

# Thermal Degradation of Epoxy/Silica Composites Monitored via Dynamic Mechanical Thermal Analysis

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## SYNOPSIS

A dynamic mechanical thermal analyzer (DMTA) was used to monitor changes of dynamic mechanical properties during thermal degradation of two types of epoxy/silica composites, both of which are used as electrical insulation in power apparatus. It was found that the peak value of the dynamic loss factor ( $\tan \delta$ ), glass transition temperature ( $T_g$ ), and dynamic storage modulus ( $E'$ ) above  $T_g$  changed considerably with increasing thermal degradation, while  $E'$  at the glassy state only underwent a moderate change with increased thermal degradation. It is concluded that the DMTA technique is very sensitive to the structural changes in the investigated epoxy composites due to the thermal degradation. It is also confirmed by DMTA tests that further cross-linking and loss of dangling chains are occurring slowly during the stage prior to the onset of the severe degradation. © 1992 John Wiley & Sons, Inc.

## INTRODUCTION

Thermal degradation is a major problem in the application of polymers in different types of environment. Research into new evaluation methods for thermal degradation of polymers has always been of great interest among polymer researchers. Much work has been done on thermal degradation of polymers by employing instrumental techniques such as thermogravimetry and differential scanning calorimetry,<sup>1-3</sup> but there have been no reports on DMTA being used for characterizing polymer degradation. This research aimed to investigate the basic DMTA responses to thermal degradation in polymers and to explore the possible application of this technique in characterization of polymer thermal degradation, particularly for electrical power insulation.

## EXPERIMENTAL

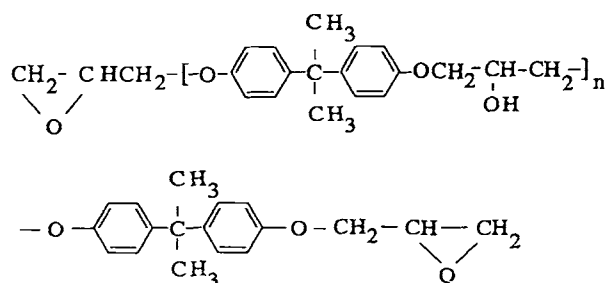
### 1. Sample Preparation

Two types of epoxy/silica formulation were used: One formulation is phthalic anhydride (32 pbw) cured bisphenol-A epoxy (100 pbw) filled with silica powder (220 pbw), which is used as electrical insulation in high-voltage switchgear. Thermally cured

sheet samples of 1 mm in thickness with this formulation were supplied by Hazemeyer-Holec Australia Pty Ltd. The other formulation is 100 pbw cycloaliphatic epoxy (Ciba-Geigy CY184) filled with 300 pbw silica powder and cured by 90 pbw hexahydrophthalic anhydride (Ciba-Geigy HT907). This formulation is used as electrical insulation in high-voltage instrument transformers.

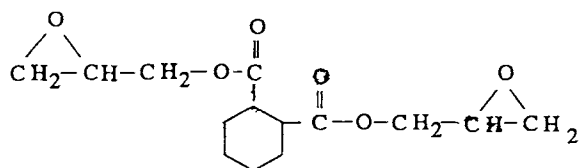
The silica filler was used in both of the formulations to simulate the real macrostructure of the materials used in the applications, where silica is used to serve several purposes including minimizing the shrinkage during curing, improving mechanical properties, and reducing the cost of the material. The median particle size of the silica powder used is determined as 2.3  $\mu\text{m}$  by a Horiba CAPA-700 particle analyzer.

The bisphenol-A epoxy and the cycloaliphatic epoxy used have the following structures, respectively:



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and



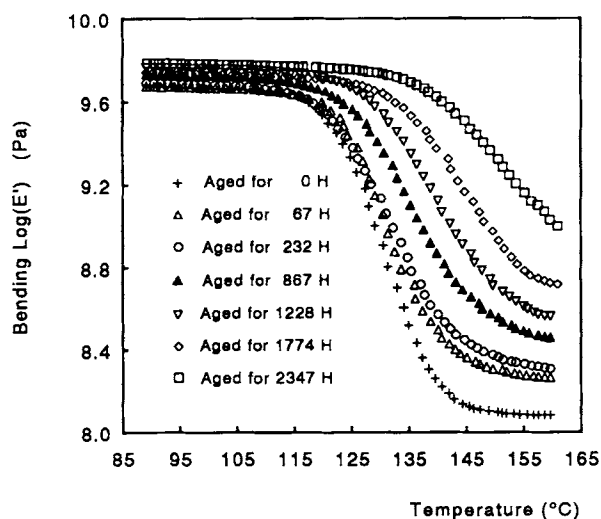
Composite sheets of about 1 mm in thickness were vacuum-cast and thermally cured. The cast sheets were then cut into small rectangular shapes suitable for the DMTA test. Dimensions of the cut rectangular specimens are  $25 \times 8 \times 1$  mm.

## 2. Thermal Degradation

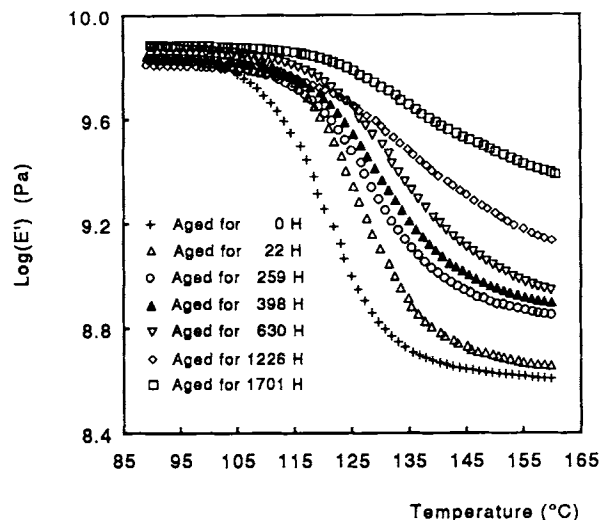
Thirty rectangular specimens of each type of epoxy were aged in a forced-convection oven set at  $160^\circ\text{C}$ . Three specimens for each type of epoxy were taken out of the oven intermittently. Then, the specimens with a certain period of thermal degradation were measured on DMTA. The mass loss of the specimens was measured with a balance having a resolution of 0.0001 g as an additional monitor of the degree of thermal degradation.

## 3. DMTA Test Method

A Polymer Laboratory Ltd. dynamic mechanical thermal analyzer (PL-DMTA) was used. The system consists of the dynamic mechanical analyzer, the temperature controller, the driving head with a controlled temperature environment, and a Compaq



**Figure 1**  $E'$  relaxations of bisphenol-A epoxy composites with different lengths of aging time.



**Figure 2**  $E'$  relaxations of cycloaliphatic epoxy composites with different lengths of aging time.

80386 computer that serves to control the measurement, to collect the real-time data, and to carry out the data analysis.

Three test modes are available with the PL-DMTA. The bending test mode with a single cantilever clamping style was used due to relatively high rigidity of the materials being investigated. All specimens were measured with 2 Hz bending frequency in the temperature range of  $30$ – $160^\circ\text{C}$ . The temperature ramping rate was  $2^\circ\text{C}/\text{min}$ .

## RESULTS

The behavior of the dynamic storage modulus ( $E'$ ) in the glass transition range with differing amounts of degradation is shown in Figure 1 for bisphenol-A epoxy and in Figure 2 for cycloaliphatic epoxy. There is an obvious trend of the increased rubbery state  $E'$  with increased time of thermal aging for both types of epoxies. This trend is quantitatively illustrated in Figure 3, which shows monotonic changes of  $E'$  at  $160^\circ\text{C}$  (which is above  $T_g$ ) with increased aging time.  $E'$  below  $T_g$  appears quite scattered with an increasing amount of degradation, but a general trend of increase with aging time, which is shown in Figure 4, is still observable.

Dynamic damping behavior, represented by loss factor ( $\tan\delta$ ), in the glass transition range with different aging time is shown in Figure 5 for bisphenol-A epoxy and in Figure 6 for cycloaliphatic epoxy. An obvious decrease in the peak value of the loss factor and a shift of  $T_g$  to higher temperatures

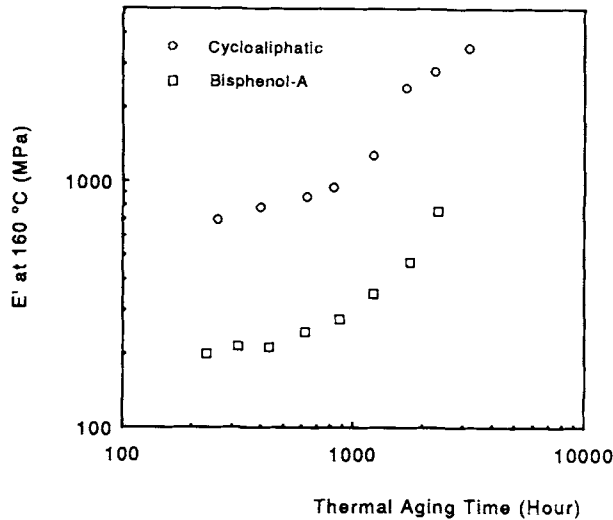


Figure 3 Change of  $E'$  above  $T_g$  with aging time.

with increased aging can be observed. These trends are shown quantitatively in Figures 7 and 8. Figure 9 shows the percentage loss of mass over the aging time for the two types of epoxy composites.

DISCUSSION

It can be seen that several DMTA parameters are sensitive to structural changes caused by thermal degradation. For instance,  $E'$  above  $T_g$  experienced an approximately 300% increase for both types of epoxies during 2000 h of aging. The possible causes for these observed changes in dynamic mechanical properties are discussed, based on some of the theo-

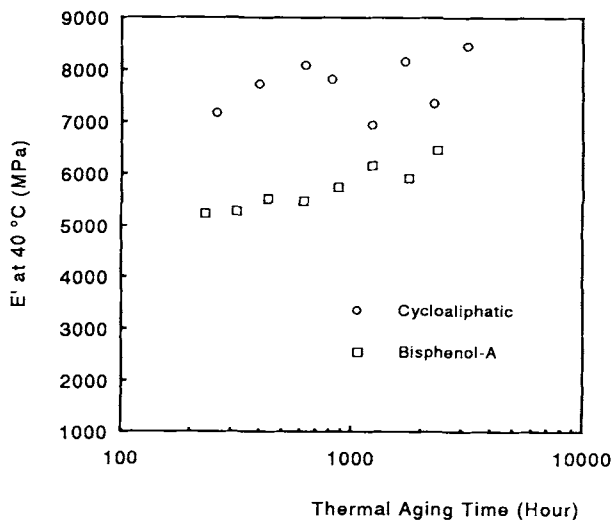


Figure 4 Change of  $E'$  below  $T_g$  with aging time.

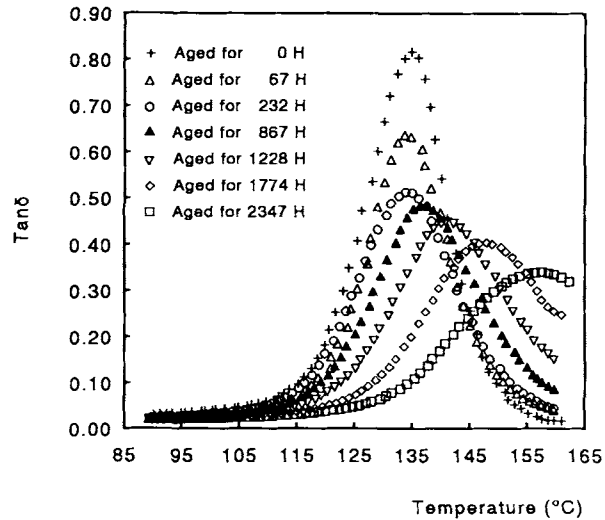


Figure 5  $Tan\delta$  relaxations of bisphenol-A epoxy composites with different lengths of aging time.

retical relationships previously obtained from studies of epoxy curing processes by other researchers.

Previous work<sup>4,5</sup> has shown that  $E'$  above  $T_g$  varies with the cross-link density of a thermosetting material with the following relationship:

$$E'_r = \frac{3\phi dRT}{M_c} \tag{1}$$

If the effect of dangling is neglected, then

$$M_c = d/\alpha \tag{2}$$

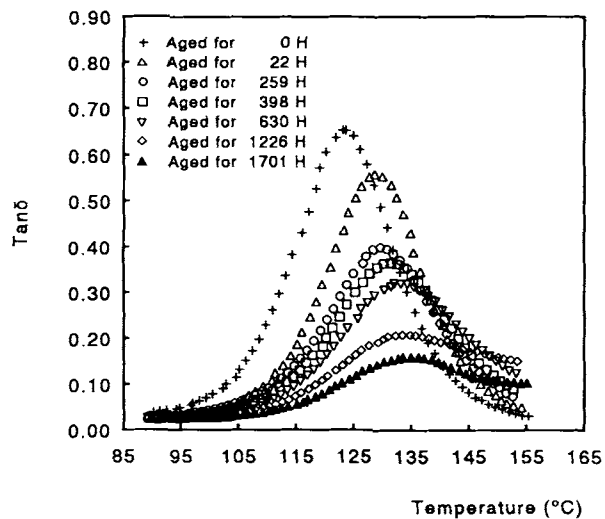


Figure 6  $Tan\delta$  relaxations of cycloaliphatic epoxy composites with different lengths of aging time.

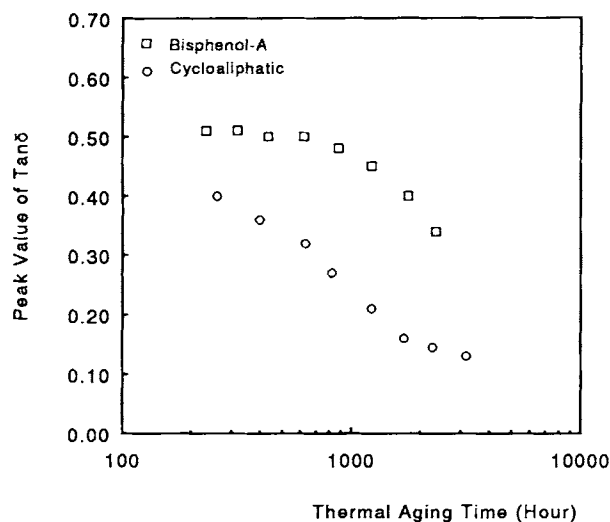


Figure 7 Decrease of  $\tan\delta$  peak value with aging time.

Thus, eq. (1) changes to

$$E'_r = 3\phi\alpha RT \quad (3)$$

where  $E'_r$  is the elastic modulus in the rubbery state;  $d$ , the density;  $R$ , the gas constant;  $T$ , the temperature in K;  $M_c$ , the molecular weight between cross-links;  $\alpha$ , the cross-link density; and  $\phi$ , the front factor. The value of  $\phi$  is close to unity.

Equation (3) shows that  $E'_r$  is directly proportional to the cross-link density. In other words, the increase of cross-link density will cause an increase in  $E'_r$ .

The relationships between  $T_g$  and  $\alpha$  have also been studied in a number of papers. Takashi proved

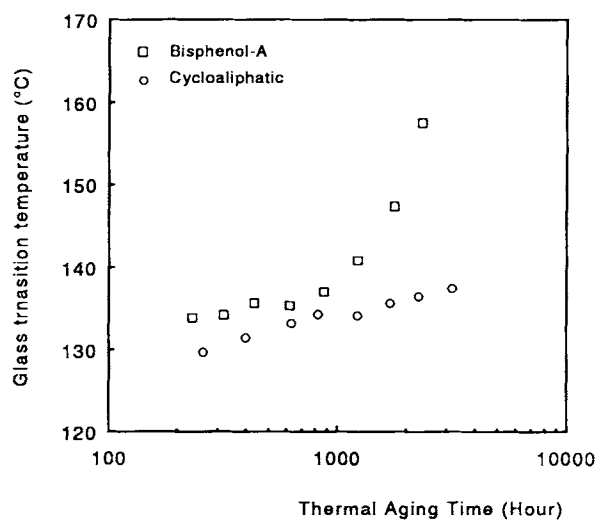


Figure 8 Increase of  $T_g$  with aging time.

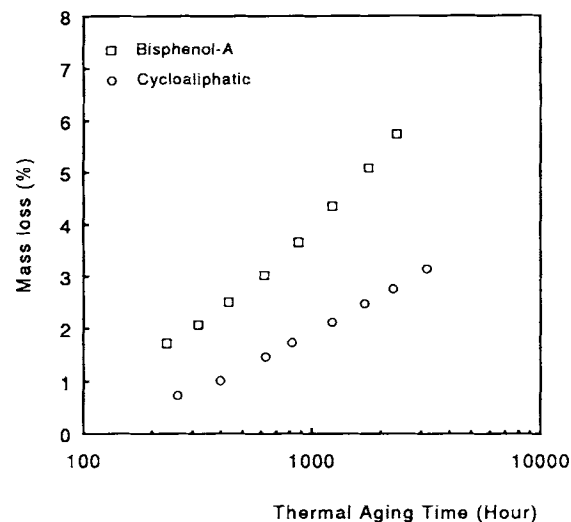


Figure 9 Mass loss with thermal aging time.

Eq. (4) was applicable to many types of cured epoxy resins<sup>6</sup>:

$$T_g = K_1 \log K_2 \alpha \quad (4)$$

Here,  $K_1$  and  $K_2$  are constants for the same groups of resins. This relationship also predicts an increase in  $T_g$  if cross-link density is increased.

Although the relationships of (3) and (4) were drawn from studying the effect of different curing processes on the cross-link density, it is valid to assume that they can also be used to describe the relationships between  $E'_r$ ,  $T_g$ , and  $\alpha$  in cured resins with different amounts of thermal degradation. Therefore, we can argue that the increased  $E'$  in the rubbery state and  $T_g$  (Figs. 3 and 8) during the thermal degradation must result from an increased cross-link density because the other parameters in eqs. (3) and (4) should remain unchanged. However, in our experiment, all the specimens were postcured before the start of thermal aging and no exothermal peaks were detected on DSC in the temperature range up to 250°C. This means that the speed of the further cross-linking during the degradation stage could be several orders slower than that during the resin curing stage.

The other main degradation process was the loss of mass (Fig. 9). The decreasing peak value of  $\tan\delta$  (Figs. 5-7) seems to support the point that the lost part was mainly the dangling chains in the cross-linked network since losing dangling chains would generally make the material less viscous and thus produce less energy loss in the transition region. The general trend of increasing  $E'$  in the glassy state, as

shown in Figure 4, also supports this point. It has been shown that  $E'_g$  (storage modulus in the glassy state) is proportional to the cohesive energy density  $\delta^2$  of the system.<sup>6</sup> Losing dangling chains can subsequently increase  $\delta^2$  of the system and, thus,  $E'_g$ , whereas scissioning of the cross-linked main chains would cause a lower  $\delta^2$  and lower  $E'_g$ .

## CONCLUSION

A number of DMTA parameters, such as  $E'$  in the rubbery state, peak value of  $\tan \delta$ , and  $T_g$ , are very sensitive to the structural changes experienced by the epoxies during the thermal degradation, and structural changes such as further cross-linking and loss of dangling chains in the cross-linked network can be identified by the DMTA method.

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