

# Glass-Transition Temperature–Conversion Relationship for an Epoxy–Hexahydro-4-methylphthalic Anhydride System

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**ABSTRACT:** The DGEBA–MHHPA epoxy system has found increasing applications in microelectronics packaging, making crucial the ability to understand and model the cure kinetics mechanism accurately. The present article reports on work done to elucidate an appropriate model, modified from the empirical DiBenedetto's equation, to relate the glass-transition temperature ( $T_g$ ) to the degree of conversion for a DGEBA–MHHPA epoxy system. This model employs the ratio of segmental mobility for crosslinked and uncrosslinked polymers,  $\lambda$ , to fit the model curve to the data obtained. A higher ratio value was shown to indicate a more consistent rate of increase of  $T_g$  in relation to the degree of conversion, while a lower value indicated that the rate of  $T_g$  increase was disproportionately higher at higher degrees of conversion. The best fit value of  $\lambda$  determined by regression analysis for the DGEBA–MHHPA epoxy system was 0.64, which appeared to be higher than for those previously obtained for other epoxy systems, which ranged from 0.43–0.58. The highest  $T_g$  value obtained experimentally,  $T_{g\text{ max}}$ , was 146°C, which is significantly below the derived theoretical maximum  $T_{g\infty}$  value of 170. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 511–516, 2000

**Key words:** glass transition; conversion; theoretical maximum glass-transition temperature

## INTRODUCTION

Interest in the low-viscosity, highly transparent, and excellent electrical insulation epoxy DGEBA–MHHPA system has received increasing attention because of its application in the microelectronics industries, such as for use in high-grade LEDs, IC die encapsulation, conductive ink paste, and adhesives, as well as in structural components using resin transfer molding techniques. From an application standpoint, the effective use of any thermosetting system requires the ability to predict the cure kinetics of the system,<sup>1,2</sup> to precisely locate the sol–gel transition in order to form and process the polymer,<sup>3</sup> and to maximize

the glass-transition temperature ( $T_g$ ) for the system. Physically,  $T_g$  is the temperature of transition between a glassy state and a liquid or rubbery state. Because of the dramatic change in the physical properties of the polymer at this transition,  $T_g$  is an important material parameter in a polymer application because it becomes the upper bound for the service temperature of a noncrystallizable amorphous material.<sup>4</sup> This is simply the result of the considerable drop in the bulk resin modulus once the material transforms from a glassy to a rubbery phase when it reaches  $T_g$ . Although a higher  $T_g$  is always desirable, there is of course a limiting maximum value of  $T_g$  for each thermosetting system used. Not optimally achieving this limiting maximum value in applications is often a concern. As such, a main objective in the curing of thermosetting polymers is knowing the maximum possible value to which the glass-tran-

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sition temperature can be increased, as well as knowing the curing profile that enables that value to be achieved.

Although generally the  $T_g$  increases with an increase in the degree of conversion, its relationship is not necessarily linear. As the cure process begins, the resin, comprising a mixture of monomers or oligomers sometimes dissolved in solvents, begins to form end-to-end linear chain extensions, followed by side-to-side chain crosslinking. Initially, the extension process dominates, effectively making the resin a thermoplastic material, with the material transforming from a liquid to a soft solid. This is usually the stage suitable for production of prepregs since the resin can exhibit flow during shaping or molding. Further heating will result in chain crosslinking dominating the reaction, ending up with a fully hardened thermosetting material. This reaction is typically associated with a significant shrinkage because the molecular chains are being pulled closer together by the crosslinks. As the degree of conversion increases, the network of crosslinked molecules also increases. This may subsequently impede the ability of molecules to further increase crosslink density, which means in effect that further increase in  $T_g$  value will also be impeded. Depending on the segmental mobility of the molecules through the crosslinked network and the segmental mobility of the molecules through the uncrosslinked network, further increases in the  $T_g$  value may or may not be significant as the conversion reaches its maximum. The reaction rate typically depends on the difference between the  $T_g$  at that time and the temperature of crosslinking. Molecular motion is significantly decreased, together with the rate of reaction, when the difference becomes very small. Once the  $T_g$  exceeds the crosslinking temperature, that is, vitrification occurs, the reaction substantially decelerates and consequently slows down the increase of the glass-transition temperature. The possibility thus exists that crosslinking at a temperature lower than the theoretical maximum glass-transition temperature would result in a final  $T_g$  lower than the theoretical maximum value. The possibility also exists that chemical degradation resulting from overheating could in effect act as an upper limit to the curing temperature that is to be set. At each stage of crosslinking the thermal degradation of the resin changes as the molecular weight and the amount of crosslinks increase. Obviously then, an isothermal approach to the crosslinking process would not be optimal. Incremental nonisothermal crosslinking profiles

would be more appropriate.<sup>5</sup> The efficient prediction of the  $T_g$  would thus require a model that is independent of the cure profile or history.

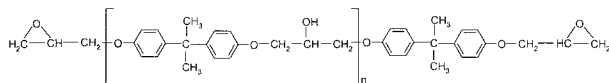
A unique relationship between the crosslinking density or degree of conversion of a thermosetting polymer and its glass-transition temperature, which is independent of the cure history, previously has been demonstrated.<sup>6-19</sup> One approach is based on using the DiBenedetto equation,<sup>6,7</sup> shown to have a physical basis,<sup>10</sup> listed as eq. (1):

$$\frac{T_g - T_{gu}}{T_{gu}} = \frac{(\varepsilon_\infty/\varepsilon_0 - c_\infty/c_0)x}{1 - (1 - c_\infty/c_0)} \quad (1)$$

$T_{gu}$  is the glass transition of the uncrosslinked polymer, and  $x$  is the crosslink density, defined as "the fraction of all segments that are crosslinked,"  $\varepsilon$  is the lattice energy,  $c$  is the segmental mobility, and the subindexes 0 and  $\infty$  refer to the uncrosslinked and the fully crosslinked polymers, respectively. The segmental mobility,  $c$ , although shown as having simply an initial and a final value, is of course a variable changing constantly with the change in the molecular structure during the cure process, and as such, eq. (1) is a simplification of the actual process. This is the main limitation of this model, and it becomes apparent when used for highly crosslinked systems. The  $T_g$ -conversion data for highly crosslinked systems such as a multifunctional epoxy novolac system, has been shown previously to have its  $T_g$  increase rapidly in the later stages of cure.<sup>18,21</sup> This is apparently because these systems appear to have a considerable change in the configurational entropy caused by the act of crosslinking itself, which is not reflected in the physical basis of the model. This deviation has been shown to result from both a high crosslinking density and from steric restrictions on the freedom of the chain segments in the region around the junctions.<sup>18</sup>

However, a version of the DiBenedetto equation, modified for easier application, has been used more frequently,<sup>7,10-11,20-22</sup> where  $x$  is replaced by the degree of conversion,  $\alpha$ , and  $T_{gu}$  is replaced by  $T_{g0}$ . It has been demonstrated that this version of the DiBenedetto equation is derived from entropic considerations of an idealized system consisting of a mixture of a fully cured network and an unreacted monomer phase, based on these thermodynamic considerations<sup>22</sup>

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1 - (1 - \lambda)\alpha} \quad (2)$$



**Figure 1** Structure of DGEBA epoxy.

where  $\lambda$  is an adjustable, structure-dependent parameter. Pascault and Williams<sup>10,11</sup> used a relationship among  $T_{g0}$ ,  $T_g$ , and  $_{gel}T_g$  to estimate  $\lambda$ , obtaining values that ranged between 0.46 and 0.58 for several amine–epoxy systems, while another report<sup>23</sup> gave  $\lambda = 0.43$  for a dicyanate ester system.

More recently Venditti and Gillham<sup>24</sup> proposed a relatively simple equation, based on thermodynamic considerations put forth by Couchman<sup>22</sup> to predict the  $T_g$ -versus-mole fraction of constituents of a linear copolymer, to model the  $T_g$ -conversion relationship for thermosetting systems

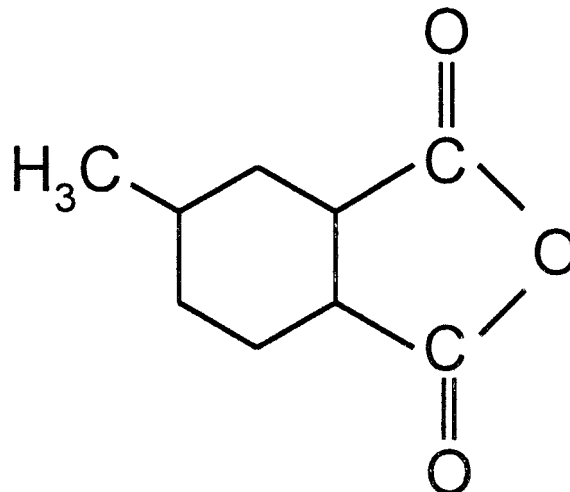
$$\ln(T_g) = \frac{(1 - \alpha)\ln(T_{g0}) + \frac{\Delta C_{p\infty}}{\Delta C_{p0}} \alpha \ln(T_{g\infty})}{(1 - \alpha) + \frac{\Delta C_{p\infty}}{\Delta C_{p0}} \alpha} \quad (3)$$

in which the parameter  $\lambda$  here is theoretically taken to be equal to  $\Delta C_{p\infty}/\Delta C_{p0}$ , where  $\Delta C_{p\infty}$  and  $\Delta C_{p0}$  are the differences in heat capacity between the glassy and rubbery–liquid states at  $T_g$  for 100% and 0% conversion, respectively. The  $\lambda$  value so obtained using eq. (3) and applying it to a whole range of thermosetting materials ranged from 0.31 to 0.62.

## EXPERIMENTAL

The epoxy resin used in this study was the diglycidyl ether of bisphenol A (DGEBA; Epikote 828, Shell Chemicals,  $n = 0.2$ ,  $M_w = 383$ ), with the structure as indicated in Figure 1. The hardener used was the Hexahydro-4-methylphthalic anhydride (MHHPA) (Aldrich). Its structure is shown in Figure 2. The tertiary amine catalyst used was the 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30) (Fig. 3).

Three molar ratios of DGEBA–MHHPA were used in our study (1:0.8, 1:1, and 1:1.2) to characterize the effect of the molar ratio on the  $T_{g\infty}$ . The tertiary amine catalyst was 1% by weight of the DGEBA epoxy resin in all three compositions. Isothermal cure of the samples was conducted at 100°C, 120°C, 140°C, and 160°C within the DSC cell. A Perkin–Elmer calorimeter (DSC-7) was used to measure the  $T_g$  and the heat evolution of the reaction, from which  $T_g$ -versus-conversion was determined. At specific time intervals the cure was

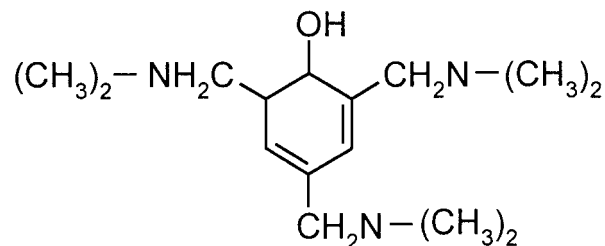


**Figure 2** Structure of hexahydro-4-methylphthalic anhydride.

stopped, and the sample was removed and immediately quenched in the refrigerator to avoid additional reaction. The samples were then scanned from  $-60^\circ\text{C}$ – $250^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$ .  $T_g$  was determined as the midpoint of the transition of the heat capacity, indicated by the inflection in the DSC scan. The degree of conversion,  $\alpha$ , was determined as the ratio of the difference between the total heat of reaction for full curing and the remaining heat of reaction, divided by the total heat of reaction for full curing.

## RESULTS AND DISCUSSION

One of the key objectives of any cure optimal process is to achieve the maximum possible  $T_g$  value. In practice it is nearly impossible to achieve the theoretical maximum  $T_g$  value. As such, the maximum achievable  $T_g$  value usually may not reach the theoretical  $T_{g\infty}$ , taken to be the glass-transition temperature of the thermoset at 100% conversion of reactive groups. The measured value of  $T_{g\infty}$  must in



**Figure 3** Structure of 2,4,6-tris(dimethylaminomethyl)phenol.

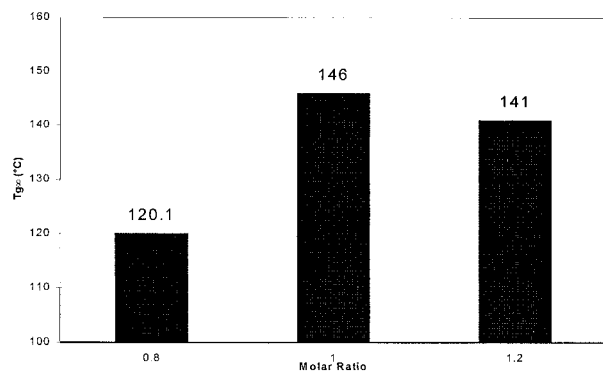


Figure 4 Effect of stoichiometric ratio on  $T_g$ .

most cases be taken as an approximation of or as the maximum achievable  $T_{g\infty}$ . Experimentally, based on the extensive number of tests performed to determine the  $T_g$  value, it has been ascertained that for the system presently tested, the maximum achievable  $T_g$  obtainable practically would have been achieved by curing at 140°C for 12 h. Further curing after this would bring only a very minimal incremental increase in the  $T_g$ .

Based on the above definition and the premise of the maximum achievable value for  $T_g$ , the  $T_{g\infty}$  values for the DGEBA–MHHPA systems with different molar ratios have been experimentally measured using differential scanning calorimetry (DSC) and are plotted in Figure 4 with ratios of 0.8, 1.0, and 1.2. At the ratio of 0.8 (representing an excess of epoxy resin) the  $T_{g\infty}$  was significantly lower at 120°C. This was probably because insufficient hardener resulted in a lower crosslink density. At a ratio of 1.2 (representing an excess of the anhydride hardener) the  $T_{g\infty}$  obtained was also lower, at 141°C. This is because the excess unused hardener actually had a plasticity effect on the cured system, which lowered the  $T_g$ . From the plot in Figure 4, it can be observed that the highest  $T_{g\infty}$ , at 146°C, was obtained at the stoichiometric ratio of 1:1.

These results clearly confirm that accurate compliance to the optimal stoichiometric ratio is critical to the maximization of the  $T_g$ . Figure 5 plots the results of the  $T_g$  values obtained from samples that had been cured isothermally at 100°C, 120°C, 140°C, and 160°C against the cure time in minutes. Except for the 160°C plot, for a given curing time, the  $T_g$  increased with increasing curing temperature. The lower  $T_g$  value obtained for curing at 160°C, compared to curing at 140°C, results from the volatility of the anhydride at this high temperature. The results also show a two-stage progressive increase in the  $T_g$  values. At the first stage ( $T_{\text{cure}} > T_g$ ), the  $T_g$  increased

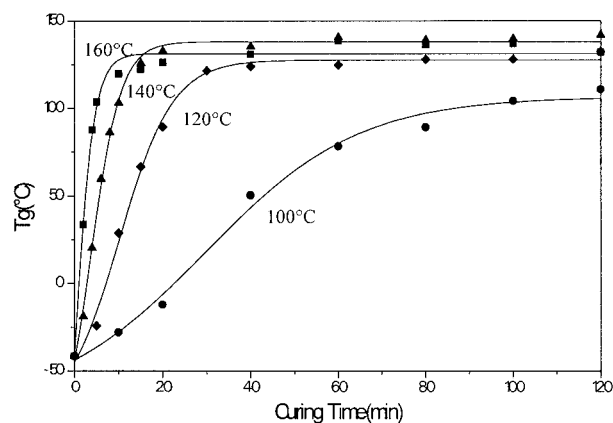


Figure 5 Plots of conversion versus curing time at different curing temperatures.

rapidly, but as the  $T_g$  approached  $T_{\text{cure}}$ , the rate of increase dropped significantly. The point dividing these two stages is thus the vitrification point.

The cure reaction prior to vitrification would be typically dominated by the rate of the chemical reaction of cure. As the crosslink density increases with the progress of the chemical reaction, the difference between the transient  $T_g$  value and the cure temperature decreases. The increase in the crosslink density in turn would reach a state so as to seriously hinder the physical movement of the molecules, at which time the reaction would be dominated by a diffusion type control and the overall crosslink conversion rate would decrease by orders of magnitude because of a relative lack of mobility of the reactive groups.

Aside from determining the value of  $T_{g\infty}$ , the DSC results can also be used to obtain two other critical values— $T_{g\infty}$ , and  $_{\text{gel}}T_g$ . The former is the  $T_g$  of the uncured resin, while the latter is the value of the  $T_g$  at the gel point. The values of  $T_{g0}$ ,  $T_{g\infty}$ , and  $_{\text{gel}}T_g$  obtained from the DSC tests have been ascertained and are tabulated in Table I.

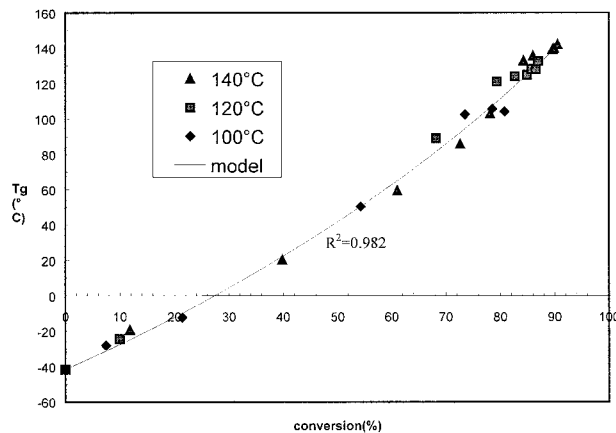
In order to correlate the  $T_g$  values to the % conversion, the conversion–curing time results have been combined with the  $T_g$ –curing time results, as shown in Figure 6, which plots the  $T_g$  against the conversion for the three isothermal curing temperatures.

Table I Critical Thermal Parameters of DGEBA–MHHPA System

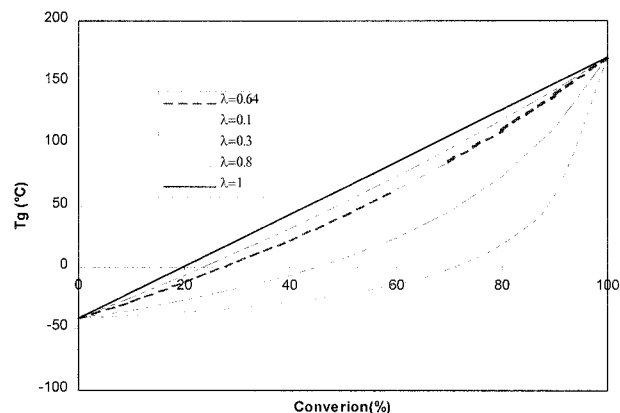
$T_{g0}$	−41.7°C
$T_{g\infty}$	146°C
Gel $T_g$	26.4°C
$\alpha_{\text{gel}}$	0.43

The experimentally obtained results generally fell on an approximately single curve. As such, it can be concluded that a one-to-one relationship exists between the  $T_g$  value and the % conversion, which is independent of the cure temperature (for the range of our tests). This result is in agreement with the work of other investigators.<sup>6-12</sup> Equation (3) was then used as a model to fit the experimental data so obtained. The values of  $T_{g0}$  and  $T_{g\infty}$ , the glass-transition temperatures of uncured and fully cured systems, respectively, were taken from Table I. The resulting regression analysis performed using eq. (3) to the experimental data in Figure 6 gave a high degree of correlation, judging from the obtained value of the squared co-efficient of correlation ( $R^2$ ) of 0.98. It was determined that  $\lambda$  was 0.64, apparently higher than for those previously obtained for other epoxy systems, which ranged from 0.43–0.58, but is similar to the value obtained by Monserrat ( $\lambda = 0.69$ ) for another epoxy-anhydride system.<sup>24</sup> By extrapolating the modeled curve in Figure 6 to 100% conversion, the theoretical value  $T_{g\infty}$  is seen to have a value of about 170°C. The highest  $T_g$  value obtained in the experiment,  $T_{g\max}$ , shown in Table I, was only 146°C, which is far below  $T_{g\infty}$ . Evidently, to reach  $T_{g\infty}$  by an isothermal cure method is practically impossible. A curing process with several steps would probably be more suitable to get the optimal final  $T_g$ .

The practical importance of the value of  $\lambda$  is shown in Figure 7, for which is plotted the  $T_g$ -conversion curve for various values of the parameter  $\lambda$ , ranging from 0.1 to 1.0. A low ratio results in a skewed curve, showing that the increase in the  $T_g$  value lags significantly behind the increase in the degree of conversion. A higher ratio would



**Figure 6**  $T_g$ -Conversion relationship of DGEBA-MHHPA system.



**Figure 7** Dependence of  $T_g$ -conversion curve on the parameter  $\lambda$ .

indicate that the increase in the  $T_g$  values follows more closely and consistently with the increase in the degree of conversion. More importantly, it can be seen that a system with a low value of  $\lambda$  would invariably result in a significantly higher difference in  $(T_{g\infty} - T_{g\max})$ , and a higher  $\lambda$  value would indicate an ability to achieve a maximum  $T_g$  value closer to its theoretical maximum.

## CONCLUSION

The glass-transition value for an mHHPA epoxy system has been successfully related to the conversion value using the DiBenedetto equation, giving a high value of  $\lambda$ , the ratio of segmental mobility for crosslinked and uncrosslinked polymers, at 0.64. The highest  $T_g$  value obtained experimentally,  $T_{g\max}$ , was 146°C, which is significantly below the derived  $T_{g\infty}$  value of 170.

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