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Communications to the Editor

Effects of Prior Cooling Rates on T_g and Sub-T_g Heat Flow Transitions of Cured Epoxy Resin

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Introduction. Glasses usually exist in a nonequilibrium state, and relaxation toward equilibrium is commonly referred to as physical aging. Physical aging of amorphous polymers has been widely studied in recent decades.[1] Mostly, three-step thermal cycles were applied involving cooling, isothermal annealing and subsequent reheating. Sub-T_g endothermal heat flow transition peaks were observed in annealed samples that were rapidly quenched from above T_g.[2] Then some nonexponential and nonlinear theories of glass transition have also been used to fit the experimental data,[3−7] taking into account a distribution of relaxation times and the self-retarding nature of the enthalpy relaxation. Besides these phenomenological models which have been proposed to describe structural relaxation from a macroscopic point of view, Mazeau and co-workers[8] attributed sub-T_g specific heat peaks to the defects in excess of the equilibrium concentration and the nonequilibrium configuration of molecular segments. Controversy also exists in the explanations. Recently, modulated differential scanning calorimetry (MDSC) was used to study the two relaxation peaks of polystyrene (PS) by Hourston et al.[9] who believed that the lower temperature relaxation peak might be the β relaxation found in the dynamic mechanical spectrum. The effects of physical aging to free volume have also been wisely studied.[10,11]

In our previous work,[12] the sub-T_g heat flow transition of polysiloxane-modified epoxy resin was related to the motion of the internal stress-relaxed molecular chains. Furthermore,[13] fully and partially cured epoxy resins based on DGEBA have been studied, and the same declaration has been made. In this work, the relationship of glass transition temperature of unaged samples with cooling treatments from above T_g and the sub-T_g heat flow transition have been studied. We hope this work will aid in understanding the molecular mechanism of sub-T_g heat flow transition on the view of internal stress relaxation and free volume.

Experimental Section. Diglycidyl ether of bisphenol A (DGEBA; E51, Shanghai Resin Factory, epoxy equivalent weight = 190) epoxy resin was employed. Equal stoichiometric amounts of 4,4′-diaminodiphenyl methane (DDM) and 2,3,2′,3′-tetramethyl-4,4′-diaminodiphenyl methane (TDDM) were added, respectively, as curing agents at 100 °C while the epoxy was stirred. After that, the mixture was poured into a polished steel mold over a period of 5 min, and then the mixture was cured at 100 °C for 2 h, 130 °C for 2 h, 160 °C for 4 h, and then 180 °C for 8 h in a vacuum.

To fully cured epoxy resin was added an equal stoichiometric amount of 4,4′-diaminodiphenyl sulfone (DDS) as curing agent at 150 °C while the epoxy was stirred and then the mixture was cured at 150 °C for 2 h, 180 °C for 2 h, and then 202 °C for 8 h in a vacuum. To partially cured epoxy resin was added an 80% stoichiometric amount of DDS at 150 °C. Then the mixture was cured at 150 °C for 4 h and then 180 °C for 8 h in a vacuum. The degrees of cure were determined by the residual heat of reaction at various time through DSC scans to ensure that the curing reaction was complete.

In the presence of an accelerator, *o*-cresol novolac epoxy resin (YDCN-702, Tohto Kasei, Japan) was cured by phenol novolac resin (NOV) (H-1, Sumitomo, Japan) and synthesized phenol novolac acetate resin (NOVA) according to our previous work.[14] No detectable OH content could be observed by FTIR and NMR in cured *o*-cresol epoxy resin.

The structures of the components are shown in Chart 1.

These samples were equilibrated at 30 °C above the calorimetric T_g for 10 min to eliminate the thermal history and then were cooled at different rates. Liquid nitrogen is used to quench the samples. Each cooled specimen was aged at $T_g - 50$ °C for different times, 0.25, 1, 3, 8, and 42 h, to make sure that sub-T_g heat flow transition can be observed if it does happen. Physical aging was carried out in an aging oven with a temperature accuracy of ±0.1 °C in a N_2 atmosphere.

Specimens were put into aluminum crucibles, and the weight of each specimen was about 10−15 mg. A SETARAM DSC92 instrument was used for the DSC studies with the heating rate of 10 °C/min.

Results and Discussion. As shown in Figure 1, quenched samples of epoxy cured with DDM were aged at 116 °C which was $T_g - 50$ °C; sub-T_g heat flow transition can be observed at about 136 °C for a short annealing time. With increasing annealing time, the transition moves to higher temperatures, while the upper heat flow transition remains essentially unchanged and two merge into one which is lower than the original T_g after a long annealing time. All of these observations are in good agreement with previous work,[2−9,12,13] and they have been accepted as general features of the structure relaxation of thermoplastic and thermosetting polymers.

Samples of epoxy resin cured with DDM were cooled from above T_g with different rates and then they were reheated to observe the change of T_g. In Figure 2, it is clear to see that T_gs are strongly influenced by the prior

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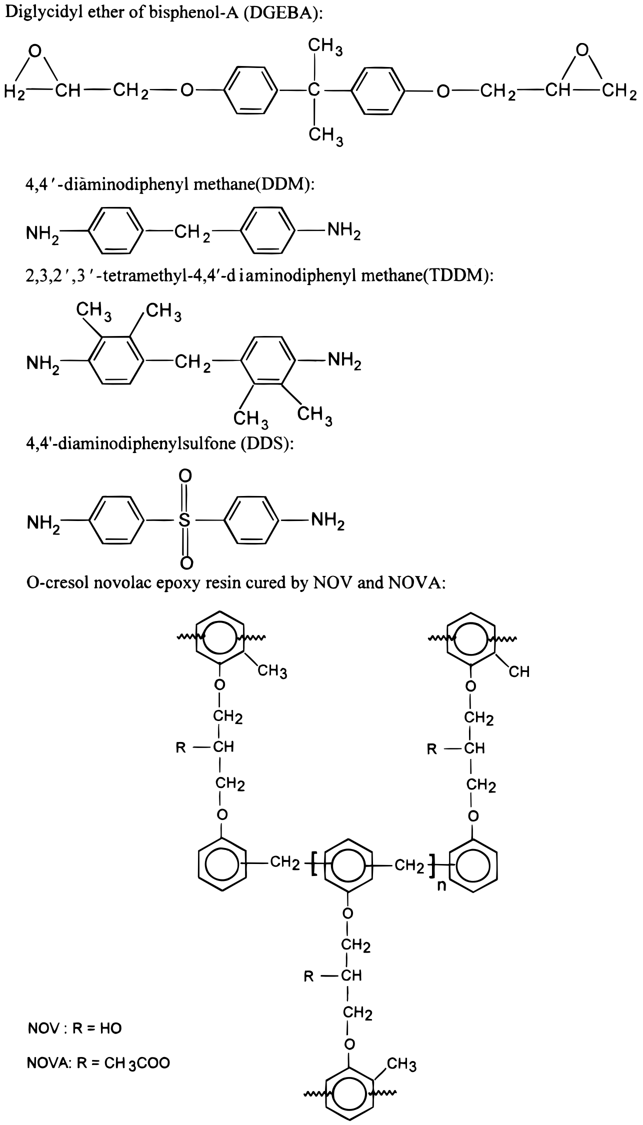
Chart 1



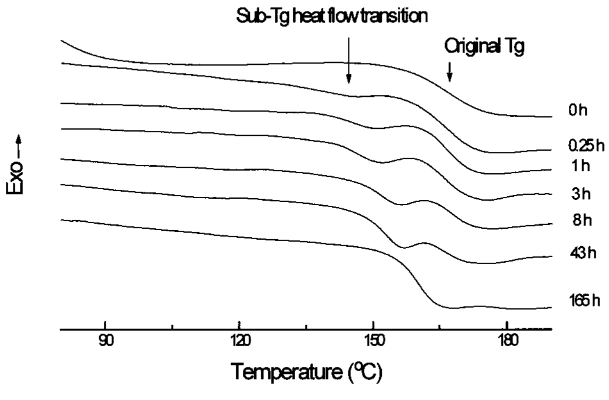


Figure 1. Effects of aging time at 116 °C on the DSC traces of epoxy resin cured with DDM.

cooling rates and there exits a lowest T_g. With the decreasing of cooling rate, T_g decreases first, however, after it reaches the lowest point at prior cooling rate of 20 °C/min; it then increases instead. Furthermore, as shown in Table 1, the disparity between original T_g and sub-T_g heat flow transition, ΔT_g, decreases with the prior cooling rate and sub-T_g heat flow transition cannot be observed at all when cooling rate is lower than that to appear the lowest T_g, which is 20 °C/min.

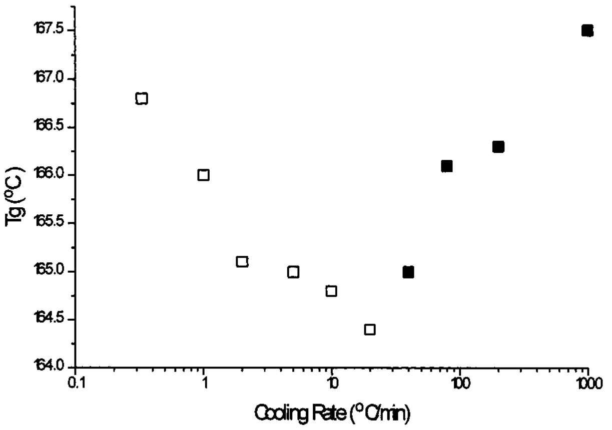


Figure 2. Change of T_g of epoxy resin cured with DDM with prior cooling rates. Take the cooling rate of quench in liquid nitrogen as 10^3. ((□) sub-T_g heat flow transition appears after aging; (■) sub-T_g heat flow transition does not appear after aging.)

Table 1. Change of ΔT_g of Cured Epoxy Resin with Prior Cooling Rates

cooling rate (°C/min)	ΔT_g ($T_g(2)^a - T_g(1)^b$)					
	DDM[d]	TDDM[e]	NOV[f]	NOVA[g]	100%[h]	80%[i]
10^3 [c]	20.1	25.5	32.3	17.6	35.5	23.7
200	18.1	24.0	23.8		20.4	21.1
80	14.4		21.3	15.9	16.7	
40	12.4	24.0		15.3	12.8	18.6
20		22.9				18.2
10		18.9		15.0		16.2
5		14.2		14.6		
2						

[a] Original T_g. [b] Sub-T_g heat flow transition. [c] Quenched in liquid nitrogen. [d] Epoxy resin cured with DDM. [e] Epoxy resin cured with TDDM. [f] NOV-cured *o*-cresol novolac epoxy resin. [g] NOVA-cured *o*-cresol novolac epoxy resin. [h] Epoxy resin cured with an equal stoichiometric amount of DDS. [i] Epoxy resin cured with an 80% stoichiometric amount of DDS.

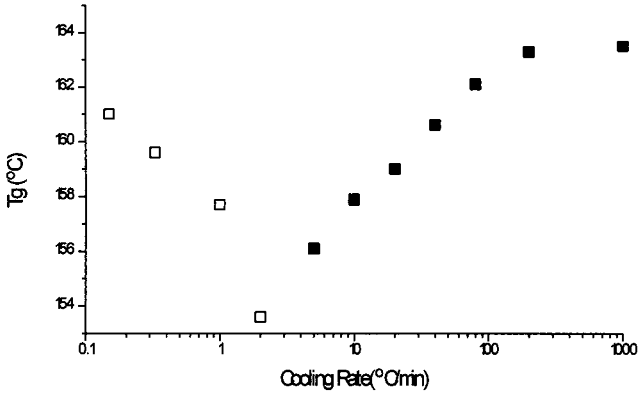


Figure 3. Change of T_g of epoxy resin cured with TDDM with prior cooling rates. Take the cooling rate of quench in liquid nitrogen as 10^3. ((□) sub-T_g heat flow transition appears after aging; (■) sub-T_g heat flow transition does not appear after aging.)

To discuss the further relationship of T_g, sub-T_g heat flow transition, and the cooling rates, three systems of cured epoxy resin were studied. Figure 3 gives the change of T_g with prior cooling rates of epoxy resin cured with TDDM, in which four methyl groups are introduced to the 2,3 and the 2′,3′ positions of DDM. However, it can be seen that the lowest T_g appears at a prior cooling rate of 2 °C/min, which is much lower than that of the epoxy resin cured with DDM, and the sub-T_g heat flow transition appears only when the prior cooling rate is

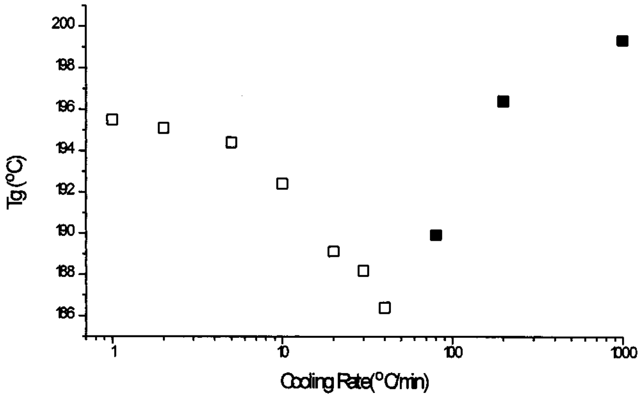


Figure 4. Change of T_g of *o*-cresol novolac epoxy resin cured with NOV with prior cooling rates. Take the cooling rate of quench in liquid nitrogen as 10^3. ((□) sub-T_g heat flow transition appears after aging; (■) sub-T_g heat flow transition does not appear after aging.)

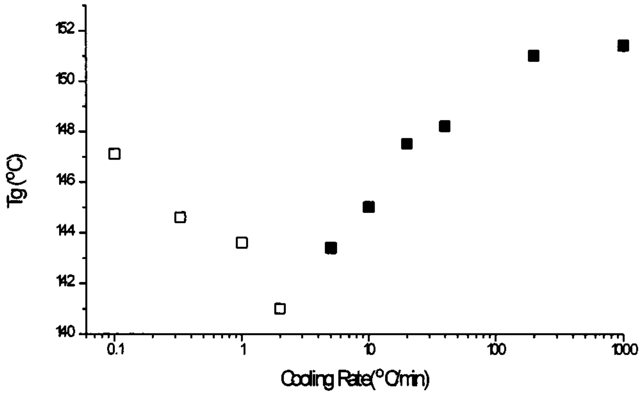


Figure 5. Change of T_g of *o*-cresol novolac epoxy resin cured with NOVA with prior cooling rates. Take the cooling rate of quench in liquid nitrogen as 10^3. ((□) sub-T_g heat flow transition appears after aging; (■) sub-T_g heat flow transition does not appear after aging.)

higher than that. Further, it can be seen in Figure 3 that the disparity of T_gs is much larger than that in Figure 2, which are about 10 and 3 °C, respectively.

For NOV and NOVA cured *o*-cresol novolac epoxy resin, it can be seen that the lowest T_g appears at 2 °C/min in Figure 5 which is much lower than 40 °C/min in Figure 4. However, as shown in Table 1, ΔT_g of NOVA is lower than that of NOV. In Figures 6 and 7, the lowest T_g of 80% cured epoxy resin appears at the cooling rate of 5 °C/min, which is lower than that of fully cured epoxy resin, 20 °C/min; meanwhile, it can de seen in Table 1 that the ΔT_g of fully cured epoxy resin is larger than that of the 80% cured one.

It has been observed that the original T_g was attributed to the motion of the internal stress relaxed molecular chain, while the sub-T_g heat flow transition was attributed to the motion of the internal stress unrelaxed molecular chain.[12,13] When the epoxy resin is cooled from above T_g, the molecular network of the sample is frozen in the nonequilibrium state with internal stress and extra free volume, and the internal stress will hinder the molecular relaxation of epoxy networks to approach the equilibrium state. With the increase in the prior cooling rate, the departure from the equilibrium state would be farther and the internal stress and extra free volume would be higher. Mijovic[15] observed that T_g decreased with the annealing time and described it as the result of the existence of an internal stress relaxation the epoxy network. Baratheeswaran and Gupta[16] found that the higher the T_g, the higher the internal stress. After T_g reaches the lowest point, the main factor to influence the position of T_g would be the arrangement of the network toward an equilibrium state, and therefore T_g increases again.

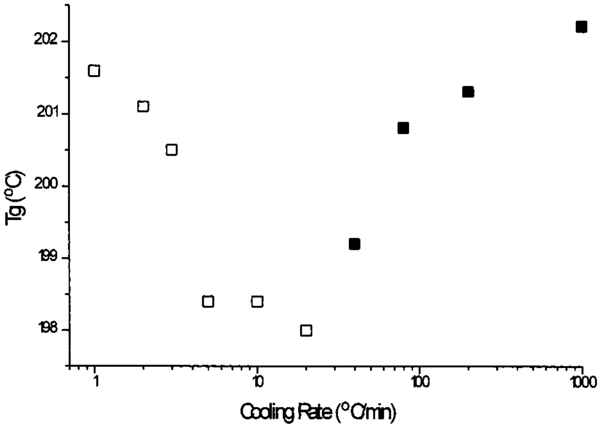


Figure 6. Change of T_g of epoxy resin fully cured with DDS with prior cooling rates. Take the cooling rate of quench in liquid nitrogen as 10^3. ((□) sub-T_g heat flow transition appears after aging; (■) sub-T_g heat flow transition does not appear after aging.)

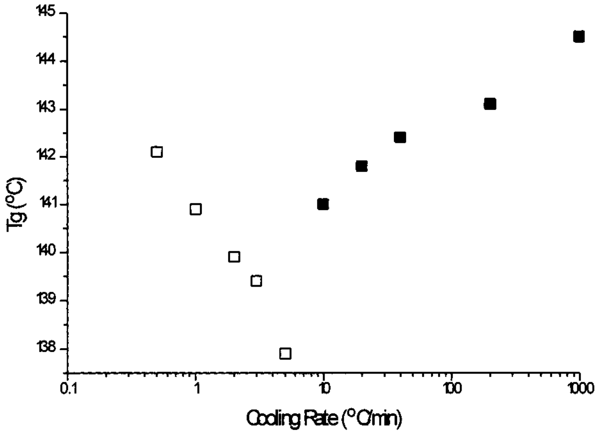


Figure 7. Change of T_g of epoxy resin 80% cured with DDS with prior cooling rates. Take the cooling rate of quench in liquid nitrogen as 10^3. ((□) sub-T_g heat flow transition appears after aging; (■) sub-T_g heat flow transition does not appear after aging.)

The methyl substituent of TDDM, the hydrogen bonding of the NOV system, and the higher cross-linking density of the fully cured epoxy resin would cause difficulty in the rotation of the molecular chain and the relaxation of the network and thereby would introduce higher internal stress. Thus, as shown in Table 1, ΔT_g, the disparity of T_g and sub-T_g heat flow transition, was influenced by these factors.

In Figures 2−7, the substituent groups, the bulky accetate groups, and the lower cross-link densities would make the network looser and introduce more extra free volume in the network and cause the network to reach equilibrium state in the longer period. Therefore, the lowest T_g appears at lower prior cooling rate.

References and Notes

(1) Hutchinson, J. M. *Prog. Polym. Sci.* **1995**, *20*, 703.

(2) Berens, A. R.; Hodge, I. M. *Macromolecules* **1982**, *15*, 756.
(3) Hodge, I. M.; Berens, A. R. *Macromolecules* **1982**, *15*, 762.
(4) Ramos, A. R.; Hutchinson, J. M.; Kovacs, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1655.
(5) Hodge, I. M. *Macromolecules* **1987**, *20*, 2897.
(6) Ribelles, J. L.; Greus, G. A. R.; Calleja, R. D. *Polymer* **1990**, *31*, 223.
(7) Montserrat, S. *J. Polym. Sci. Part B: Polym. Phys.* **1994**, *32*, 509.
(8) Muzeau, E.; Vigier, G.; Vassoille, R.; Perez, J. *Polymer* **1995**, *36*, 611.
(9) Hourston, D. J.; Song, M.; Hammiche, A.; Pollock, H. M.; Reading, M. *Polymer* **1996**, *37*, 243.
(10) Wimberger-Friedl, R.; de Bruin, J. G. *Macromolecules* **1996**, *29*, 4992.
(11) Jo, W. H.; Ko, K. J. *Polym. Eng. Sci.* **1991**, *31*, 239.
(12) Shen, J.; Shao, Z.; Li, S. *Polymer* **1995**, *36*, 3479.
(13) Chen, X.; Li, S. *Polym. Eng. Sci.* **1998**, *38*, 947.
(14) Luo, X. W.; Ping, Z. H.; Ding, J. P.; Ding, Y. D.; Li, S. J. *J. Macromol. Sci.* **1997**, *A34*, 2279.
(15) Mijovic, J. *J. Appl. Polym. Sci.* **1982**, *27*, 3211.
(16) Brahatheeswaran, C.; Gupta, V. B. *Polymer* **1993**, *34*, 289.

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