

USING DYNAMIC MECHANICAL ANALYSES TO PROBE THE GLASSY STATE RESPONSE OF A *Sub-T_g* ANNEALED MODEL EPOXY NETWORK¹

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Abstract

Using dynamic mechanical analyzers the relaxation behavior of a loosely cross-linked model epoxy resin was investigated before and after room temperature aging. Preliminary results indicate a stiffening of the storage moduli occurs below $-50\text{ }^{\circ}\text{C}$, the β relaxation temperature of the epoxy network, with a subsequent softening of the network above room temperature and a drop in the apparent glass transition temperature (T_g) of the material with aging.

Introduction

Research on the physical aging of glassy polymers began with the discovery by Kovacs [1] that the volume of the polyvinyl acetate (PVAC) system slowly decreased (densified) with time, when rapidly quenched from above its glass transition temperature (T_g). This research area expanded to include most engineering resins when the 1961 results of Peilstocker [2,3] on molded polycarbonate (PC) were linked to physical aging [4]. He observed that PC, whose molecular structure is based on bisphenol-A (see Figure 1), becomes brittle after engineering parts are held $12\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$ below its T_g ($142\text{ }^{\circ}\text{C}$). This embrittlement was associated with the rearrangement of existing ordered regions in the PC polymer during the aging process.

Research on bisphenol-A epoxy resins composed of the diglycidyl ether of bisphenol-A (DGEBA) monomer have been mixed with respect to the physical aging of the polymer network when subjected to sub- T_g annealing. For example, the strain-to-failure of the network formed by curing DGEBA with nadic methyl anhydride (NMA) and the catalyst benzyldimethylamine (BDMA) decreases from 12 % to 6 % after 56 days at $23\text{ }^{\circ}\text{C}$ [5]. Physical aging has also been observed in amine cured epoxy resin systems and in an uncross-linked 28,000 g/mol linear epoxy resin tested under wet conditions [6]. In contrast, DGEBA homo-polymerized with piperidine (subsequently

designated as DGEBA-H_p), has been found to be independent of the imposed thermal histories [7] when analyzed under dynamic mechanical stimuli. Interestingly, the latter epoxy network system has been reported to be approximately thermo-rheologically simple [8].

Although the physical aging phenomenon is often characterized by enthalpy changes associated with the time dependent volume change [9], it is also of interest to understand how the structure of individual polymer's network influence physical aging and the impact these subtle changes may have on their engineering properties. Since the recoverable structural changes due to the aging process may be associated with localized ordering that influences the glassy state molecular motions of the polymer, dynamic mechanical analyzers (DMAs) were chosen as the primary measurement devices for detecting and quantifying any changes in molecular mobility.

For these techniques to be most effective, the molecular architecture of the polymer network must be controlled in a manner that allows its systematic manipulation. To this end, this investigation involves the use of an amine cured epoxy resin whose cross-link density is altered by controlling the relative molecular mass of the DGEBA oligomer. Therefore, thermoset resins with different cross-link densities were made with a DGEBA monomer (mass average relative molecular mass = 340 g/mol, i.e., $n=0$ in Figure 1) and a DGEBA oligomer whose relative average molecular mass is 6,300 g/mol (average $n = 24.6$ in Figure 1).

Citing only a few examples, previous epoxy research on physical aging, with the exception of the research conducted by Plazek and Choy [10,11], have altered the relative molecular mass of the curing agent [6,12] and the curing agent stoichiometry [13] to effect changes in the cross-link density. Although these systems are industry relevant, the mass and flexibility of the curing agent may have a pronounced impact of relaxation behavior of the epoxy network. In addition, off-stoichiometric epoxy systems may contribute to the presence of dangling ends in the cured network. Therefore, the molecular structure of these types of systems could obscure any effects the DGEBA repeat unit may have on the aging rate and its

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impact on mechanical property changes in bisphenol-A based polymers. In this study, the choice of the 6,300 g/mol DGEBA oligomer may also provide some insight into how the carbonyl (CO) linkage between bisphenol-A units in PC influences the physical aging process since the CO linkage is replaced with a $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2$ linkage in the DGEBA oligomer (see Figure 1).

Experimental

The procedure for preparing the 6,300 g/mol DGEBA oligomer and the curing conditions for the DGEBA epoxy resins cross-linked with 4,4'-diaminodiphenyl sulfone (DADPS) have been described previously [14]. An important aspect of this preparation procedure relative to earlier DGEBA/DADPS systems [10,11] is that the laboratory preparation of the 6,300 g/mol advanced resin allowed the functionality to be maintained at 2. The resin was also cured with a slight excess of amine curing agent to further minimize the presence of dangling ends in the cured network. Also, the network formed from the 6,300 g/mol advanced resin has an increased possibility of trapped entanglements in the cured network since the highest relative molecular mass DGEBA oligomer investigated by Plazek and Choy had an oligomer functionality of only 1.4 and a 2,600 g/mol relative molecular mass.

In this paper, the term loosely cross-linked network will be used to denote the network formed by the reaction of the 6,300 g/mol advanced resin with DADPS. This resins was also tested after allowing the sample to age at room temperature for 90 d. The term tightly cross-linked network will be used for the epoxy resin formed by the reaction of the DGEBA monomer with DADPS.

Analyses were performed on a DMA equipped with force rebalancing transducers and liquid nitrogen (LN_2) dewars capable of controlling the oven temperature below and above room temperature. Frequency-temperature sweeps were performed on the test specimens. Data was taken at 10 points per decade over a frequency range of 0.1 rad/s to 100 rad/s. To ensure optimal overlap during the construction of the master curves, the -150°C to 280°C temperature range was covered using 4°C temperature steps and a 2 min initial soak time after each temperature step.

Data Reductions

Master curves were generated from the dynamic mechanical data by employing only horizontal shifts to the $\tan \delta$ data. After these shifts were obtained, vertical shift factors were then employed to the storage modulus, G' , data. The best superposition was obtained in the glassy

and T_g regions where localized and long-term relaxation behaviors, respectively, are expected to dominate [15].

Two methodologies were used to determine the activation energies in the glassy region, since the apparent activation energy for viscoelastic relaxation is formally calculated by the following equation:

$$\Delta H_a = R \frac{d \ln a_T}{d(1/T)} \quad (1)$$

In the first method, the average activation energy, $\langle \Delta H_a \rangle$, of the β relaxation was calculated. Since the shift factors, a_T , for the glassy region relaxations (i.e., β , γ , etc.) are usually described by the Arrhenius form, $\langle \Delta H_a \rangle$ was calculated from equation 2 by using a_T values in a $\pm 30^\circ\text{C}$ window about the -50°C reference temperature, T_{ref} , for the β relaxation.

$$\ln(a_T) = \frac{\langle \Delta H_a \rangle}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \quad (2)$$

Observing that ΔH_a can also be determined, independent of a model, by taking the first derivative of a plot of the $\ln(a_T)$ versus $1/T$, a C2-cubic spline was fit to the data to obtain the variation of the apparent activation energies for viscoelastic relaxations with temperature.

Finally, the viscoelastic parameters at T_g were obtained from the DMA data using the *modified* Williams, Landel, and Ferry (W-L-F) equation integrated with the single parameter ordering model that includes the standard assumption that the fractional free volume, $f(T)$, increases linearly with temperature [16,17].

$$f(T) = f(T_g) + \alpha_f (T - T_g) + \delta \quad (3)$$

where $f(T_g)$ is the fractional free volume at T_g , α_f has the dimensions of a thermal expansion coefficient and δ is the dimensionless variable that can be obtained from the Kovacs, Aklonis, Hutchinson, and Ramos (KAHR) multi-parameter model [18] by assuming a single ordering parameter. The concept of a single ordering parameter, δ , being used to describe the volume departure from equilibrium is based on the research of Tool [19,20] and Davies and Jones [21] and is expressed as

$$\delta = \frac{(v - v_{\infty})}{v_{\infty}} \quad (4)$$

where v is the instantaneous specific volume and v_{∞} is the equilibrium value of the specific volume at the temperature and pressure. Therefore, the *modified* W-L-F equation used in this paper has the following form:

$$\ln(a_T) = \frac{-C_1[(T - T_g) + C_3]}{(T - T_g + C_2 + C_3)} \quad (5)$$

where

$$C_1 = B/f_g$$

$$C_2 = f_g/\alpha_f$$

$$C_3\{\delta, T\} = \delta\{t, T\}/\alpha_f$$

In the above expressions t denotes time and $X\{*\}$ indicates that the variable X is a function of the variables included in the brackets. It should be noted that Kovacs et al. [17,18], McKenna [22] and others [16,23] have noted the limitations of the above expression in studying physical aging phenomena.

By using the universal constants for C_1 and C_2 (i.e., $C_1^g = 17.44$ and $C_2^g = 51.6$), the expected values of $f(T_g)$ and α_f for many polymers were found to be 0.025 and $4.8 \times 10^{-4} \text{ deg}^{-1}$, respectively [15]. For the DGEBA epoxy resins investigated here, the constants C_1 and C_2 were determined by fitting the conventional W-L-F equation (i.e., $C_3 = 0$ in equation 5) to T_g and above data, while $C_3\{\delta, T\}$ was obtained by fitting equation 5 to the data below T_g .

Results and Discussions

To facilitate inter-comparisons and comparisons with previous data, the G' and G'' DMA responses versus temperature of the un-aged and aged loosely cross-linked networks and the un-aged tightly cross-linked network are shown in Figure 2 and Figure 3 at 6.308 rad/s (≈ 1 Hz). In Figure 2, the aged loosely cross-linked network G' moduli are stiffer than the un-aged specimen in the temperature region below -50 °C., while between -50 °C and room temperature the G' moduli are comparable. Surprisingly,

above room temperature the aged specimen softens by approximately 5 % relative to the un-aged specimen to a value that is comparable to the un-aged tightly cross-linked network (see insert A in Figure 2). Furthermore, there is an apparent (4 to 5) °C reduction in the T_g of the aged specimen (see Figure 3) without a corresponding change visually in the cross-link density of the loosely cross-linked network (see insert B in Figure 2). Mathematically the G' moduli in the rubbery plateau region indicate that the difference between the G' of the un-aged and aged samples is much less than 1 %.

The reproducibility in the rubbery plateau region suggests that the 5 % reduction in G' observed in the aged sample above room temperature is real. Furthermore, to maintain continuity of the data, each test segment was restarted to retrace the last (10 to 15) °C from the previous test segment. In insert A of Figure 2 the effect is shown of this retracing on the G' moduli as T_g is approached. The retraced G' for both loosely cross-linked systems are slightly higher, while those of the tightly cross-linked system were lower. This suggests that in the loosely cross-linked networks, the de-aging process that occurs as T_g is approached stiffens G' . These results are consistent with the observed softening between room temperature and T_g of the aged loosely cross-linked network relative to the un-aged network.

The apparent reduction in the T_g (also known as the α relaxation) with aging in the loosely cross-linked network is accompanied by the disappearance of the γ relaxation that occurs at -128 °C in the un-aged network and a slight increase in the peak maximum of the β relaxation of the aged network that exhibits a consistent -73 °C peak maximum in both specimens (see Figure 3). From thermally stimulated depolarization (TSD) studies on the diglycidyl ether of butanediol (DGEB) cured with ethylenediamine (EDA) and uncured DGEBA, the γ relaxation has been attributed to the motion of the ether linkage and its neighboring segments, while the β relaxation has been ascribed to the cured network segment denoted by $R_2NCH_2CH(OH)CH_2O$ [24]. The γ relaxation is also depressed in the un-aged tightly cross-linked specimen, with the β and α relaxations in this network occurring at -56 °C and 217 °C, respectively. Using the nomenclature adopted by Keenan et al. [25], the peak at 39 °C in the G'' relaxation versus temperature trace of the tightly cross-linked network (see Figure 3) has been labeled an ω relaxation. The presence of this peak centered around 100 °C in the tetraglycidyl-4,4'-diaminodiphenylmethane epoxy (TGDDM) cured with

DADPS has been ascribed to unreacted molecular segments and/or inhomogeneities in the sample arising from dissimilar cross-linking resins [25,26]. However, in this study the absence of this peak in the loosely cross-linked network suggests that the ω relaxation may be associated with movement of the DGEBA/DADPS cross-links.

Motivated by the differences observed in the DMA data of the un-aged and aged loosely cross-linked specimens, master curves for the systems under study were constructed. The $\tan \delta$ of the un-aged loosely cross-linked epoxy resin in the T_g and β relaxation regions are shown in Figure 4 and Figure 5, respectively. The peak values in the T_g region decrease as the temperature is increased from 116 °C to 129 °C. Similar behavior was observed in the aged loosely cross-linked epoxy resin and the tightly cross-linked epoxy resin (not shown). These results are consistent with results of Cavaille et al. [26,27] on atactic polystyrene and DGEBA epoxy resin cured with 4,4' diaminodiphenylmethane (DDM). Plazek [28] cited the polystyrene research as evidence that polystyrene's rheological behavior is thermo-rheologically complex.

For polystyrene near T_g , Cavaille et al. surmised that the predominant change that contributes to this polymer's thermo-rheological complex behavior is an increase in the segmental correlation length that also involves regions of entanglements. These changes lower the contribution to the modulus (between rubbery-plateau and glass regions), so that the time-temperature superposition is vitiated. In the case of the DGEBA/DDM epoxy resin, they concluded that the predominant effect of increasing the temperature is the change in the temperature dependence of relaxation times of correlated motions of chain segments and/or an increase in the segmental correlation length involving regions of cross-linking in the epoxy resin that vitiates time-temperature superposition. Plazek chose to associate this type of non-reproducibility with polymers that have a relatively high steepness factor [29].

From the earlier quoted observations that DGEBA- H_p is approximately thermo-rheologically simple and noting that DGEBA- H_p networks formally contains no hydroxyl groups, it is possible that the reduction of the $\tan \delta$ peak with increasing temperature in the amine cured DGEBA epoxy networks may be associated, at least partially, with the hydroxyl-hydroxyl hydrogen bond interactions that exists in the epoxy resin network. Consistent with this interpretation, Schwarzl and Staverman [30] suggest from a chemical point of view that thermo-rheological simple behavior in non-crystalline polymers should only be expected for polymers that do not contain strong polar groups, since both the changes of crystalline structure and

of interaction of polar groups depend on temperature in a way different from that of the viscosities of flow in the amorphous, nonpolar parts of the material.

To make the comparison between the un-aged and aged samples in the β relaxation region of the loosely cross-linked resin system, only horizontal shifts were made to the frequency-temperature data, with optimization of the overlap in $\tan \delta$ being the basis for master curve generation. In contrast to the DMA results published on DGEBA- H_p , thermo-rheological complex behavior is clearly evident in the β relaxation region, with overlap between the temperature isotherms occurring only at the higher frequencies. With the peak maxima locations remaining constant for both samples, the up-turns observed in the $\tan \delta$ data of the un-aged loosely cross-linked network at the low frequencies of each temperature isotherm are absent in the aged specimen. In both specimens, however, the peak maximum in this region decreases with decreasing temperature, indicating more rigidity and less energy dissipation as the temperature is decreased. It should be noted that this contrast the behavior observed in the T_g region.

Being careful to use the same procedure to shift the temperature isotherms in both specimens, apparent activation energies, $\langle \Delta H_a \rangle$, in the β relaxation region were found for the un-aged and aged specimens, with the values being (39.5 ± 1.4) Kcal/mol and (42.3 ± 1.4) Kcal/mol, respectively. The "±" represents one standard deviation about the mean value and is taken as an estimate of the standard uncertainty. The correlation for each fit was greater than 0.997. These activation energies are 2 to 3 times the 15 Kcal/mol value observed in the DGEBA- H_p epoxy network [7]. At 1 rad/s the T_g of the DGEBA- H_p epoxy network is about 93 °C, while that of the loosely cross-linked DGEBA/DADPS network is about 120 °C. Since the β relaxation in both epoxy networks are at least 140 °C below their respective glass transition temperatures, the difference in the $\langle \Delta H_a \rangle$ at -50 °C, where both networks have β relaxations, may again be associated with the restriction of molecular motion by the hydrogen bonded hydroxyl groups in the network.

The separation of 2 standard deviations between the un-aged and aged samples suggests that the difference between these two values may be significant. Using the C2-cubic spline method, the change in the apparent activation energy with temperature was calculated for the two specimens in the β and T_g relaxation regions.

These plots are shown in Figure 7 and Figure 8, respectively.

In Figure 7 a small peak centered at $-50\text{ }^{\circ}\text{C}$, the peak maximum of the β relaxation region, emerges in the aged sample that is not present in the un-aged sample. The peak maximum is approximately 10 Kcal/mol higher than the background level in the un-aged sample. Similar analyses on the un-aged tightly cross-linked sample indicate that this peak is also absent.

Furthermore, analyses of the un-aged and aged loosely cross-linked epoxy resins in the T_g region (see Figure 8) indicate that the peak activation energies for the two specimens (178 Kcal/mol and 174 Kcal/mol, respectively) are approximately equal. This result is consistent with the aging effect being erased as T_g is approached, since the frequency sweep from 0.1 rad/s to 100 rad/s at each temperature takes approximately 20 min.

Using creep data Plazek and Ngai [29] reported a value of 269 Kcal/mol for the apparent activation energy for the T_g relaxation of a 1450 g/mol DGEBA oligomer cross-linked with DADPS. Differences in oligomer functionality, molecular weight, cure conditions, and testing method may be the cause of the much lower values obtained in this report. For completeness, the apparent activation energy for the tightly cross-linked epoxy resin (DGEBA = 340 g/mol) investigated in this report is 249 Kcal/mol. Finally, the emergence of the peak at $-50\text{ }^{\circ}\text{C}$ has been interpreted as occurring from localized changes in the network structure that restrict molecular motion, with the working hypothesis for this restricted mobility being due to hydrogen bonding between the network chains.

Preliminary calculations of the ordering parameter, δ , which quantifies the volume departure from equilibrium, indicate, as expected, that δ decreases uniformly as T_g is approached. However, there appears to be a discrepancy in the expected magnitude of the fractional free volume at T_g , $f(T_g)$, and the difference between the glass and rubbery thermal expansion coefficients, α_f , obtained from using the DMA shift factors in equation 5, with initial values of 0.07 and 0.003 deg^{-1} being obtained. The value of $f(T_g)$, although higher than the values obtained by Kitoh and Suzuki [31] on related DGEBA amine systems (≈ 0.02), has the correct magnitude. However, the value of α_f obtained from the DMA data appears to be too high

by an order of magnitude, with Kitoh and Suzuki using stress relaxation data and Plazek and Choy [11] using creep data to obtain values of approximately 0.0003. Interestingly, calculations performed by Gerard et al. [32] from DMA data on DGEBA cured with 4,4'-diaminodiphenylmethane (DDM) are consistent with the values $f(T_g)$ and α_f obtained in this research, with the values from their research being 0.04 and 0.001, respectively, if the B constant in equation 5 is taken to be 1. The source of this discrepancy is being investigated.

Conclusions

DMA analyses of the aged loosely cross-linked DGEBA/DADPS network indicates a stiffening of the G' in the region below $-50\text{ }^{\circ}\text{C}$, the β relaxation, and a softening of this same modulus above room temperature as T_g is approached, with a concurrent (4 to 5) $^{\circ}\text{C}$ decrease in the T_g of the aged specimen. Although these results are intriguing, two distinct samples from the same plaque were analyzed. Therefore, it is possible that the differences observed here are associated with the non-uniform curing of the plaque. To further explore the phenomena observed in this report, future research will focus on using the same specimen in its aged and un-aged states to obtain the DMA data. As previously stated the apparent discrepancy in the T_g viscoelastic parameters derived from DMA data relative to those from stress relaxation and creep data is being investigated further.

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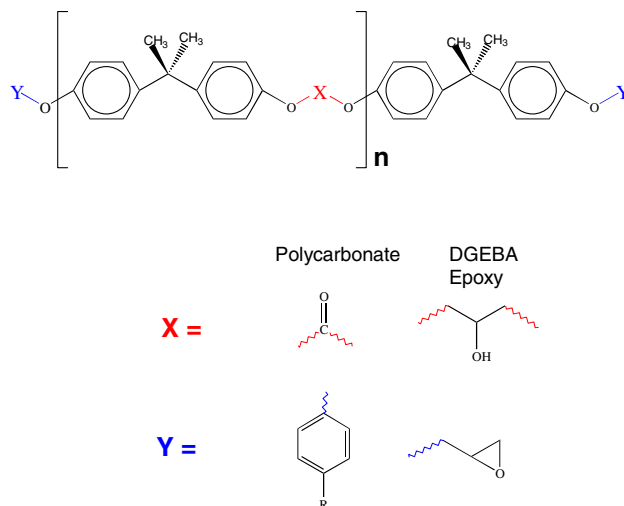


Figure 1. Oligomeric Structure of Polycarbonate (PC) and Diglycidyl Ether of Bisphenol-A (DGEBA)

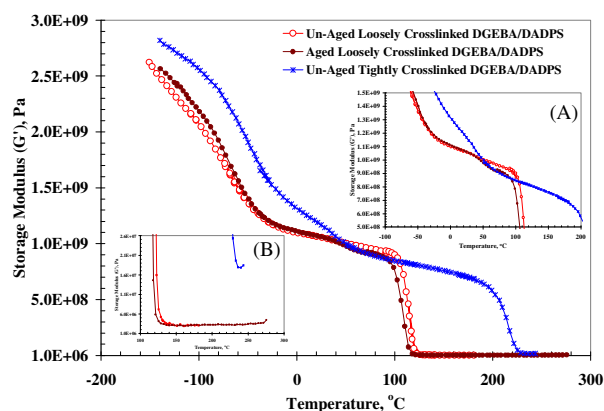


Figure 2. Storage Moduli (G') of model epoxy networks at 6.308 rad/s. Insert (A) shows the change in behavior from the glassy region to the glass transition region. Insert (B) shows the rubbery plateau region. (note: A linear G' scale is used to more clearly show differences).

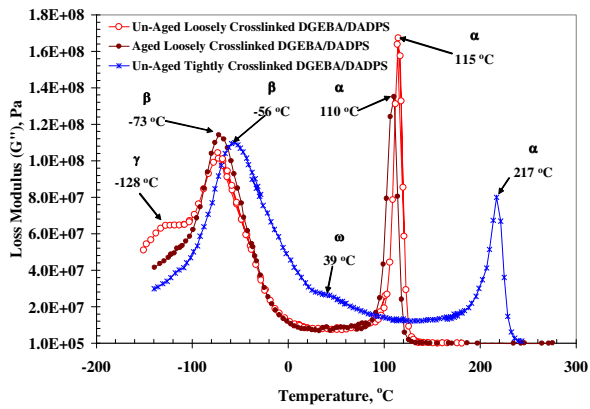


Figure 3. Loss Moduli (G'') of model epoxy networks at 6.308 rad/s. Relaxation peaks are labeled following the convention of Ochi et al. [1]. (note: A linear G'' scale is used to more clearly show differences).

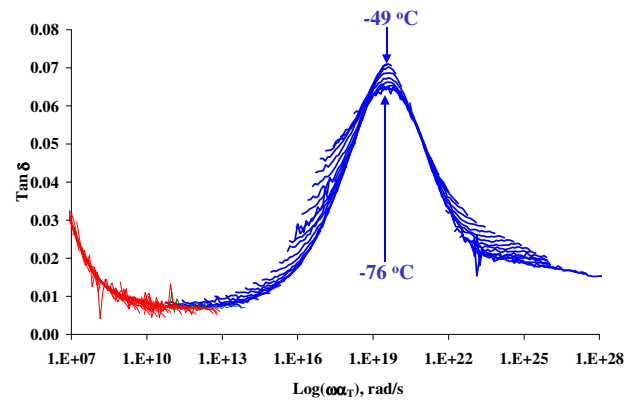


Figure 6. $\text{Tan } \delta$ Master Curve in β region of Aged Loosely Cross-linked DGEBA/DADPS Epoxy Resin.

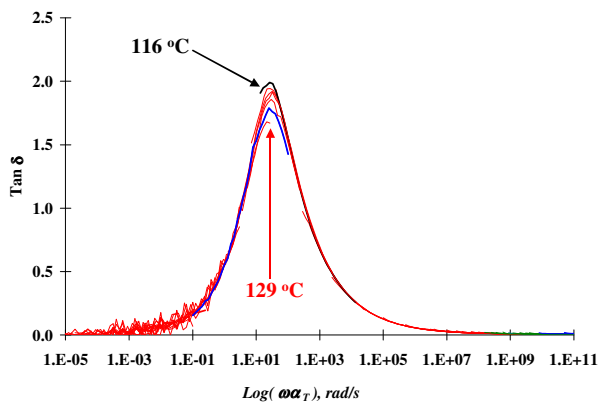


Figure 4. $\text{Tan } \delta$ Master Curve in T_g region of Un-aged Loosely Cross-linked DGEBA/DADPS Epoxy Resin.

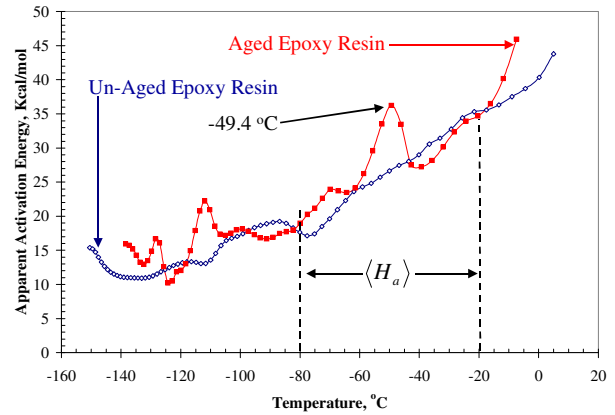


Figure 7. Apparent activation energies vs. temperature in glassy region of Un-aged and Aged Loosely Cross-linked DGEBA/DADPS Epoxy Resins.

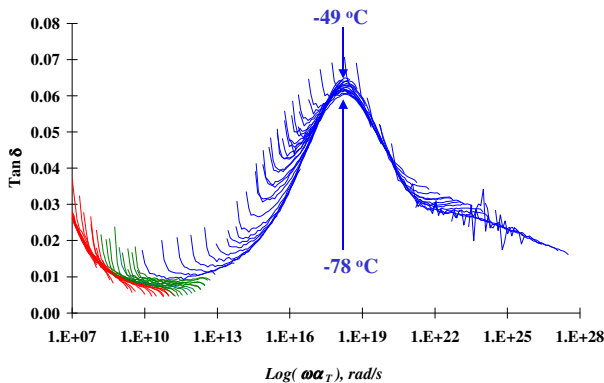


Figure 5. $\text{Tan } \delta$ Master Curve in β region of Un-aged Loosely Cross-linked DGEBA/DADPS Epoxy Resin.

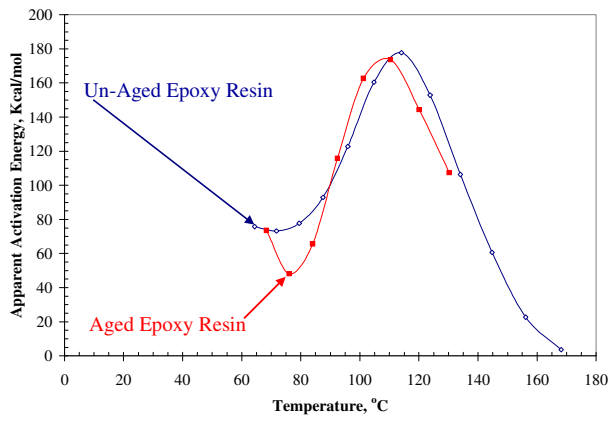


Figure 8. Apparent activation energies vs. temperature in T_g region of Un-aged and Aged Loosely Crosslinked DGEBA/DADPS Epoxy Resins.

Key Words: Physical Aging, Epoxy, Dynamic Mechanical Analysis, Master Curve.