# Physical Aging of Polydimethylsiloxane-Modified Epoxy Resin

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**ABSTRACT:** The thermal expansion coefficient and physical aging behavior of cured epoxy resins modified with amino-terminated polydimethylsiloxane were investigated. The epoxy resin was tetramethyl biphenol diglycidyl ether. Two factors influenced the thermal expansion behavior and the free volume relaxation of the polysiloxane-modified epoxy systems. One was the miscibility between the epoxy resin and the polysiloxane and the flexibility of the chains in the network system. The intrinsic thermal expansion of the network chains and the volume relaxation increased as a result of building polysiloxane molecules into the network structure. The other factor was the size and concentration of the dispersed polysiloxane particles. The increased local free volume at the interface between the epoxy matrix and the polysiloxane particle resulted in a higher thermal expansion coefficient and led to a large driving force for the volume relaxation during annealing. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1291–1300, 1998

**Key words:** tetramethyl biphenol diglycidyl ether; polydimethylsiloxane; morphological parameter; thermal expansion coefficient; physical aging

## INTRODUCTION

It has been known for a long time that mineral and organic glasses are in a metastable state, more or less far from thermodynamic equilibrium. This metastable state of glasses is characterized by thermodynamic parameters such as entropy and enthalpy of the structural state. Many physical properties are linked to this structural state: mechanical and dielectric losses, glass-transition temperature, creep and internal stress relaxation, yield behavior, and toughness.

The physical aging of linear polymers has been widely studied; however, in recent years more attention has been paid to physical aging of network polymers. One of the characteristics of the quenched glassy state is the excess trapped free volume that is manifested by the lowering of the bulk polymer density. Thermodynamic state functions, such as enthalpy and specific 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 aging phenomenon is the time-dependent approach toward equilibrium, and it is typically viewed as a recovery phenomenon. Basically, volume relaxation and enthalpy relaxation take place in physical aging. The two parameters are nearly identical in their time-dependent behaviors.

Epoxy resins are widely utilized as packaging

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and insulating materials and adhesives in the electric and electronic industries because of their excellent heat, moisture, solvent, and chemical resistance; superior electrical and mechanical properties; and good adhesion to many substrates. Tetramethyl biphenol diglycidyl ether (TMBPDGE) is commonly used as a base material for the encapsulation of microelectronic devices because it has a high rubbery modulus, a low glassy modulus, and a broad glass transition compared with bisphenol-A type epoxy resin.[1,2] However, it is known that epoxy resins, including the biphenol type resin, are relatively brittle polymers with poor resistance to crack growth. It is also known that when epoxy resins are cured, they can contract and develop internal stresses.[3,4] This shrinkage and internal stress cause reduced durability against moisture and heat cycle.

To reduce the internal stress or to improve the fracture toughness of epoxy resins, several methods have been proposed. One method involves the preformation of a stable dispersion of rubbery particles in the uncured epoxy resin via preliminary reaction of epoxy resin using functionalized polysiloxanes. Organosiloxane polymers are known for their excellent thermal and thermooxidative stabilities, very low glass-transition temperature ($T_g = -123°C$), high moisture resistance, and good electrical properties.[5] However, the solubility parameter of polydimethylsiloxane (PDMS), 7.4–7.8, is much lower than that of the epoxy resin, which is about 10.9.[6] PDMS is therefore not compatible with epoxy resin unless it has functional groups that react with epoxy groups. We previously reported that epoxy modified with the composition of amino-terminated PDMS (ATPDMS) differing in molecular weight increased fracture toughness ($K_{IC}$).[7]

The physical aging of linear glassy polymers has been well documented, and research[8–11] has shown that physical aging also exists in network epoxy glasses. Shen et al.[12] suggested that physical aging is an effective method for investigating the internal stress of the modified epoxy resin. They investigated epoxy systems modified with two kinds of low molecular weight polysiloxanes: aminopropyl dimethyl-terminated polysiloxane and phenyl-terminated polysiloxane. Their results showed that after annealing the neat and the modified cured epoxy resins at sub-$T_g$ (−30°C), two kinds of relaxation (internal stress relaxation and enthalpy relaxation) took place simultaneously during annealing. Furthermore, the extent and the rate of relaxation were closely related to the kind of modifiers and their ratio. Therefore, in their study, the physical aging phenomena were studied to monitor the internal stress of the modified epoxy resin.

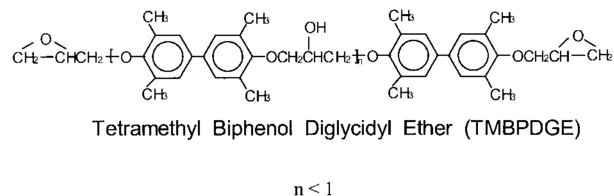


**Figure 1** Molecular structure of TMBPDGE.

The objective of this study is to investigate the thermal expansion coefficient and the physical aging behavior of cured epoxy systems in relation to the composition of ATPDMS differing in molecular weight.

## EXPERIMENTAL

### Materials

TMBPDGE (YX-4000, Yuka Shell Co., 184 epoxy equivalent weight) was used as the epoxy resin (Fig. 1), 4,4′-Diamino diphenylmethane (DDM) was used as the curing agent. ATPDMS was from Shin-Etsu Chemical Co., and the structure and molecular weights are shown in Table I.

### Preparation of ATPDMS-Modified Epoxy Resin

The modified TMBPDGE was prepared by reacting TMBPDGE with ATPDMS in the melt state at 135°C. Into a four-necked, round-bottom flask (equipped with a heating mantle, mechanical stirrer, and thermocouple), TMBPDGE was charged, heated to 135°C, and then vigorously stirred under a dry nitrogen atmosphere. ATPDMS was then added dropwise while maintaining the reaction temperature at 135°C.

The degree of the reaction was monitored by titrating tertiary amine with bromophenol blue indicator solution in the reaction mixture (Table II). Epoxy equivalent weights of ATPDMS-modified epoxy resins were determined by the titration method with cresol red indicator solution. All polysiloxane-modified epoxies contained 10 phr PDMS.

### Specimen Preparation

The epoxy resin was degassed at 105°C under reduced pressure while stirring. Then a stoichiometric amount of curing agent (DDM) was added,

**Table I Polydimethylsiloxane Used for Modification of TMBPDGE**

| Polysiloxane | Structural Formula | Molecular Weight |
|---|---|---|
| AT900 | $R-Si(CH_3)_2-O-[Si(CH_3)_2-O]_n-Si(CH_3)_2-R$ | 900 |
| AT1680 | | 1,680 |
| AT3000 | | 3,000 |
| AT3880 | | 3,880 |
| AT7000 | | 7,000 |
| AT12000 | $R = CH_2CH_2CH_2NH_2$ | 12,000 |

assuming that one epoxy group corresponded to one active hydrogen of the amino group. Because the curing agent was in the solid state at room temperature, this agent was melted in an oven at 105°C and then added to the epoxy resin. The mixture was stirred at 105°C until the curing agent was dissolved completely in the epoxy resin and was then poured into the mold. This resin system was cured at 130°C for 2 h and then at 180°C for 6 h to obtain a cured specimen. The cured samples were scanned at 10°C $min^{-1}$ on a Dupont DSC 2010 to ensure that the materials were fully cured.

### Microstructural Characterization

The mean particle size and the particle size distribution of the polysiloxane particles were determined by Philips 535M scanning electron microscopy (SEM) on the fractured surfaces of cured ATPDMS-modified samples that were vacuum coated with gold.

The magnification was chosen to provide a region containing about 100 particles of the dispersed domains. Using equations previously described,[13] the size distribution was determined by measuring individual particles.

### Determination of Thermal Expansion Coefficient

Determination of the thermal expansion coefficient ($\alpha$) was made using a thermal mechanical analyzer (DuPont TMA 943) with a heating rate of 10°C $min^{-1}$. The size of the specimens was 5L × 5B × 5W mm. The test specimen was placed in the instrument between the bottom of an outer quartz jacket and an inner quartz rod. The rod is part of a balanced beam assembly that is used to minimize the load on the specimen during testing (1 g). The whole assembly is surrounded by a furnace. The thermal expansion coefficient in the glassy state ($\alpha_1$) below the $T_g$ was taken from 60 to 100°C.

### Isothermal Aging

A DuPont DSC 2010 instrument was used for the DSC studies. Samples were placed into sample

**Table II Percentage of Amines of ATPDMS-Modified Epoxy Resins**

| Composition | Reaction Time[a] (min) | Primary | Secondary | Tertiary |
|---|---|---|---|---|
| AT900 | 60 | 1 | 2 | 97 |
| AT1680 | 60 | 5 | 3 | 92 |
| AT3000 | 90 | 15 | 12 | 73 |
| AT3880 | 120 | 18 | 4 | 78 |
| AT900/AT1680 (1 : 1) | 60 | 1 | 2 | 97 |
| AT900/AT3000 (1 : 1) | 90 | 1 | 7 | 92 |
| AT900/AT3880 (1 : 1) | 120 | 2 | — | 98 |
| AT900/AT7000 (1 : 1) | 250 | 2 | 3 | 95 |
| AT900/AT12000 (1 : 1) | 400 | 1 | 1 | 98 |

The resins were in a comparatively homogeneously dispersed state of polysiloxane particles (ATPDMS content: 10 phr).
[a] Preliminary reaction time is when the polysiloxane particles are homogeneously dispersed before aggregation takes place (amine percentage was determined at this time).

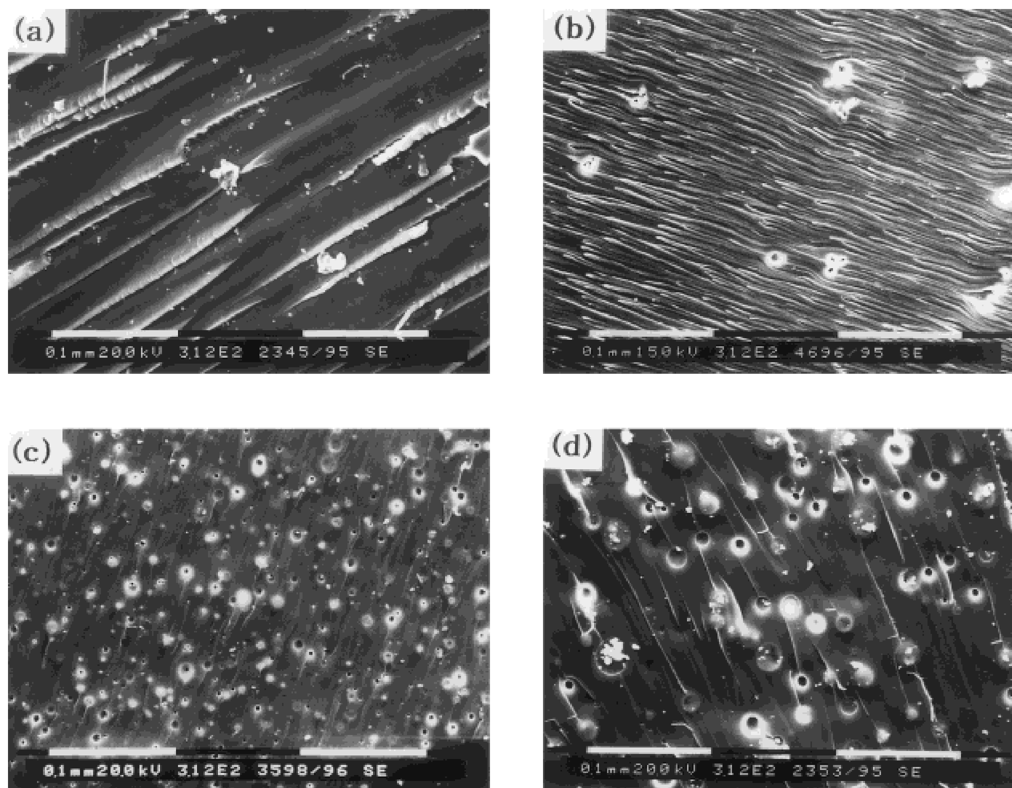


**Figure 2** Morphology of the fracture surfaces of cured epoxy resins modified with various ATPDMSs (10 phr): (a) control, (b) AT900, (c) AT900/AT3000 (1 : 1 weight ratio), and (d) AT3000.

pans, equilibrated at 10°C above $T_g$, and then quenched with liquid nitrogen. They were annealed at once at constant sub-$T_g$ temperature (140°C) for various time periods and quenched with liquid nitrogen at the end of the annealing. Annealed and unannealed specimens were scanned with a heating rate of 10°C min$^{-1}$ to see the effect of the isothermal aging at 140°C.

## RESULTS AND DISCUSSION

### Morphology

SEM micrographs of the fracture surfaces generated at room temperature for the unmodified epoxy resin and several polysiloxane-modified epoxy resins are shown in Figure 2. A sea-island structure is observed in all polysiloxane-modified epoxy resins. The shape of these polysiloxane particles is almost spherical and the details of the morphology are reported elsewhere.[7] Table III shows the morphological parameters obtained from the SEM micrographs.

### Thermal Expansion Behavior

The values of the thermal expansion coefficient ($\alpha_1$) in the glassy state are described in Table IV. The dependence of $\alpha_1$ on the size and the concentration of polysiloxane particles is depicted in Figure 3.

The lowest molecular weight polysiloxane-modified epoxy system (AT900-modified epoxy system) shows the highest value of $\alpha_1$ (107 $\mu$m/m °C). AT900 is partially miscible with the epoxy resin.[7] In this case, the presence of polysiloxane chains in the epoxy network structure results in an increased intrinsic thermal expansion of the network chains. In other words, the degree of miscibility between the epoxy resin and the polysiloxane determines this thermal expansion behavior. The higher molecular weight polysiloxanes are completely immiscible with the epoxy resin. The value of $\alpha_1$ increases as the polysiloxane particle size decreases and the particle concentration increases (Fig. 3). It is known that the addition of a polysiloxane with a higher thermal expansion coefficient than the matrix to the epoxy matrix

**Table III Morphological Parameters Determined by SEM[7]**

| Composition[a] | Number-Average Diameter ($\mu$m) | Concn Polysiloxane Particles ($\times 10^7$ cm$^{-3}$) |
|---|---|---|
| AT1680 | 7.8 | 13.0 |
| AT3000 | 10.2 | 7.6 |
| AT3880 | 12.4 | 3.0 |
| AT900/AT3000 (1 : 1) | 3.0 | 98.2 |
| AT900/AT7000 (1 : 1) | 3.5 | 44.3 |
| AT900/AT12000 (1 : 1) | 4.4 | 33.1 |

[a] All ATPDMS-modified epoxy systems contain 10 phr ATPDMS.

leads to the buildup of radial tensile stresses in the particle–matrix interface, accompanied by tangential compressive stresses in the surrounding matrix after cooling from the cure temperature to room temperature.[14,15] These stresses might increase the local free volume in the epoxy matrix.[16,17]

When the epoxy resin is modified with the mixture of AT900 and the other higher molecular weight polysiloxanes, two factors described above influence the thermal expansion behavior of the polysiloxane-modified epoxy systems. The intrinsic thermal expansion of the matrix increases as the result of the presence of low molecular weight polysiloxane molecules in the epoxy network structure. In this case, the degree of shrinkage in the epoxy matrix is similar to that in the dispersed phase after cooling from the cure temperature to room temperature. Therefore, the local free volume in the interface decreases. These results show that in the epoxy systems modified with the mixture of AT900 and higher molecular weight polysiloxanes, the effect of the polysiloxane particle concentration on the thermal expansion is lower compared to the single component ATPDMS-modified epoxy systems because the thermal expansion coefficient of the epoxy matrix approaches that of the dispersed phase.

In this study, annealing at 140°C significantly reduces the value of $\alpha_1$ (Table V). This is most likely due to the physical aging during the annealing below $T_g$. The unmodified epoxy system exhib-

**Table IV Thermal Expansion Coefficient ($\alpha_1$) of Polysiloxane-Modified Epoxy Systems**

| Composition[a] | Thermal Expansion Coefficient ($\mu$m/m °C) |
|---|---|
| Control | 87.3 |
| AT900 | 107 |
| AT1680 | 101 |
| AT3000 | 83.6 |
| AT3880 | 79.4 |
| AT900/AT1680 (1 : 1) | 99.2 |
| AT900/AT3000 (1 : 1) | 91.3 |
| AT900/AT3880 (1 : 1) | 93.5 |
| AT900/AT7000 (1 : 1) | 87.2 |
| AT900/AT12000 (1 : 1) | 81.5 |

[a] All ATPDMS-modified epoxy systems contain 10 phr ATPDMS.

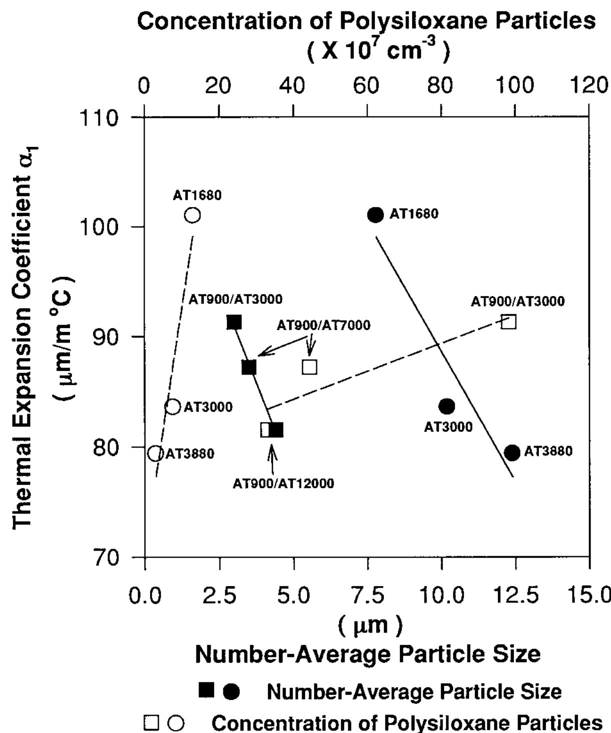


**Figure 3** Dependence of $\alpha_1$ on the number-average particle size and the concentration of polysiloxane particles.

**Table V Thermal Expansion Coefficient ($\alpha_1$) after Sub-$T_g$ Annealing at 140°C**

| | Thermal Expansion Coefficient ($\mu$m/m °C) | |
|---|---|---|
| Composition[a] | 30-min Annealing | 12-h Annealing |
| Control | 62 | 53.4 |
| AT900 | 70.6 | 67.7 |
| AT1680 | 69.1 | 68.2 |
| AT3000 | 66 | 62 |
| AT3880 | 62.3 | 59.5 |
| AT900/T3000 (1 : 1) | 66.5 | 64.5 |
| AT900/T7000 (1 : 1) | 64.2 | 65.6 |
| AT900/T12000 (1 : 1) | 65.1 | 62.8 |

[a] All ATPDMS-modified epoxy systems contain 10 phr ATPDMS.

its a relatively low value of $\alpha_1$ but a considerable decrease of $\alpha_1$ during the sub-$T_g$ annealing (Table V). The mobility of the biphenyl segment in the unmodified epoxy system is considerably low.[1] The motion of networks is frozen in the large free volume state with the decrease in the mobility of network segments, and the system that has more rigid network chains has a large free volume in the glassy region. This means that the free volume is not the only decisive factor to influence the degree of relaxation, but the flexibility of the chain also plays an important role in the process. The short and stiff epoxy–DDM crosslinks are very effective restraints for the chain mobility. The value of $\alpha_1$ is relatively low because of the low mobility of the biphenyl unit. Therefore, it is expected that the unmodified epoxy system with its high constraints on molecular motion will relax more slowly. The unmodified epoxy shows the continued relaxation during 12 h of annealing while in the polysiloxane-modified epoxy systems the relaxation is nearly complete after 30-min annealing.

## Physical Aging Behavior

In general, it is reported that the stress relaxation and the free volume relaxation occur simultaneously during annealing. Matsuoka et al.[18] has 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[10] observed that $T_g$ decreases with the annealing time, and this is attributed to the existence of internal stress relaxation. It was also observed by Brahatheeswaran and Gupta[19] that internal stresses relaxed on sub-$T_g$ aging due to free volume collapse, and the rate of stress relaxation was 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 nonequilibrium 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 equilibrium state. The rate of this relaxation process depends on both the temperature and time of annealing. Associated with this time-dependent free volume change is the decrease in enthalpy. Although it has been shown that enthalpy is a better characterization parameter than the volume,[20] the two parameters are nearly identical in their time-dependent behavior.

The relaxation characteristics as determined by DSC for the unmodified epoxy system are shown in Figure 4. The polysiloxane-modified epoxy systems show similar behavior (Fig. 5). A new heat-flow transition ($T_{g1}$) appears at low temperature and coexists with the original glass transition ($T_{g2}$).

It is found that the difference ($\Delta T_g$) of the low temperature transition ($T_{g1}$) and the high temperature transition ($T_{g2}$) decreases with the addition of various ATPDMSs. In Figure 6, $\Delta T_g$ decreases as the annealing time increases. The AT900-modified epoxy system shows the lowest $\Delta T_g$ and the smallest change of $\Delta T_g$ during the entire annealing time. Conversely, the unmodified epoxy system shows the highest $\Delta T_g$. The $\Delta T_g$ of the epoxy modified with the mixture of AT900 and AT3000 is lower than that of the epoxy modified with AT3000 alone. One explanation for

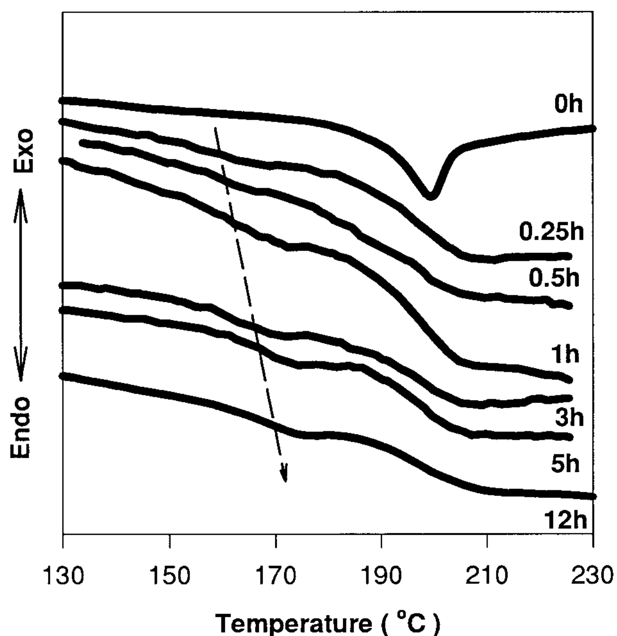


**Figure 4** Effect of annealing time on the DSC thermogram of unmodified epoxy resin annealed at 140°C for various time periods.

this interesting observation is that the change is caused by stress release during the annealing. It is well known that the separation $\Delta T_g$ is considered to be associated with the existence of the

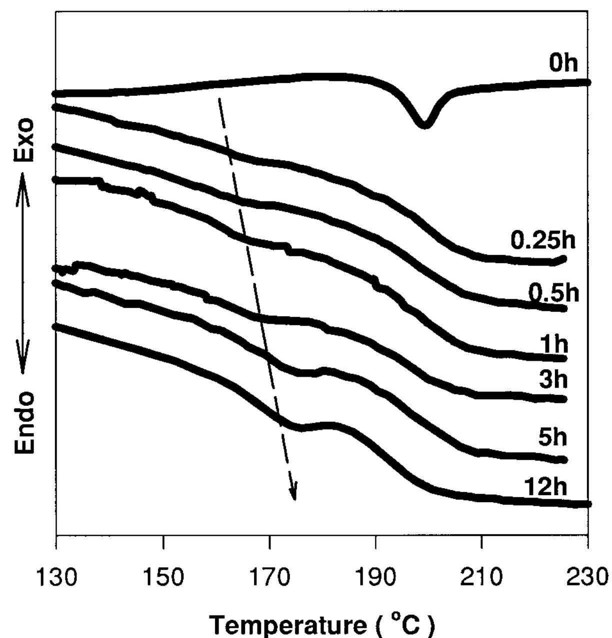


**Figure 5** Effect of annealing time on the DSC thermogram of the AT3000-modified epoxy resin annealed at 140°C for various time periods.

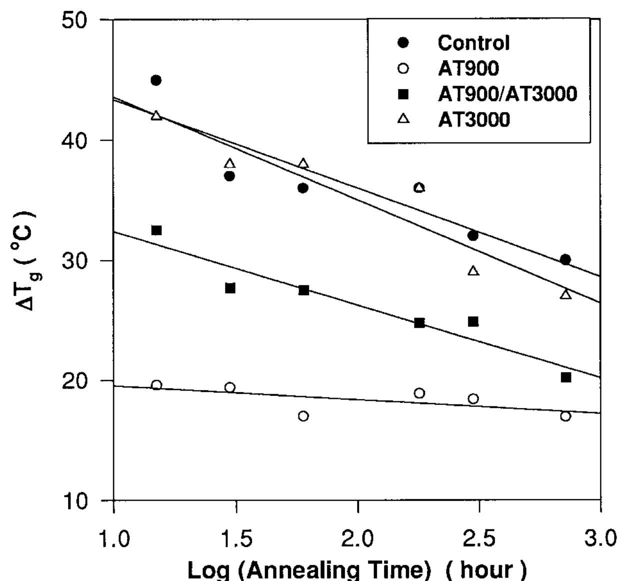


**Figure 6** Dependence of $\Delta T_g$ on annealing time for ATPDMS-modified epoxy resins at 140°C.

internal stress and the degree of separation reflects the relative value of the internal stress.[12] The smaller the value of $\Delta T_g$, the less internal stress exists.

The dependence of $\Delta T_g$ on the particle size and the concentration of polysiloxane particles was also investigated. Figures 7 and 8 show that the $\Delta T_g$ decreases as the particle size decreases and the particle concentration increases.

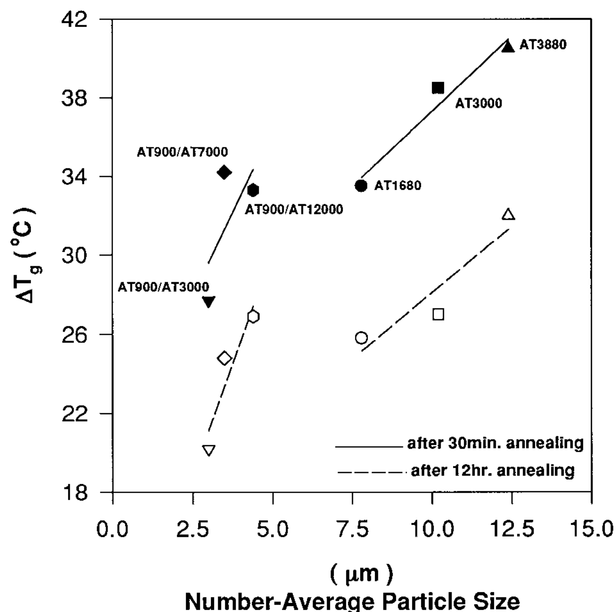


**Figure 7** Dependence of $\Delta T_g$ on the number-average particle size of polysiloxane at 140°C annealing.

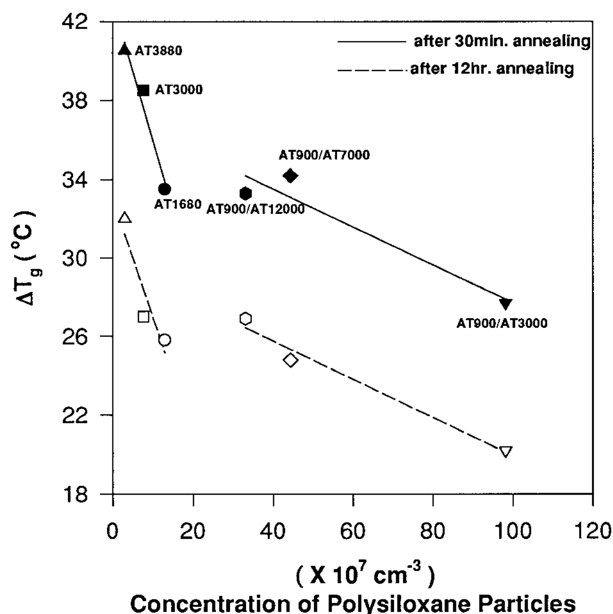


**Figure 8** Dependence of $\Delta T_g$ on the concentration of polysiloxane particles at 140°C annealing.

In the case of the unmodified epoxy system, two heat flow transitions ($T_{g1}$, $T_{g2}$) appear and the value of $\Delta T_g$ decreases with the increase of the annealing time. These phenomena are due to the existence of inhomogeneities in the morphology of the thermosetting resin. For a long time the concept of one indefinitely large molecule forming a homogeneous network has been used to describe the morphology of crosslinked thermosets. However, an apparent inadequacy of such a morphological model in explaining various properties of thermosets has led to a formulation of the concept of inhomogeneous thermoset morphology. Mijovic and Koutsky[21] reported that various bulk epoxy resin formulations were shown to be characterized by nodular morphology. They proposed that the model of higher crosslink density regions immersed in a lower crosslink density matrix most adequately described the morphology of thermosets. They explained the above phenomena as follows: a sudden quenching from the cure temperature to a temperature well below the $T_g$ introduces a certain amount of frozen-in stresses in the sample. In terms of the inhomogeneous thermoset morphology, the majority of these stresses are induced in the regions of lower crosslink density where the molecular motions of polymeric chains are less restricted. Therefore, this network is trapped during sudden quenching and exists in a nonequilibrium state with higher free volume and internal stress. During the annealing, however, the existing nonequilibrium state is altered by the molecular rearrangements that occur in the glassy state. On the morphological level, such transformations (referred to as the sub-$T_g$ annealing) are believed to lead to the formation of a more closely packed and aligned matrix (Fig. 9). This ordering of the less crosslinked matrix is achieved by the small-scale molecular motions. The network releases extra free volume and internal stress 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 $T_{g1}$, to higher temperature, and a lower value of $\Delta T_g$ (Table VI).

As mentioned earlier, the low mobility of the biphenyl unit leads to less relaxation of free volume. This fact can be confirmed in Table VII. The $\Delta T_g$ of the unmodified epoxy system after 12-h annealing is higher than that of the other systems.

However, except for the AT900-modified epoxy system, another effect might be considered in the polysiloxane-modified epoxy systems. The higher molecular weight polysiloxanes are not miscible with the epoxy resin, and they are dispersed as particles in the epoxy matrix. The polysiloxane particles tend to have higher shrinkage than the epoxy matrix during quenching, and this results in an increased local free volume at the interface of the epoxy matrix and the polysiloxane particle.

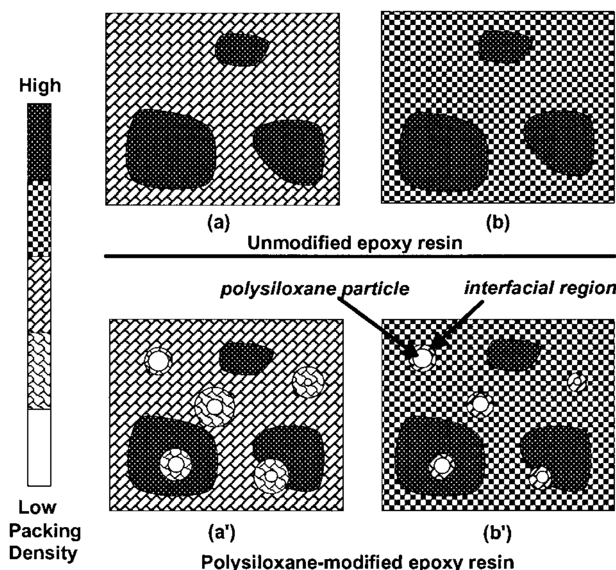


**Figure 9** A schematic representation of packing densities in the epoxy matrix during the sub-$T_g$ annealing: (a,a′) immediately after quenching and (b,b′) annealed for several hours.

**Table VI Glass-Transition Temperatures (°C) of ATPDMS-Modified Epoxy Systems after Various Annealing Times at 140°C**

| | | Annealing Time (h) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0.25 | 0.5 | 1 | 3 | 5 | 12 |
| Control | $T_{g1}$ | 154.0 | 160.0 | 160.5 | 162.5 | 167.5 | 168.0 |
| | $T_{g2}$ | 199.5 | 197.5 | 196.5 | 198.5 | 199.5 | 199.0 |
| | $\Delta T_g$ | 43.5 | 37.5 | 36.5 | 36 | 32 | 30 |
| AT900 | $T_{g1}$ | 156.9 | 157.2 | 161.2 | 160.0 | 163.4 | 165.7 |
| | $T_{g2}$ | 176.5 | 176.6 | 178.3 | 178.9 | 181.8 | 182.6 |
| | $\Delta T_g$ | 19.6 | 19.4 | 17.1 | 18.9 | 18.4 | 16.9 |
| AT900/AT3000 (1 : 1) | $T_{g1}$ | 158.7 | 161.9 | 163.0 | 164.1 | 166.6 | 171.5 |
| | $T_{g2}$ | 191.2 | 189.6 | 190.5 | 188.9 | 191.4 | 191.7 |
| | $\Delta T_g$ | 32.5 | 27.7 | 27.5 | 24.8 | 24.8 | 20.2 |
| AT3000 | $T_{g1}$ | 158.5 | 160.0 | 159.0 | 160.5 | 168.0 | 169.0 |
| | $T_{g2}$ | 200.0 | 198.5 | 197.5 | 197.0 | 197.0 | 193.0 |
| | $\Delta T_g$ | 41.5 | 38.5 | 38.5 | 36.5 | 29.0 | 27 |

All ATPDMS-modified epoxy systems contain 10 phr polysiloxane.

Therefore, the local free volume at the interface region increases during quenching as the particle size decreases and the particle concentration increases. The high initial free volume accelerates the initial relaxation of free volume and internal stress and leads to the small value of $\Delta T_g$.

In the AT900-modified epoxy system, as mentioned earlier, AT900 is partially miscible with the epoxy resin and the polysiloxane chains bonded chemically with the epoxy resin chains. It is known that the molecular chains bonded between the polysiloxane and the epoxy resin are very flexible so that they can move more freely and rapidly than pure epoxy resin chains when the samples are annealed. Therefore, the molecular chains pack more rapidly; that leads to a higher relaxation rate of free volume and a lower value of $\Delta T_g$. The miscibility of polysiloxane with epoxy resin and the flexibility of the chain play an important role in the process.

**Table VII Glass-Transition Temperatures (°C) and $\Delta T_g$ of Cured Epoxy Resins Modified with Various ATPDMSs after Annealing**

| | Annealing Time | | |
|---|---|---|---|
| Composition | 0 min $T_g$ | 30 min $\Delta T_g$ | 12 h $\Delta T_g$ |
| Control | 198.0 | 37.5 | 30 |
| AT900 | 171.8 | 19.4 | 16.9 |
| AT1680 | 195.5 | 33.5 | 25.8 |
| AT3000 | 193.0 | 38.5 | 27 |
| AT3880 | 197.0 | 40.5 | 32 |
| AT900/AT3000 (1 : 1) | 189.5 | 27.7 | 20.2 |
| AT900/AT7000 (1 : 1) | 192.0 | 34.2 | 24.8 |
| AT900/AT12000 (1 : 1) | 192.5 | 33.3 | 26.9 |

All PDMS-modified epoxy systems contain 10 phr polysiloxane.

In the epoxy modified with the mixture of AT900 and other high molecular weight polysiloxanes, the miscibility between the epoxy resin and the polysiloxane and the flexibility of the chains affect the volume relaxation in addition to the local free volume at the interface between the epoxy matrix and the polysiloxane particle. The miscibility and the flexibility may be more important than the local free volume at the interface in these processes. Figure 10 makes this explanation clear. The particle size and concentration of polysiloxane play important roles in affecting the extra free volume effectively. The thermal expansion coefficient in the glassy state ($\alpha_1$) is indirectly related to the chain flexibility of the epoxy matrix, and $\Delta T_g$ is inversely related to $\alpha_1$.

In this limited study, the synergistic effect of the local free volume at the interface and the chain flexibility in the volume relaxation are not observed. A detailed investigation of the interface surrounding the rubber particle during the annealing process is needed.

## CONCLUSION

This study investigated the thermal expansion coefficient and physical aging behavior of cured epoxy

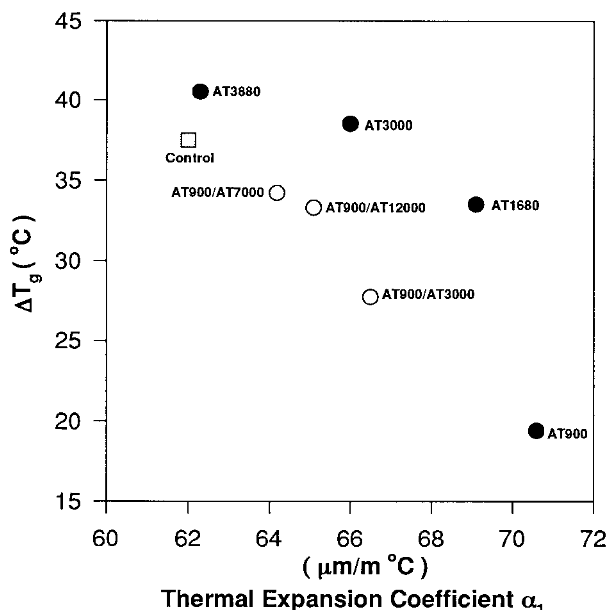


**Figure 10** Relationship between the thermal expansion coefficient ($\alpha_1$) and $\Delta T_g$ (after 30-min annealing).

systems in relation to the addition of various ATPDMSs that differed in their molecular weights. The main conclusions from this study are the following:

1. The thermal expansion coefficient of polysiloxane-modified epoxy resins in the glassy state is affected by two factors. One factor is the miscibility between the epoxy resin and the polysiloxane. As the miscibility increases, flexible polysiloxane chains are incorporated into the epoxy network, which increase the intrinsic thermal expansion of the epoxy matrix. Another factor is the mismatch of the degree of shrinkage between the epoxy matrix and the polysiloxane particle when cooled from the cure temperature to room temperature. The mismatch will cause the additional localized free volume at the interface, which results in a higher thermal expansion coefficient. Therefore, small particle size and high concentration of polysiloxane particles increases the $\alpha_1$ of the epoxy resin.
2. When the polysiloxane-modified epoxy resin is annealed at the sub-$T_g$, a new $T_g$ appears below the original $T_g$. The difference between the new $T_g$ and the original $T_g$ ($\Delta T_g$) decreases as a function of the annealing time at 140°C. These phenomena originate from the frozen-in internal stresses that relax on sub-$T_g$ annealing due to free volume collapse. The increased local free volume at the interface between the epoxy matrix and the polysiloxane particle leads to a high $\alpha_1$ and a high driving force for relaxation. The flexibility of the chains in the network system also plays an important role in the process. The effect of the flexibility is especially more important than that of the local free volume.
3. The values of $\Delta T_g$ are inversely proportional to the values of $\alpha_1$.

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