Cure Reaction for Modified Diallylbisphenol A/Diaminodiphenylsulfone/Bismaleimide

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ABSTRACT: The glass-transition temperature as a function of curing conversion for a modified diallylbisphenol A/diaminodiphenylsulfone/bismaleimide (BMI) resin was investigated at different temperature regimes and modeled using a modified Di Benedetto equation. Although the relationship between the glass-transition temperature and conversion of the BMI system conforms to the Di Benedetto equation for $\alpha < 0.6$ and at lower cure temperatures, at higher cure temperatures the results deviated significantly from the equation; thus, it was an inadequate model for the system. Fourier transform IR analysis showed that the major crosslinking reactions did not occur during cure for the modified BMI at and below 150°C. However, as the cure temperature was increased, the crosslinking reactions responsible for 3-dimensional network structures became more dominant. At 190°C the $C—N—C_{stretch}$ vibration of the uncured maleimide ring converted into succinimide rings in the curing process. Simultaneously, a decrease was observed for the absorbance bands of $=C—H_{bending}$ (maleimide). The higher cure temperatures induced a significantly faster initial crosslinking rate and also resulted in a shorter period of time after which further crosslinking was retarded, because the increase in the crosslinks also physically slowed further crosslinking activity. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 227–235, 2002

Key words: cure reaction; bismaleimide; glass-transition temperature; conversion; Di Benedetto equation

INTRODUCTION

Bismaleimide (BMI) resins have found increasing applications in the aerospace and electronic industries, bridging the temperature gap from epoxy systems to the very high temperature polyimide systems. BMI systems have a slightly lower glass-transition temperature (T_g) compared to polyimides; however, they have a significantly lower moisture absorption, better processing properties, and lower cost (Fig. 1). Also, although brittleness is a major drawback of polyimides, which is due to their aromatic molecular structure, modified BMI resins using various components (aromatic diamines, diallyl bisphenol A, and certain epoxies) have been shown to adequately improve the elasticity of BMI resins by increasing the distance between crosslinks.[1–10]

To the extent that the T_g forms the upper bound limit for the service temperature of the material,[11] optimization of the T_g becomes critical during processing. The standard procedure to ensure optimal T_g values precludes the existence of a unique relationship between the degree of conversion (α) and the T_g. In most thermoset systems this relationship has been shown to be independent of the thermal cure history.[12–14] To date, most of the models used, whether based on an
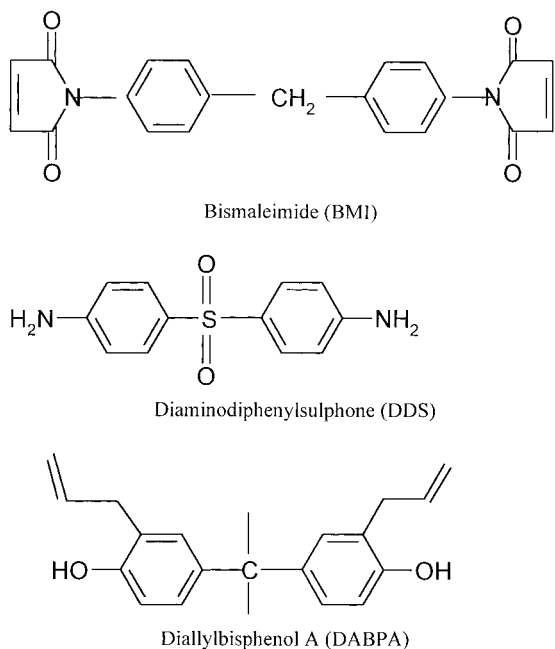
Figure 1 The chemical structures of the components used in the modified bismaleimide system.

empirical or phenomenological approach,[15–25] have been modifications of the Di Benedetto equation, which is[16]

$$[(T_g - T_{gu})/T_{gu} = (\varepsilon_\infty/\varepsilon_0 - C_\infty/C_0)x]/[1 - (1 - C_\infty/C_0)] \quad (1)$$

where T_{gu} is the glass transition of the un-crosslinked polymer; x is the crosslink density, defined as the "fraction of all segments that are crosslinked"; ϵ is the lattice energy; C is the segmental mobility; and the subindexes 0 and ∞ refer to the uncrosslinked and fully crosslinked polymers, respectively.

Equation (2) shows one of the modified Di Benedetto equations derived from entropic considerations of an idealized system. This system consists of a mixture of a fully cured network and a monomer, based on thermodynamic considerations put forth by[23]

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

Here λ is an adjustable, structure-dependent parameter that is theoretically equal to $T_{g0}/T_{g\infty}$ $= \Delta C_{p\infty}/\Delta C_{p0}$, where $\Delta C_{p\infty}$ and ΔC_{p0} are the differences in the heat capacity at constant pressure

among the glassy, rubbery, and liquid states at the T_g for 100 and 0% conversion, respectively. Pascault and Williams[21,22] use a relationship among T_{g0}, $T_{g\infty}$, and $_{gel}T_g$ to estimate λ, which ranged between 0.46 and 0.58 for several amine-epoxy systems. Another report gave[24] $\lambda = 0.43$ for a dicyanate ester system from a plot of $(T_{g\infty} - T_{g0})/(T_g - T_{g0})$ versus α^{-1}.

Venditti and Gillham[25,26] proposed a relatively simple equation to model the T_g and conversion relationship for thermosetting systems that is based on the thermodynamic considerations put forth by Couchman[21] to predict the T_g versus the mole fraction of constituents of a linear copolymer:

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

To date, the equation in varying modifications has been found to fit the T_g and conversion data of epoxy systems with relatively uncomplicated curing reactions. These systems include amine-based epoxy,[24–26] dicyanate ester,[27,28] and epoxy–hexahydro-4-methylphthalic anhydride epoxy systems[29] in which the T_g increases rapidly in the later stages of cure.

In contrast, similar reports of T_g and conversion for more complicated systems involving multiple and often simultaneous reaction paths (e.g., BMI systems) are scarce. The only conversion and T_g work reported is that of Tungare and Martin, which was performed for a BMI and an aromatic diamine.[30] No similar work was found for other more common systems [e.g., BMI-diallylbisphenol A (DABPA)]. For the former system two chemical reactions were shown to exist during curing, as illustrated in Figure 2. The first reaction involved the amine addition reaction leading to extension of the network chains, while the other involved a homopolymerization reaction resulting in chain extension and crosslinking. The results obtained in this work did not follow the Di Benedetto equation. This is because the equation assumes a simple single reaction system or at least a single generalized reaction throughout the duration of cure. More recent work[31] involving solid-state ^{15}N-NMR showed that there are three primary competing reactions for a BMI-methylenedianiline curing system. The three cure reactions were identified as the homopolymerization of BMI, the
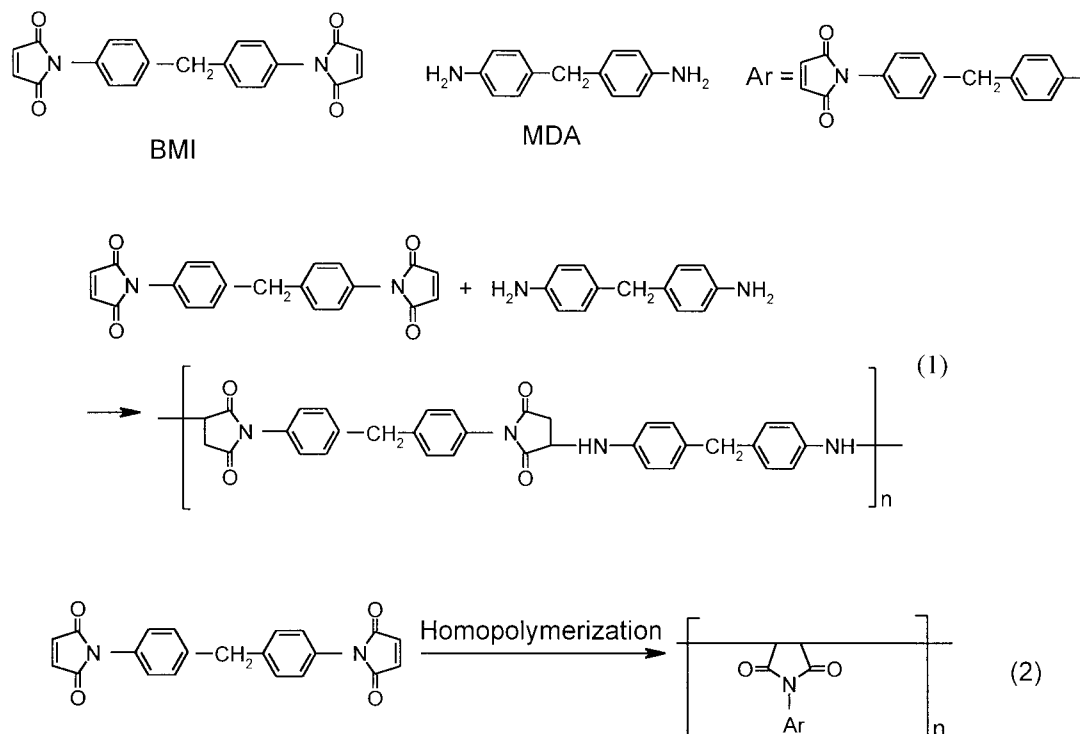
Figure 2 The chemical reactions in the bismaleimide-methylenedianiline system.

chain extension reaction between the primary amine and the double bond of the maleimide ring, and the ring opening or aminolysis reaction. It therefore follows that it would be too simplistic to model these kinds of complex reaction systems assuming only one general reaction path. For similar reasons we also recently showed that a combination of different cure kinetic models was required to accurately represent a similar modified BMI system.[32]

This article reports on our investigation relating the glass-transition temperature and conversion for a BMI system consisting of three main components: BMI (4,4′-methylenebis-[maleimido-benzene]), DABPA (2,2′-diallylbisphenol A), and 4,4′- diaminodiphenylsulfone (DDS). The major reaction types occurring in this type of system containing diallybisphenol have been proposed in the literature[33,34] (Fig. 3): ene, a Diels–Alder reaction, homopolymerization, rearomatization, and alternating copolymerization.

EXPERIMENTAL

The chemical structures of the individual components of the BMI resin system are shown in Fig-ure 1. The details of the synthesis and properties can be found elsewhere.[1,6] The degree of conversion was determined with a Perkin–Elmer DSC7 differential scanning calorimetry (DSC) instrument using an isothermal method to analyze the variation of the conversion versus the curing time.[29,35] The method was able to continuously monitor the rate and extent of the reaction during isothermal curing. The percentage of conversion was calculated by first obtaining the total DSC exothermic heat of the reaction using the DSC7. The total exothermic heat of the curing reaction was determined from the maximum heat released during isothermal and dynamic curing of the modified BMI resin.

The glass-transition temperature was measured with the Perkin–Elmer DSC7 as well. Each sample for a glass-transition temperature test was cured in the DSC pan for the prescribed duration and at the selected temperature, then it was quenched and rescanned from room temperature to 300°C at 20°C/min to obtain its glass-transition temperature. The T_g was determined as the temperature at which the increment in the C_p reaches half of the total ΔC_p value (Fig. 4), where the ΔC_p is the difference in the specific heat between the glassy and rubbery states. The ΔC_p
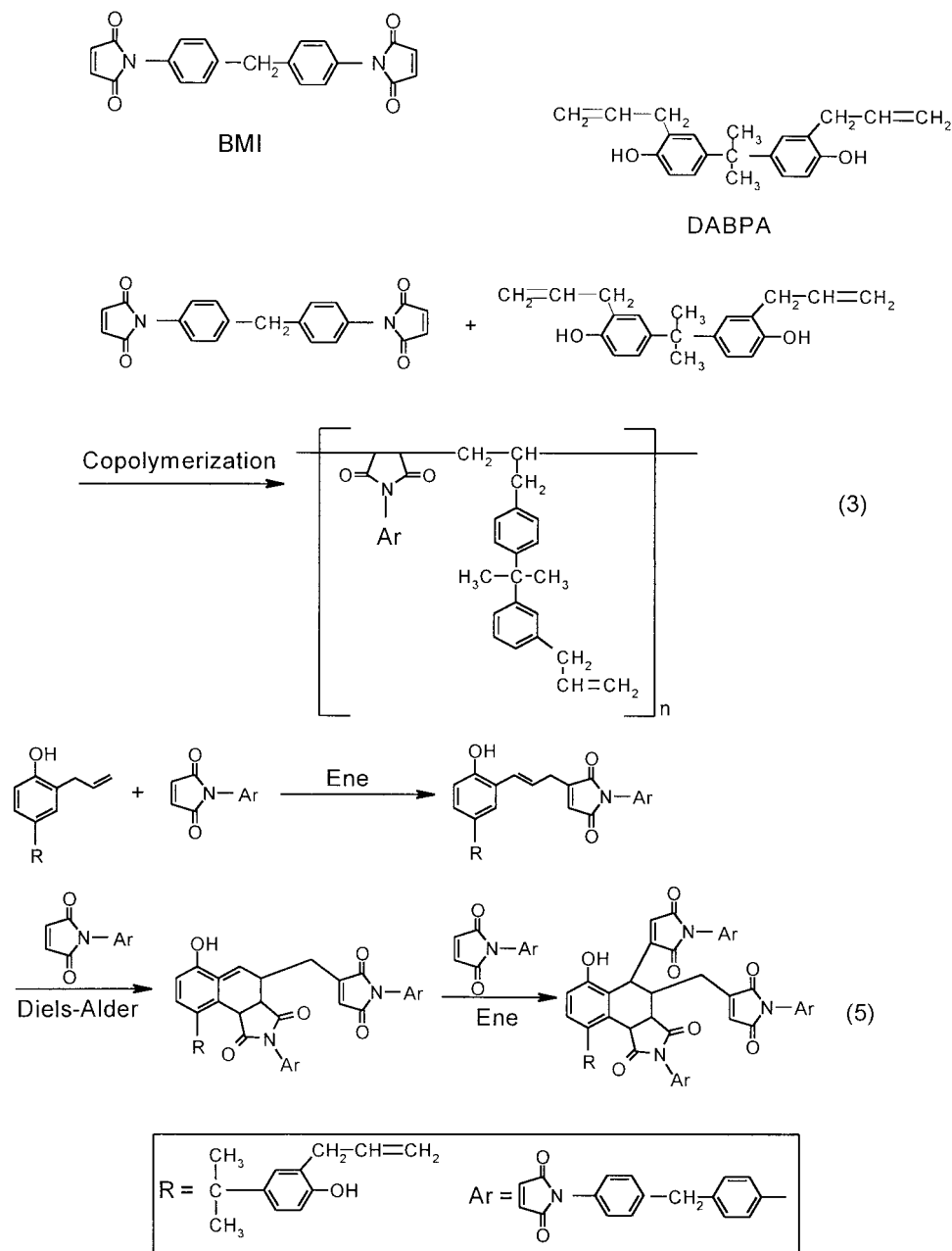
Figure 3 The chemical reactions in the bismaleimide-diallylbisphenol A system.

was shown to be approximately constant at conversion values less than 25%, showing a steady and significant decrease thereafter.[29,35] Because of the high crosslinking density of BMI systems, the ΔC_p is often not sufficiently distinct to attain an accurate T_g value. Therefore, for this work the peak temperature of the derivative normalized heat flow is considered as the T_g. Based on this approach, the reproducibility of the T_g was $\pm 2°C$. There were five isothermal curing temperatures: 150, 170, 190, 210, and 220°C.

A real-time Fourier transform IR (FTIR) study of the samples was carried out by following the *in situ* curing process at different curing temperatures (160–200°C) using a Nicolet Magna 560 FTIR spectrophotometer with a DTGS KBr detector and an XT-KBr beam splitter. The instrument was equipped with a single reflection attenuated total reflectance accessory (Graesby Specac) with an accurate temperature control of $\pm 0.1°C$. Each of the samples was cured for a time period of 2 h. The experimental parameters were selected to
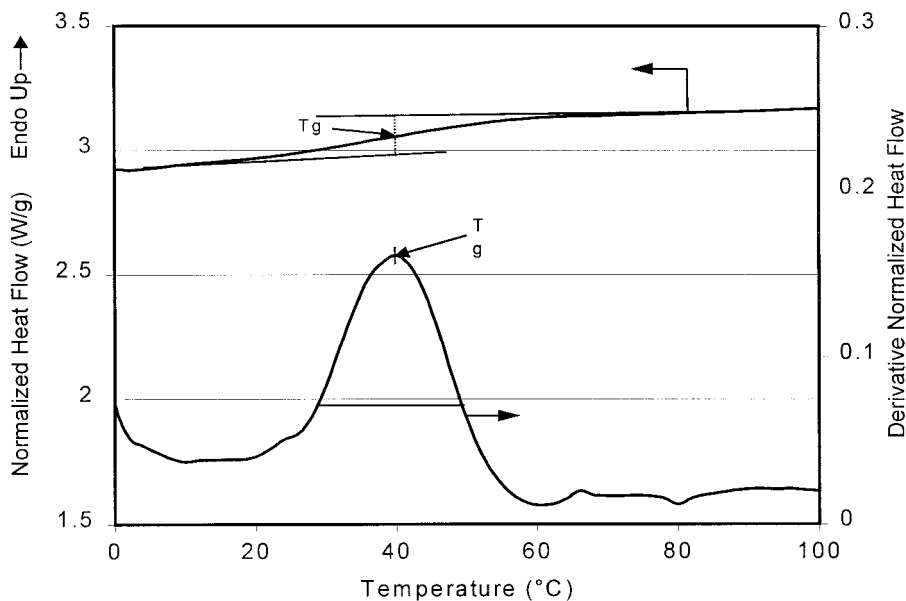
Figure 4 A typical DSC curve.

collect the spectra in real time at 10-s intervals during the curing process.

RESULTS AND DISCUSSION

Figure 5 shows the plot of the percentage of conversion measured using the DSC7 versus various isothermal curing temperatures. In all cases, the percentage of conversion increased rapidly with curing time but subsequently reached a limiting value asymptotically. In all but one case, a higher isothermal cure temperature resulted in a shorter cure time being required to reach a given degree of conversion. The results for isothermal curing at 220°C was the exception: it showed the conver-
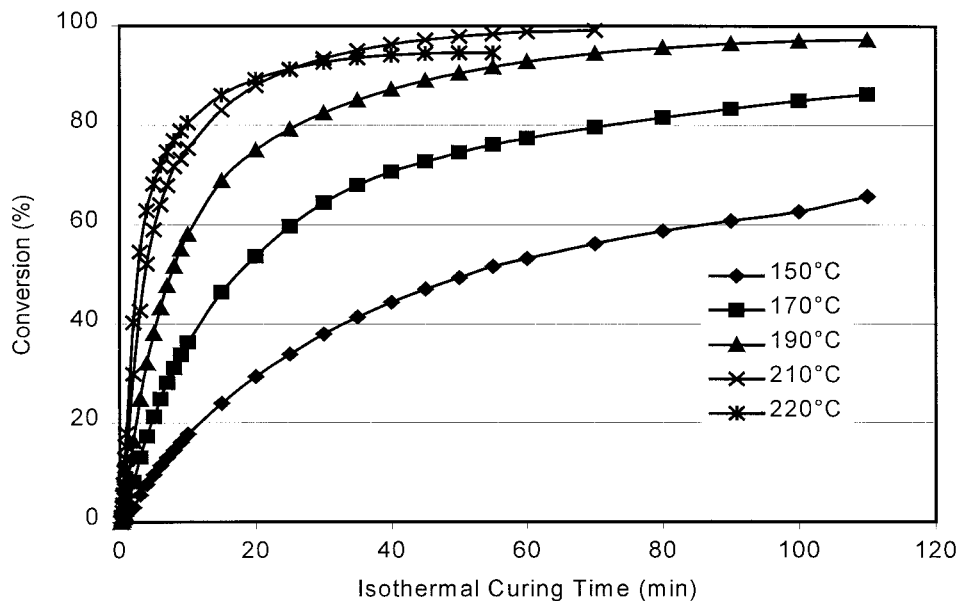

Figure 5 The variations of conversion of the modified bismaleimide with the isothermal curing time.
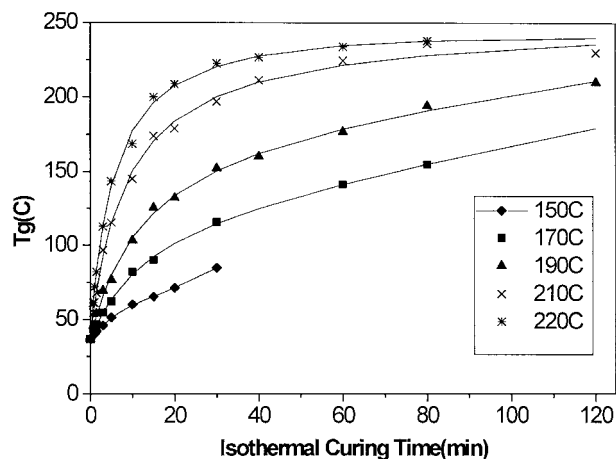
Figure 6 The variations of the glass-transition temperature with the isothermal curing time at 150, 170, 190, 210, and 220°C.

sion of BMI to be lower than that for curing at 210°C at the initial stage. This was likely due to the degradation of the initially uncured resin at 220°C.

Figure 6 plots the results of the T_g against the cure time at different isothermal curing temperatures. The plots indicate similarity with the earlier results (the T_g generally increasing asymptotically to reach a limiting maximum value with the cure time), and the higher isothermal cure temperatures achieve a higher conversion for the same cure time. As the cure time increases, the concentration of chemical groups and their mobility are reduced and diffusion controlled reactions become more dominant, resulting in a lower rate of increase of conversion. The increase in the T_g depends on a few factors, including the decrease in the chain-end concentration, the formation of crosslink points, and a further decrease in the configurational entropy due to a departure from Gaussian behavior at high crosslink density.[12] The decreased rate of increase in the conversion leads to a decreased rate of increase of the crosslink density and thus a decreased rate of increase for the T_g.

Using the respective data from Figures 5 and 6, the T_g versus the conversion plot was obtained as shown in Figure 7 for isothermal curing temperatures of 150 and 170°C. The results in Figure 7 indicate that a linear relationship exists between α and T_g as long as $\alpha < 0.6$, which is independent of the isothermal curing temperature. However, as α exceeds 0.6, significant deviations from the linear relationship existed for curing at 170°C.

Typically, a linear relationship between the glass-transition temperature and conversion indicates that a linear molecular structure is formed during curing. Fox and Flory[35] utilized the following equation for linear polymers to relate the glass-transition temperature and the molecular weight:

$$T_g = T_g(\infty) - (A'/M_{mon})(1 - p) \qquad (4)$$

where $T_g(\infty)$ is the glass-transition temperature of a polymer with infinite molecular weight, M_{mon} is the molecular weight of a monomeric structural unit, p is the probability that the monomeric structural unit (or an end group) has reacted, and A' is a material-specific constant. In the modified BMI the probability that a maleimide group has reacted can be given by the α. Accordingly, eq. (4) can be revised to eq. (5)[15]:

$$T_g = T_g(\infty) - A_1(1 - \alpha) \qquad (5)$$

where $A_1 = A'/M_{mon}$. A linear regression analysis statistical method was used to determine the $T_g(\infty)$ and A_1 by using the experimental data in Figure 7. Respective values of 155 and 116°C were found.

Because $T_g(\infty)$ is deduced to be 155°C, this is theoretically the highest glass-transition temperature that could be achieved by a truly linear 1:1 BMI/DDS system.

Figure 8 plots the results of the T_g values against the corresponding measured value for α for isothermal curing at 190, 210, and 220°C. The
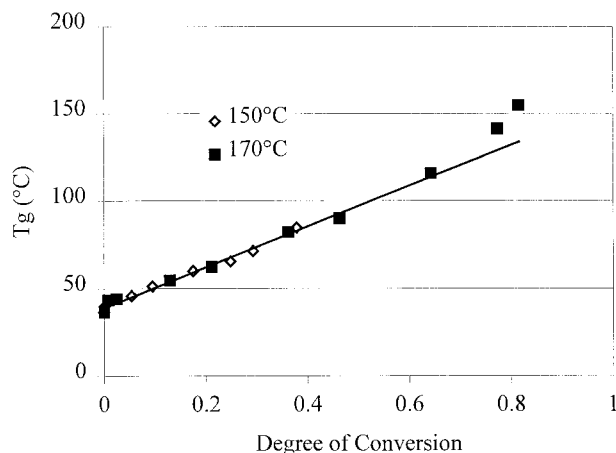

Figure 7 The glass-transition temperature (T_g) versus the degree of conversion for modified bismaleimide at 150 and 170°C
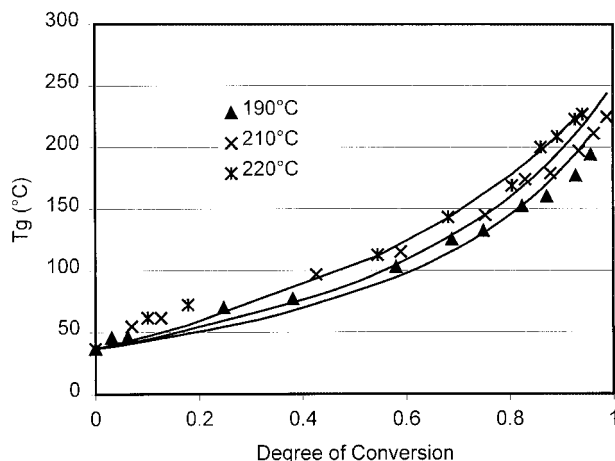
Figure 8 The variation of the glass-transition temperature (T_g) with conversion at 190, 210, and 220°C. (—) The T_g profiles predicted by the Di Benedetto equation.

T_g values obtained for a given α differed significantly with the isothermal curing temperature, and the higher isothermal cure temperatures resulted in a higher T_g value for the same α value. Evidently, the T_g and conversion relationship for the modified BMI system was dependent on the cure temperature at higher cure temperatures in contrast to the assumption in the Di Benedetto equation.

Where the Di Benedetto equation is valid, a one to one relationship between the T_g and α exists, indicating that there is no significant difference in the molecular structure for materials cured at different temperatures. For the present modified BMI system, evidently changing the cure temperature resulted in a molecular structure variation, which correspondingly resulted in a change in the glass-transition temperature.

An attempt was also made to use eq. (2) to model the data in Figure 8 for each respective cure temperature. The statistical results for the nonlinear regression analysis are tabulated in Table I, and the corresponding curves are drawn in Figure 8. Table I shows that the R^2 values were close to unity in all three cases, indicating a very good fit. It can thus be concluded that the modified BMI system fits the Di Benedetto type equations very well for a given isothermal cure temperature, but the relationship is not independent of the isothermal cure temperature.

The λ values obtained were 0.37, 0.34, and 0.43 for 190, 210, and 220°C, respectively. These values are relatively low in all three cases compared to those obtained for epoxy systems with λ values between 0.48 and 0.64.[29] A lower value would indicate that the modified BMI system has a comparatively lower ratio of segmental mobility for crosslinked and uncrosslinked polymers, resulting in a higher rate of increase for the T_g value for a lower conversion value than for higher conversion. In contrast, a high ratio would have resulted in a more consistent increase in the T_g, whatever the conversion value.

To explain the variation in the glass-transition temperature with the curing conversion for the modified BMI at different isothermal curing temperatures, an attempt was made to follow the nature of different chemical reactions during the process of curing using a FTIR spectrophotometer. Figure 9 shows the real-time spectra of a representative sample cured at 190°C. It is evident from the figure that the peak at 1148 cm^{-1} decreases in intensity while the one at 1180 cm^{-1} increases in intensity with the curing time. The peak at 1148 cm^{-1} is representative of the C—N—C$_{\text{stretch}}$ of the uncured maleimide ring while that at 1180 cm^{-1} is a similar vibration arising out of a succinimide ring (which increases in concentration as the maleimide rings get converted into succinimide rings as a result of consumption of the double bond in the curing process). Simultaneously, a decrease in the absorbance bands at 826 and 690 cm^{-1} with the cure time was observed. The 826 cm^{-1} band corresponds to the bending mode of vibration of =C—H (maleimide) bonds whereas the band at 690 cm^{-1} corresponds to the out of plane vibration of =C—H (maleimide) bonds. Evidently, the decrease reflected the disappearance of =C—H maleimide bonds.

Figure 10 plots the intensity of the band at 1180 cm^{-1} (normalized against the aromatic C=C$_{\text{stretch}}$ vibration at 1510 cm^{-1}) with the curing time. The intensity of the normalized peak height ratio for cure temperatures below 160°C was not very significant, indicating that reactions like ene, Diels–Alder, and copolymerization,

Table I Values for λ and R^2

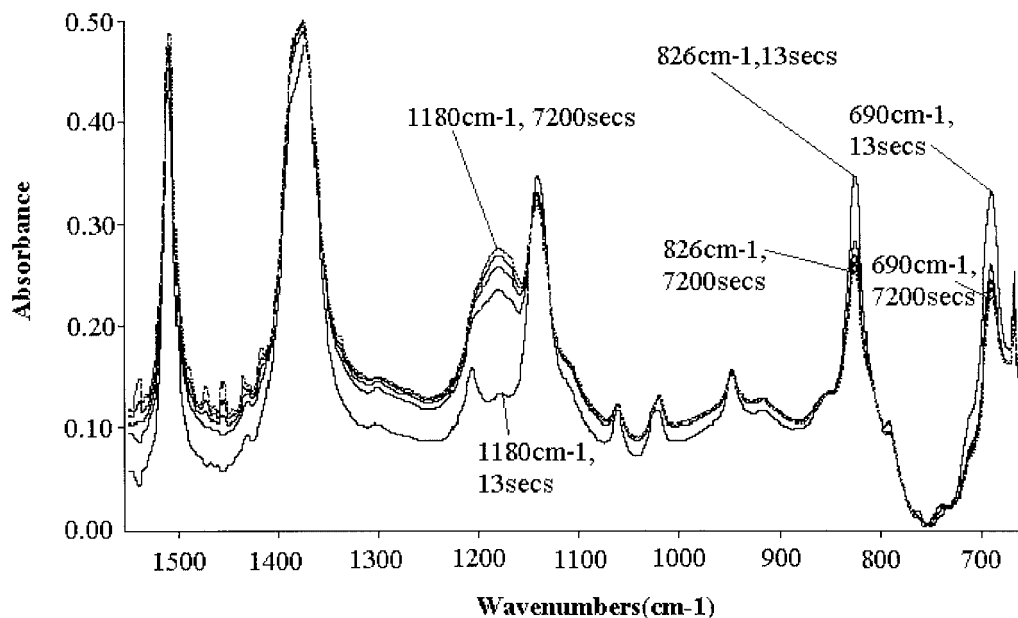|	Cure Temperature (°C)		
	190	210	220
λ	0.37	0.34	0.43
R^2	0.97	0.96	0.99

Figure 9 The *in situ* FTIR spectra for the modified bismaleimide at 190°C.

which involve crosslinking and hence contribute largely to the intensity of this peak,[33,34] are not extensive. It is only at 160°C and above that the normalized peak height ratio significantly increases with the cure time. This is evidence for the fact that at lower cure temperatures the linear chain extension was dominant, so that the peak at 1180 cm^{-1} was not predominant. However, as the cure temperature is increased, the crosslinking reactions responsible for 3-dimensional network structures dominate as reflected by the increase in the peak height in Figure 10. The higher cure temperatures induce a signifi-
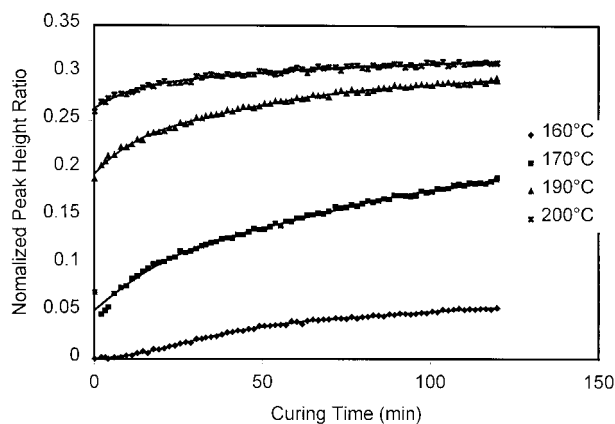
cantly faster initial crosslinking rate but also result in a shorter period of time after which further crosslinking was retarded, the latter presumably due to the fact that the increase in the crosslinks also physically slow further crosslinking activity.

CONCLUSION

While the relationship between the glass-transition temperature and the conversion of the modified DABPA/DDS/BMI conform to the Di Benedetto equation for $\alpha < 0.6$ and at lower cure temperatures, at higher cure temperatures the results obtained deviated significantly from the equation, indicating that the equation was an inadequate model for the system. FTIR analysis showed that the major crosslinking reactions did not occur during cure for the modified BMI at and below 150°C. However, as the cure temperature was increased to 190°C, the crosslinking reactions responsible for 3-dimensional network structures became dominant. The C—N—C$_{stretch}$ uncured maleimide ring converted into succinimide rings in the curing process. Simultaneously, a decrease was observed for the absorbance bands of $=$C—H$_{bending}$ (maleimide) and $=$C—H$_{out\ of\ plane\ bending}$ (maleimide) bonds. The higher cure temperatures induced a significantly faster initial crosslinking

Figure 10 The normalized peak height ratio of 1180 versus 1510 cm^{-1} at different curing temperatures.

rate but also resulted in a shorter period of time after which further crosslinking was retarded, the latter presumably attributable to the fact that the increase in the crosslinks also physically slowed further crosslinking activity.

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