Glass-Transition Temperature in the Curing Process of Bismaleimide Modified with Diallylbisphenol A

F. Boey, Y. Xiong, S. K. Rath

School of Materials Engineering, Nanyang Technological University, Nanyang Avenue, 639798 Singapore

ABSTRACT: The T_g–conversion relationship, during the thermal curing of different stoichiometric formulations of 1,1'-(methylene-di-4,1-phenylene) bismaleimide (BMI), modified with *o,o'*-diallyl bisphenol A (DABA), was investigated. The DiBenedetto equation was used to model this relationship for the formulation of DABA-1 (BMI : DABA, 1 : 1). Based on this model, the T_g–conversion relationship of formulation DABA-0.5 (BMI : DABA, 1 : 0.5) was modeled. The high consistency between the model curve and experimental data showed that the change of T_g, attributed to copolymerization between BMI and DABA in DABA-0.5, in the low-conversion regime, was the same as that in DABA-1. This also verifies that, for the formulation DABA-0.5, copolymerization and homopolymerization do not overlap with each other. The reactions progressed sequentially and homopolymerization occurred after completion of copolymerization. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3244–3247, 2004

Key words: bismaleimide; diallylbisphenol A; copolymerization; curing of polymers; glass transition

INTRODUCTION

Bismaleimides (BMI) have gained increased importance given their comparatively higher service temperatures in contrast to those of epoxy systems, and better processing behavior compared to that of other polyimides. The latter, although having higher glass-transition temperatures, nevertheless usually suffer from processing problems because of their insolubility, infusibility, and the volatiles evolved as a result of ring formation[1] during cure.

The main drawback in the use of neat BMI resin is its highly brittle characteristic after curing, caused by its aromatic molecular structure and high crosslink density. Efforts to reduce its brittleness invariably reduce the crosslink density in the neat resin system by the introduction of a second component. Among the more promising approaches of resin modification have been the addition of reactive elastomers,[2] use of the Michael addition chain reaction,[1,3] copolymerization with allyl-terminated copolymers,[4,5] eutectic mixtures,[6] and modification with thermoplastics.[7,8] So far, the copolymerization of BMI with allylphenyl/allylphenol compounds has been shown to be the most effective method for toughening BMI. The most promising modifier has been diallylbisphenol A (DABA). The modified BMI offers easy processability and cured networks with excellent toughness. Allylphenol compounds coreact with BMI to give linear chain extension by the "ene"-type reaction, followed by a Diels–Alder reaction occurring at high temperature. This chain extension results in tougher networks with only minimal reduction in the thermal properties.

Complete curing of BMI is difficult to obtain in practice because of the high crosslink density and early onset of vitrification, which prevents further curing. As curing proceeds, the increasingly crosslinked network itself becomes a barrier against diffusion and mobility, thus preventing further extension of the curing network. Therefore, taking measurements of the theoretical heat flow for complete curing of BMI, and its T_g, are very difficult: the relatively high value of BMI's T_g (of the order of 400°C and more) is beyond the range of most DSC units. Also, the onset of the glass-transition regime often coincides with the degradation temperature of the cured resin. Thus, for highly crosslinked systems like BMI, the T_g finally obtained is typically significantly below the theoretical maximum T_g attainable.

To measure the maximum possible T_g, the ability to determine the theoretical maximum T_g for the system is required. Second, different reactions, as well as their sequence of occurrence, result in different lengths as well as a variety of molecular chains. The T_g of the final product is a property reflecting cumulative summation of all these factors.[9] Both the above points form the basis of the results and discussion of this article.

For a given thermosetting system, the T_g is uniquely related to the conversion. The famous DiBenedetto equation[10] [eq. (1)] attempted to correlate the various parameters of a curing system:

Correspondence to: F. Boey (mycboey@ntu.edu.sg).

$$\frac{T_g - T_{gu}}{T_{gu}} = \frac{(\varepsilon_\infty / \varepsilon_0 - C_\infty / C_0)x}{1 - (1 - C_\infty / C_0)x} \qquad (1)$$

where T_{gu} is the glass-transition temperature of the uncrosslinked system; 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 system, respectively. The segmental mobility c is the phenomenological constant used to express the measure of mobility of the molecules during cure. Although shown as having simply an initial and a final value in DiBenedetto's equation, it is a function of the molecular structure during the course of the cure process. As such, eq. (1) is a simplification of the actual process, which becomes apparent when used for highly crosslinked systems. The T_g–conversion data for highly crosslinked systems, such as a multifunctional epoxy novolac system, was previously shown to have its T_g increase rapidly in the later stages of cure.[11] The cure process for the resin appears 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 was shown to result from both a high crosslinking density and from steric restrictions on the freedom of chain segments, in the region around the junctions.

By assuming an idealized system consisting of a mixture of a fully cured network and an unreacted monomer phase, a more commonly used version of the DiBenedetto equation was derived from entropic considerations.[12] In the following equation, x is replaced by the degree of conversion α and T_{gu} is replaced by T_{g0}:

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

where λ is an adjustable, structure-dependent parameter. T_{g0} and $T_{g\infty}$ represent the glass-transition temperature (T_g) at zero and 100% conversion, respectively. Boey and Qiang[14] showed how the derived value of λ can indicate a higher rate of increase for the T_g value for a lower conversion value than for a higher, or a more consistent increase in the T_g value whatever the value of conversion. Clearly, eq. (2) is better suited for a multireaction system such as the modified BMI system studied here.

EXPERIMENTAL

1,1'-(Methylene-di-4,1-phenylene) bismaleimide (BMI) and the o,o'-diallyl bisphenol A (DABA) were purchased from Hu Bei Feng Guang Chemicals (China) and Ciba-Geigy (Summit, NJ), respectively. Three different stoichiometric formulations (1 : 1, 1 : 0.5, and 1 : 2.12) of BMI
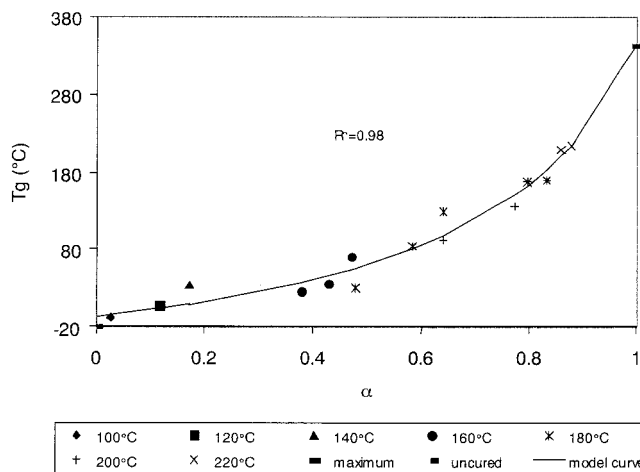

Figure 1 Relationship between T_g and conversion of the formulation DABA-1.

and DABA were prepared, by mixing both components at desired molar ratios at room temperature. Individual formulations are referred to as DABA-r, with r representing the number of moles of DABA to 1 mole of BMI. Subsequently, samples were stored at subzero temperature, to prevent resin advancement. DSC studies were performed using a modulated DSC (DSC 2920; TA Instruments, New Castle, DE), equipped with a refrigerated cooling system. The samples with different conversions were obtained by isothermal curing of the fresh samples at 100, 120, 140, 160, 180, 200, and 220°C, for different times, followed by quenching to room temperature. Subsequently, the cured samples were rerun in a dynamic temperature scan, at 5°C/min. T_g was determined as the midpoint of the exothermic transition of the heat capacity curve. The conversion α was determined by an isothermal method, and the results of kinetic studies of the system were communicated in a previous report.[13]

RESULTS AND DISCUSSION

Figure 1 plots the experimental results for the whole curing course of the formulation DABA-1. The T_g and conversion data were obtained from DSC, for samples cured at different isothermal temperatures. As observed from Figure 1, the whole range of T_g and conversion values may be plotted as an approximate single curve. This is an indication that the T_g–conversion relationship for the curing system DABA-1 is unique and the relationship is independent of the curing profile. Therefore, a model equation should exist to represent this relationship. While attempting to study this system, we used the modified DiBenedetto equation [eq. (2)] to model the relationship, given that this has successfully been used to model the T_g–conversion relationship for many thermoset systems.

The modified DiBenedetto equation [eq. (2)[rsqb] contains three unknown parameters: T_{g0}, $T_{g\infty}$, and λ. In practice, it is nearly impossible to achieve the theoretical maximum T_g value—the T_g of fully cured polymer ($T_{g\infty}$)—for BMI-based systems, for reasons discussed earlier. An alternate approach is to accept the experimentally measured maximum T_g to be an approximation of $T_{g\infty}$. Following this approach, we determined the $T_{g\infty}$ of DABA-1, by dynamically curing the sample up to 300°C at 5°C/min and subsequently holding at that temperature for 20 min. The upper limit of 300°C was selected based on our previous studies, whereby it was thermogravimetrically established that the sample undergoes significant degradation, upon heating beyond 350°C.[9]

By rewriting the modified DiBeneditto equation [eq. (2)[rsqb] for DABA-1, we obtain

$$\frac{T_{g-\text{DABA}-1} - T_{g0-\text{DABA}-1}}{T_{g0-\text{DABA}-1} - T_{g0-\text{DABA}-1}} = \frac{\lambda_1\alpha}{1 - (1 - \lambda_1\alpha)} \quad (3)$$

The value of $T_{g\infty}$ for DABA-1, obtained following the above approach, was found to be 343°C. The conversion values and the corresponding glass-transition temperatures ($T_{g\text{-DABA-1}}$) were read from Figure 1. Therefore, eq. (3) contains two unknown parameters: $T_{g0\text{-DABA-1}}$ and λ. These two parameters were obtained by performing a nonlinear regression analysis, which gives a value of -7°C for $T_{g0\text{-DABA-1}}$ and λ_1 as 0.24. Upon substitution of these values into eq. (3) and simplification, we obtain

$$\frac{T_{g-\text{DABA}-1} - (-7)}{343 - (-7)} = \frac{0.24\alpha}{1 - (1 - 0.24)\alpha} \quad (4)$$

$$T_{g-\text{DABA}-1} = \frac{84\alpha}{1 - 0.76\alpha} - 7 \quad (5)$$

The solid curve in Figure 1 is based on eq. (5). The value of the squared coefficient of correlation was found to be 0.98 ($R^2 = 0.98$), indicating a high degree of correlation.

In a related previous study of the BMI/DABA curing system, we reported that there is 1 : 1 copolymerization between BMI and DABA, as long as the formulation has a stoichiometry of 1 : 1 or contains excess DABA. When the formulation contains a molar excess of BMI, the remaining BMI undergoes homopolymerization. Our results have also shown that the two reactions, BMI/DABA copolymerization and BMI homopolymerization, take place independently, with the latter occurring soon after copolymerization is complete. It was further shown that BMI homopolymerization is complete, as long as the excess BMI in the formulations is not >40%. Apparently, the copolymer of BMI/DABA provides a flexible network, which permits easier chain diffusion and mobility,

for the completion of the second reaction: homopolymerization of BMI.

In line with the above arguments, it can be reasonably said that eq. (5) essentially models the copolymerization reaction between BMI and DABA (because the formulation is stoichiometric in BMI and DABA).

Our next objective was to model the T_g–conversion relationship for other formulations of the BMI/DABA system, containing excess BMI. Before doing so, however, we proceed with the following assumptions:

1. The two reactions, BMI/DABA copolymerization and BMI homopolymerization, occur independently, with the latter occurring only after the copolymerization is complete. Before the excess BMI starts to homopolymerize, the system is a mixture of the BMI/DABA copolymer and the excess monomer of BMI.
2. The products of the two reactions, the copolymer and the homopolymer, are remarkably compatible and there is no phase separation. As a result, the T_g of the product with excess BMI is actually dependent, proportionately, on the copolymer and the excess weight percentage of BMI. Accordingly, if we choose a formulation, say DABA-0.5, the T_g of the system after complete cure could be calculated using the formula

$$T_{g-\text{DABA}-0.5}$$

$$= T_{g0-\text{BMI}}\frac{0.5 \text{ mol BMI}}{1 \text{ mol BMI} + 0.5 \text{ mol DABA}}$$

$$+ T_{g-\text{DABA}-1}\frac{0.5 \text{ mol BMI} + 0.5 \text{ mol DABA}}{1 \text{ mol BMI} + 0.5 \text{ mol DABA}} \quad (6)$$

where $T_{g\text{-DABA-0.5}}$ is the T_g of DABA-0.5, $T_{g0\text{-BMI}}$ is the T_g of the BMI monomer, and $T_{g\text{-DABA-1}}$ is the T_g of the BMI/DABA copolymer (DABA-1), which was read from Figure 1, at conversion values similar to those of DABA-0.5.

Because BMI monomer is a crystalline material, its T_g is difficult to measure. However, this was obtained indirectly, using a method as follows. As reported previously, we observed that, upon mixing with DABA, the melting peak of BMI diminishes and finally disappears. This shows that DABA is a good solvent for BMI. The T_g of one such formulation, containing a large excess of DABA (DABA-2), was measured and was found to be -16.7°C. In another experiment, the T_g of pure DABA was measured and was found to be 5°C. These two values were substituted into eq. (7) to obtain, indirectly, the T_g value of pure BMI as -60°C.

$$T_{g0-\text{DABA}-2} = T_{g0-\text{BMI}}\frac{1 \text{ mol BMI}}{1 \text{ mol BMI} + 2 \text{ mol DABA}}$$

$$+ T_{g0-\text{DABA}}\frac{2 \text{ mol DABA}}{1 \text{ mol BMI} + 2 \text{ mol DABA}} \quad (7)$$
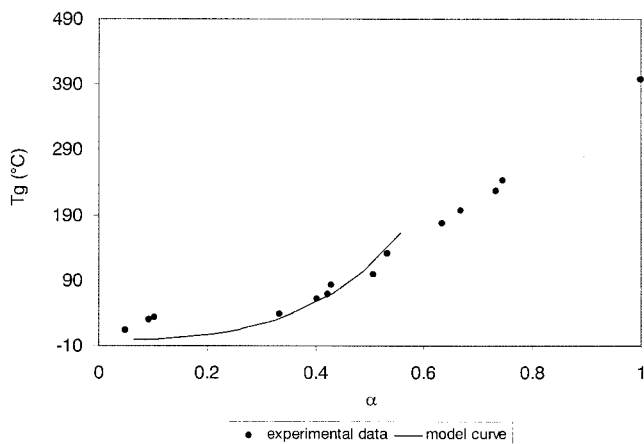
Figure 2 Modeling T_g–conversion relationship of the formulation DABA-0.5 in the copolymerization range.

The T_g–conversion relationship for DABA-0.5 was modeled using the model curve for DABA-1 and eq. (6), in the low-conversion regime. The result, for the low-conversion regime, is presented in Figure 2. As observed, there is excellent correlation between T_g and conversion in the low-conversion zone. For the high-conversion regime, the results were similarly modeled with the help of eq. (5) (the modified DiBenedetto equation), using the nonlinear regression analysis approach. The resulting model curve is presented in Figure 3. The value of λ_2 obtained in this case was 0.81 (Table I).

A comparison of the regression analysis parameters, obtained for the two formulations DABA-1 and DABA-0.5, shows that λ_2 is greater than λ_1. The influence of this parameter on T_g was previously reported by Boey and Qiang.[14] The low value of λ indicates that the increase in T_g value lags significantly behind the increase in the degree of conversion. On the other hand a higher value
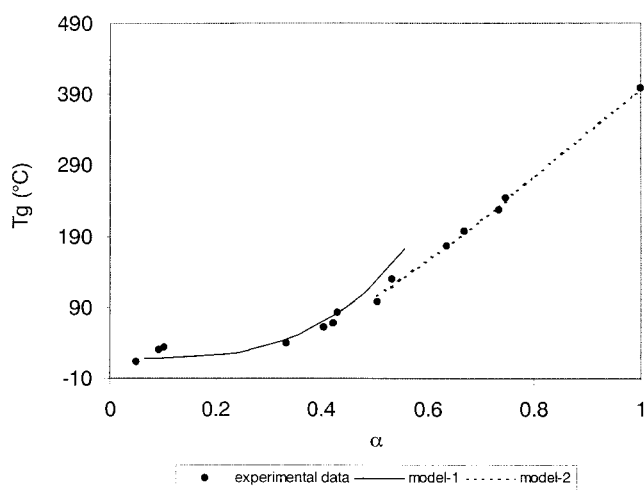
TABLE I
Nonlinear Regression Analysis Parameters

Parameter	DABA-1	DABA-0.5
λ_1	0.24	—
λ_2	—	0.81

of λ shows the T_g following closely and consistently with the degree of conversion. The significantly higher value of λ_2 indicates the T_g increase, caused by the process of BMI homopolymerization, was indeed faster than a similar increase from BMI/DABA copolymerization. In other words, the structure formed from homopolymerization was more rigid than that from copolymerization. This procedure is useful in modeling the T_g–conversion relationship for any intermediate formulation(s) of BMI and DABA.

CONCLUSIONS

The T_g–conversion relationship for BMI, modified with DABA, was successfully modeled by the DiBenedetto equation. The results of T_g–conversion modeling support our previous report that only copolymerization occurs in formulations containing BMI and DABA in stoichiometric quantities or excess of DABA. For formulations containing excess BMI, there is homopolymerization of excess BMI, which is also supported by the results of the modeling. It was found that the model can successfully be applied to similar formulations with any intermediate stoichiometry. It was also observed that the T_g increase caused by BMI homopolymerization was much faster than by BMI–DABA copolymerization.

Figure 3 Modeling T_g–conversion relationship of the formulation DABA-0.5 by two model equations.

References

1. Wang, C.-S.; Hwang, H.-J. J Polym Sci Polym Chem Ed 1996, 34, 1493.
2. Abbate, M.; Martuscelli, E.; Musto, P.; Ragosta, G. J Appl Polym Sci 1997, 65, 979.
3. Wu, W.; Wang, D.; Ye, C. J Appl Polym Sci., 1998, 70, 2471.
4. Mijovic, J.; Andjelic, S. Macromolecules 1996, 29, 239.
5. Phelan, J. C.; Sung, C. S. P. Macromolecules 1997, 30, 6845.
6. Pritchard, G.; Swan, M. Eur Polym Mater 1993, 29, 357.
7. Gopala, A.; Wu, H.; Xu, J.; Heiden, P. J Appl Polym Sci 1999, 71, 1809.
8. Mai, K.-C.; Huang, J.-W.; Zeng, H.-M. J Appl Polym Sci 1997, 66 1965.
9. Xiong, Y.; Boey, F. Y. C.; Rath, S. K.; Abadie, M. J. M. Journal, to appear.
10. DiBenedetto, A. T.; Nielsen, L. E. J Macromol Sci Rev Macromol Chem 1969, C3, 69.
11. Hale, A.; Macosko, C. W.; Bair, H. E. Macromolecules 1991, 24, 2610.
12. Couchman, P. R. Macromolecules 1978, 11, 117.
13. Xiong, Y.; Boey, F. Y. C.; Rath, S. K. J Appl Polym Sci, to appear.
14. Boey, F.; Qiang, W. J Appl Polym Sci 2000, 78, 511.