Communication: To further study the sub-$T_g$ heat flow transition of a cured epoxy resin, cured samples with different thermal history were investigated using torsion pendulum analysis (TPA) and thermal mechanical analysis (TMA). The results indicate that sub-$T_g$ heat flow transition could be related to the molecular relaxation from 20 °C to the $\alpha$-peak, and that frozen-in extra free volume is necessary for the appearance of sub-$T_g$ heat flow transition.

DSC heat flow traces of the fully cured epoxy resin quenched in liquid nitrogen from 232 °C and then aged at 162 °C (arrow A: position of Trans1 of aged samples, arrow B: end of the original heat flow).

Further Study of Sub-$T_g$ Heat Flow Transition of a Cured Epoxy Resin

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Introduction
The physical aging of polymers has been widely studied. A lot of the studies concerned with physical aging focus on long-term volume relaxation behavior. However, we are interested in the initiation of physical aging behavior, when two heat flow transitions can be observed by means of differential scanning calorimetry (DSC) curves at the glass transition area. In our previous work, the sub-$T_g$ heat flow transition of cured epoxy resins was studied and internal stress was proposed to explain it. Later, it was evidenced that this phenomenon could be related to the rigidity and crosslinking density of the epoxy resin network. In this work, torsion pendulum analysis (TPA) and thermal mechanic analysis (TMA) were utilized to study the sub-$T_g$ heat flow transition of the cured epoxy resin. The purpose of this study was to find more evidence for a possible explanation of the phenomenon of sub-$T_g$ heat flow transition of the cured epoxy resin.

Experimental Part
The epoxy oligomer used in this study was a diglycidyl ether of bisphenol-A (DGEBA; E51, Epoxy equivalent weight: 190) supplied by Shanghai Resin Factory. To obtain fully cured epoxy resin, stoichiometric amounts of 4,4’-diaminodiphenylsulfone (DDS) were added as the curing agent at 150 °C while the epoxy was stirred. The mixture was poured into a polished steel mould in a period of 5 min before it was cured at 150 °C for 2 h, at 180 °C for 2 h, and then at 202 °C for 8 h. The original $T_g$ of the sample quenched from 235 °C into liquid nitrogen was 202.2 °C. The degrees of curing were measured utilizing the residual heat of reaction at various times through DSC scans to ensure complete curing reaction, as described in the previous work.

Dynamic mechanical properties of the cured samples were studied over the temperature range 10 °C to 205 °C using inverted free-oscillation torsion pendulum analysis (Instrument Facilities of Fudan University). The rectangular specimens were 60 mm × 5 mm × 1 mm. The frequency of oscillation was adjusted to be within the range of 0.05–1.0 Hz with a heating rate of 1 °C/min.

The thermal expansion behavior was tested with a Du Pont Instrument 2940 TMA. The samples were 5 mm × 5 mm × 3.7 mm in size, and the force loaded was 0.05 N. Samples were heated from room temperature to 250 °C at a heating rate of 10 °C/min.

Results and Discussion
The Behavior of Sub-$T_g$ Heat Flow Transition of a Cured Epoxy Resin
Fully cured epoxy samples were quenched with liquid nitrogen from 232 °C and then annealed for various times...
The DSC scans of these aged samples are shown in Figure 1. It can be seen that a new heat flow transition, sub-$T_g$ heat flow transition (Trans1), appeared at 176.8°C after a short aging time, besides the original heat flow transition (Trans2) at 202.8°C. The position and magnitude of Trans1 increased with aging time, and an endothermic peak superposed. Meanwhile, the magnitude of Trans2 decreased with aging time, although the position of the trace remained unchanged. Trans2 disappeared after about 8 h and the two transitions merged to a transition, which was lower than the original one and increased with aging time. All these observations are in good agreement with previous work.[11, 12]

Physical aging of cured epoxy resin samples with different thermal history was carried out. Several samples were cooled from 232°C to $T_g \pm 40°C$ applying different cooling rates and were then aged at 150°C for 12 h. The positions of heat flow transitions of the aged samples are shown in Table 1. Additionally, some samples were cooled at 2°C/min from 242°C to a certain temperature above $T_g$, then quenched with liquid nitrogen and also aged at 150°C for 12 h. The heat flow transitions of these samples are shown in Table 2.

In Table 1, it can be seen that Trans1 decreased and the difference between Trans1 and Trans2 ($\Delta$Trans) increased with the cooling rate. The highest cooling rate (quenched in liquid nitrogen) led to the highest $\Delta$Trans and the lowest Trans1. However, when the cooling rate was appreciably low (lower than 5°C/min), Trans1 did not appear at all after aging. As shown in Table 2, Trans1 decreased and $\Delta$Trans increased with increasing quenching temperature. The sample quenched from the highest temperature had the lowest Trans1 and the largest $\Delta$Trans. When samples were quenched from below 192°C, Trans1 could not be observed at all.

**Dynamic Mechanical Analysis**

Dynamic mechanical properties data for original and aged samples are shown in Figure 2. In Figure 2a, the elastic modulus ($G$ versus $T$ curve shows significant discrepancy between samples with different thermal history. Figure 2b shows that the original sample had higher $\lg(tan\delta)$ values from 20°C to $\alpha$-relaxation, and the values decreased with aging. After aging for 8 h, the values were much lower than those of the original sample. At the same time, $\alpha$-peaks became narrower with aging time. The results show that there a kind of molecular relaxation occurred from 20°C to $\alpha$-relaxation, and this relaxation reduces with aging time.

Small, intermediate relaxation regions between $\alpha$- and $\beta$-relaxation have been reported for polycarbonate[13] and atactic polystyrene[14] and were attributed to frozen-in non-equilibrium stress during the preparation. Similar relaxations in different epoxy resins were also found[15, 16] and attributed to internal stress relaxation. In our previous work,[17] a weak and broad relaxation below the $\alpha$-peak, the so-called $\beta$-relaxation, was observed in a polysiloxane-modified epoxy resin and was attributed to residual micro-stress at the interface between polysiloxane domain and epoxy resin matrix.[10]

In this work, it should be noticed that the flat and broad relaxation peak between 20°C and $\alpha$-peak decreased with the magnitude of sub-$T_g$ heat flow transition.

Dynamic mechanical analyses for samples cooled from above $T_g$ applying different cooling rates are shown in...
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Figure 2. Dynamic mechanical analysis data for samples aged at 162°C (a) $\lg G'$ (Pa) vs $T$ and (b) $\lg(\tan \delta)$ vs $T$: (o) unaged, (+) 1 h, (a) 2 h, (●) 8 h.

Figure 3. Similar to Figure 2a, the $G'$ elastic modulus versus $T$ curve in Figure 3a shows significant difference. From Figure 3b, it can be seen that the quenched sample had the highest $\lg(\tan \delta)$ values from above 20°C, and the values decreased with cooling rate. Compared with the data of Table 1, Trans1 of the DSC curves only occurred for aged samples whose original $\lg(\tan \delta)$ values appeared as a flat and broad peak. This implies that the molecular relaxation from 20°C to the $\alpha$-peak is necessary for the appearance of the sub-$T_g$ heat flow transition.

A specimen was quenched from 235°C, then isothermal dynamic mechanical analysis was carried out at 162°C, and the results are shown in Figure 4. It can be seen that the $\lg(\tan \delta)$ values decreased with isothermal time. On the other hand, the $\lg(G')$ values increased with ongoing isothermal process. After about 6 h, the values of both $\lg(\tan \delta)$ and $\lg(G')$ did not change anymore. This suggests a kind of molecular relaxation at around 162°C, which disappears after about 6 h. Taking into account the data of Figure 1, it can be seen that this kind of molecular relaxation appears simultaneously with the phenomenon of sub-$T_g$ heat flow transition.

The results indicate that sub-$T_g$ heat flow transition might be related to the molecular relaxation from 20°C to the $\alpha$-peak.

Figure 3. Dynamic mechanical analysis data for different cooling rates (a) $\lg G'$ (Pa) vs $T$ and (b) $\lg(\tan \delta)$ vs $T$: (o) quenched, (+) 20°C/min, (a) 5°C/min.

Figure 4. Isothermal dynamic mechanical analysis data for a sample quenched at 162°C.

Thermal Mechanical Analysis (TMA)

The TMA thermograms of cured epoxy resin samples cooled from 235°C with different cooling rates, are shown in Figure 5. The quenched sample showed an abrupt drop in linear dimension at the vicinity of the glass transition region, which is considered to be related to the relaxation of the extra frozen-in free volume.[17] Further-
more, the magnitude of this abrupt drop in linear dimension decreased with cooling rate applied from 235 °C to temperatures below \( T_g \). The drop of the sample cooled at a rate of 80 °C/min is much smaller than that of the quenched one, it is even less on applying a cooling rate of 20 °C/min, and completely disappears at a rate of 5 °C/min.

Considering the results listed in Table 1, it becomes obvious that the magnitude of the abrupt drop and \( \Delta T_{\text{Trans}} \) simultaneously decreased with the cooling rate employed. The quenched sample showed the highest abrupt drop and the highest value for \( \Delta T_{\text{Trans}} \). At a cooling rate of 5 °C/min, the abrupt drop disappeared and, after aging, Trans1 could not be observed in the DSC curves either. As mentioned in our previous work, the deviation from the equilibrium state will rise, and internal stress and extra free volume will be higher on increasing the cooling rate.[17] Therefore, the results of TMA further indicate that frozen-in extra free volume is necessary for the appearance of sub-\( T_g \) heat flow transition. A minimum free volume required for the stress relaxation \( v^* \) was also found by Higuchi et al.[18] in a study concerned with the stress relaxation of polycarbonate (PC) glasses.

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