relaxation.

Along with the addition of polysiloxane dispersed as very small domains, the internal stress is greatly reduced when the sample is quenched from above T_g. In the d.s.c. scan it is found that the separation ΔT_g between T_{g1} and T_{g2} (both defined as the inflection of the d.s.c. scan) decreases with addition of PTPS or ATPS (see *Table 3*). Therefore, the separation ΔT_g is considered to be associated with the existence of the internal stress, and the degree of separation reflects the relative value of the internal stress.

The T_{g1} and T_{g2} values of samples with equal contents of PTPS and ATPS are shown in *Table 4*. The separations ΔT_g are all less than those of samples shown in *Table 3*, and it is found that the original T_g disappears from the d.s.c. scan only 4–8 h later, considerably earlier than for the other samples shown in *Table 2*. There is some relation between the nature and the internal stress of the network. The smaller the value of ΔT_g, the less internal stress exists; the earlier the original T_g disappears in the d.s.c. trace after annealing,

Table 3 Glass transition temperatures (°C) of samples with 1 h annealing

	E-20-0	E-10-0	E-0-0	E-2.5-2.5	E-5-5	E-7.5-7.5
T_{g1}	171	173	175	179	179	173
T_{g2}	203	208	215	208	210	204
ΔT_g	32	35	40	29	31	31

Table 2 Glass transition temperatures[a] (°C) of systems with different contents of PTPS and ATPS as a function of annealing time

	E-10-0		E-5-5		E-0-10		E-0-0	
t (h)	T_{g1}	T_{g2}	T_{g1}	T_{g2}	T_{g1}	T_{g2}	T_{g1}	T_{g2}
1	173	208	179	210	178	210	174	215
2	179	211	189	212	186	212	185	214
4	184	211	191	211	187	215	191	217
8	188	213	201	–	190	215	193	217
12	188	212	202	–	190	216	198	217

[a] Defined as the inflection temperature in the d.s.c. scan

Table 4 Glass transition temperatures[a] (°C) of systems with constant ratio of PTPS and ATPS as a function of annealing time

	E-2.5-2.5		E-5-5		E-7.5-7.5	
t (h)	T_{g1}	T_{g2}	T_{g1}	T_{g2}	T_{g1}	T_{g2}
1	179	208	179	210	173	204
2	188	209	189	212	182	206
4	194	–	191	211	187	208
8	195	–	201	–	190	–
12	196	–	202	–	192	–

[a] Defined as the inflection temperature in the d.s.c. scan

the more rapidly the internal stress relaxes. These phenomena further illustrate that the introduction of polysiloxane into the epoxy network does accelerate the relaxation of free volume and internal stress. When the active polysiloxane and inactive polysiloxane are added at the same time, the effects will be even more remarkable (see *Table 3*). The internal stress in these materials is under further investigation and will be reported shortly.

Dependence of enthalpy relaxation on ATPS and PTPS

It is noted that the amount of energy absorption in the d.s.c. scan is reflected in the size of the endothermic peak per unit mass of material. Thus, since the excess enthalpy decreases during annealing, the enthalpy relaxation increases with increasing annealing time and the endothermic peaks become correspondingly larger.

Table 5 shows the enthalpy relaxation of the samples with different PTPS and ATPS contents as a function of annealing time at 175°C. *Figure 3* shows these data plotted as enthalpy relaxation *versus* logarithmic sub-T_g annealing time. A linear dependence is noted. The epoxy network modified with reactive ATPS initially has the lowest enthalpy relaxation, while that modified with PTPS has the highest initial enthalpy relaxation. It is known that the molecular chains of polysiloxane are very flexible so that they can move more freely and rapidly than pure epoxy resin chains when the samples are quenched. Owing to the chemical bonding between the flexible chains and the epoxy resin chains in the ATPS-modified system, although 100% reaction is unlikely, more shrinkage occurs in the volume of the network. Therefore, the molecular chains pack more tightly, which leads to less initial free volume and therefore a lower initial enthalpy relaxation. On the other hand, with the closer solubility parameter and the lower molecular weight, the solubility of PTPS in the epoxy resin is higher than that of ATPS. The domain size of PTPS is about 2 μm while that of ATPS is about 20 μm. So the network with PTPS has a larger specific interfacial area which leads to a correspondingly greater free volume. The greater free volume gives rise to more enthalpy relaxation and initially higher enthalpy absorption.

Table 5 Enthalpy relaxation (J g^{-1}) of samples with different contents of PTPS and ATPS as a function of annealing time at 175°C

t (h)	E-10-0	E-5-5	E-0-10	E-0-0
1	0.640	0.545	0.336	0.506
2	0.780	0.743	0.593	0.620
4	0.889	0.866	0.899	0.755
8	1.026	0.973	0.930	0.921
12	1.130	0.949	1.157	1.039

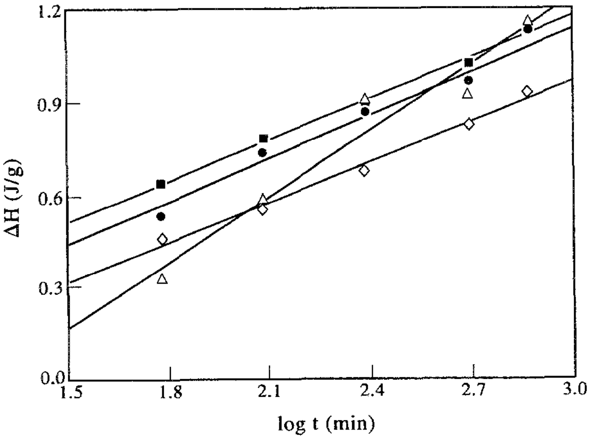

Figure 3 Plot of enthalpy relaxation *versus* logarithmic sub-T_g annealing time at 175°C: ◇, E-0-0; ■, E-10-0; ●, E-5-5; △, E-0-10

The values of enthalpy relaxation of samples with different contents of PTPS are tabulated in *Table 6*. With the content of PTPS increasing, it is observed that the initial enthalpy relaxation increases accordingly. This adds further support to the preceding observations which indicates that the introduction of PTPS contributes to the increase of the initial enthalpy relaxation.

Discussion on relaxation rate by curve fitting

The Kohlrausch–Williams–Watts (KWW) function is used to approximate a summation of exponential relaxation times[19]:

$$\Phi(t) \approx \exp[-(t_a/\tau_{ww})^{\beta_{ww}}] \qquad (3)$$

where t_a is the time of annealing, τ_{ww} is the relaxation time for the KWW function and β_{ww} is a constant related to the width of the distribution of the relaxation times ($0 < \beta_{ww} < 1$).

$$\Delta H(t) = \Delta H_e[1 - \Phi(t)] \qquad (4)$$

is used as a simple non-linear equation for enthalpy relaxation, where $\Delta H(t)$ is the enthalpy relaxation as a function of time and ΔH_e is the enthalpy which must be lost to reach equilibrium.

Equations (3) and (4) have been used to fit the data from enthalpy relaxation experiments[15]. The dependence of relaxation rate on the content of PTPS and ATPS is reflected in the constants determined by curve fitting shown in *Table 7*. The relative rates of enthalpy relaxation, characterized by the KWW relaxation time τ_{ww}, can be expressed as: E-0-10 > E-5-5 > E-10-0 > E-0-0. It is known that the amount and distribution of free volume affect the rate of the relaxation process. A high level of free volume below T_g leads to a high driving force for relaxation and initially high relaxation rates. However, the free volume is not the only decisive factor to influence the rate of relaxation: the flexibility of the chain also plays an important role in the process. In the neat epoxy network, the short and stiff epoxy–DDS cross-links are very effective restraints which prevent the chains

Table 6 Enthalpy relaxation (J g^{-1}) of samples with different contents of PTPS as a function of annealing time at 175°C

t (h)	E-0-0	E-10-0	E-20-0
1	0.506	0.640	0.723
2	0.620	0.780	0.990
4	0.755	0.889	1.080
8	0.921	1.026	1.192

Table 7 Curve-fitted constants of the samples annealed at 175°C

	E-0-0	E-10-0	E-5-5	E-0-10
β_{ww}	0.35	0.29	0.36	0.66
τ_{ww} (min)	3424	2350	629	268

from moving very far or rapidly. The ATPS is able to form crosslinks which would be longer and more flexible than the epoxy–DDS crosslinks and would allow the network to move more freely. Therefore, it is expected that the neat resin, with its great constraints on molecular motion, will relax more slowly. Since there is no chemical bonding between epoxy and PTPS to affect the flexibility of the epoxy molecular chain, the rate of enthalpy relaxation of PTPS depends mainly on the influence of free volume, while the flexibility of the chain is the main factor affecting that of ATPS. So the result shows that the influence of the flexibility on the rate of enthalpy relaxation is more evident than that of the free volume in our samples.

In summary, it is remarkable that as PTPS is added, the network has a larger initial free volume and therefore more initial enthalpy relaxation, and as ATPS is added, it relaxes much more rapidly, improving the flexibility of the network.

CONCLUSIONS

1. A new heat-flow transition T_{g1} related to the motion of the internal stress-relaxed molecular chains appears well below the original glass transition T_{g2} in the d.s.c. scan of aged samples. Both T_{g1} and T_{g2} shift to higher temperature as a result of enthalpy relaxation, and consequently they develop into one T_g of the relaxation peak. The enthalpy relaxation increases linearly with logarithmic annealing time.
2. With a solubility parameter closer to that of the epoxy resin and a lower molecular weight, PTPS is well dispersed in the epoxy resin matrix. Hence, it has a larger specific interfacial area which leads to a larger initial enthalpy relaxation. The chemical bonding between ATPS and the epoxy resin makes the molecular chains more flexible and therefore the enthalpy relaxation occurs more rapidly.
3. The introduction of polysiloxane into the epoxy network accelerates the relaxation of free volume and internal stress. The internal stress relaxation of the modified epoxy resin systems with equal amount of ATPS and PTPS takes place more rapidly than that of the epoxy resin systems only with ATPS or PTPS.
4. Physical ageing is an effective method for investigating the internal stress of the modified epoxy resin.

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