Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Cure Characterization of a New Bismaleimide Resin using Differential Scanning Calorimetry

Zhan-Sheng Guo[a]; Shan-Yi du[b]; Boming Zhang[b]; Zhanjun Wu[b]
[a] School of Aerospace Engineering and Applied Mechanics, Tongji University, Shanghai, P. R. China [b] Center for Composite Materials, Harbin Institute of Technology, Harbin, P. R. China

To cite this Article Guo, Zhan-Sheng , du, Shan-Yi , Zhang, Boming and Wu, Zhanjun(2006) 'Cure Characterization of a New Bismaleimide Resin using Differential Scanning Calorimetry', Journal of Macromolecular Science, Part A, 43: 11, 1687 — 1693

To link to this Article: DOI: 10.1080/10601320600938942

URL: http://dx.doi.org/10.1080/10601320600938942

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 43:1687–1693, 2006
Copyright © Taylor & Francis Group, LLC
ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320600938942

Cure Characterization of a New Bismaleimide Resin using Differential Scanning Calorimetry

ZHAN-SHENG GUO,[1] SHAN-YI DU,[2] BOMING ZHANG,[2]
AND ZHANJUN WU[2]

[1]School of Aerospace Engineering and Applied Mechanics, Tongji University,
Shanghai, P. R. China
[2]Center for Composite Materials, Harbin Institute of Technology, Harbin,
P. R. China

The cure characterization of a new BMI resin was investigated to ascertain a suitable cure model for the material. A series of isothermal differential scanning calorimetry (DSC) runs from 170°C to 220°C provided information about the cure characterization. All "kinetic triplet" (i. e., Arrhenius parameters A, activation energy E, and the reaction model, f(α)) of this new BMI system were calculated. It was found that the cure characterization of this new BMI could be expressed by nth-order cure reaction.

Keywords bismaleimide, cure characterization, differential scanning calorimetry, *n*th-order cure mechanism, reduced time method

Introduction

The mostly widely used composite matrixes in the aerospace industry are based on epoxy resins. In recent years, however, additional performance requirements have led to the development of poly(ether ether ketone) (PEEK), polyimides (PI), and bismaleimides (BMI). BMIs owing their popularity to superior thermal stability, mechanical strength, high fatigue resistance, and hot/wet resistance compared with those of epoxy resins, are widely used as matrix resins for advanced composites. In addition, the cure conditions for BMI resins closely mimic epoxies, so that special processing equipment is not required. Furthermore, BMI resins have found increasing applications in the microelectronic industries, bridging the temperature gap from epoxy systems to the very high temperature polyimide systems. The main disadvantage of these resins is their brittleness, which is a direct consequence of high crosslink density and inherent aromatic structure. Commercial systems are therefore formulated with various additives in order to increase their fracture toughness (1–6).

Boey et al. have attempted to describe the curing kinetics of BMIM/DABPA, amine and epoxy (2–4). They found that the reaction process was dominated by a different mechanism at different stages of the cure process, with an initial autocatalytic reaction

Address correspondence to Zhan-Sheng Guo, School of Aerospace Engineering and Applied Mechanics, Tongji University, Shanghai 200092, P. R. China. E-mail: guowinboy@163.com

shifting into an *n*th-order reaction as the reaction proceeded. However, they just investigated the cure kinetics at 170, 190, 210, and 220°C, omitted the cure information at 180 and 200°C. Acevedo et al. investigated the curing kinetics of the system containing N-phenylmaleimide and curing initiator dicumyl peroxide in the temperature range 120–160°C (7). They used the first-order model to fit their experimental data; the first-order model could be fit better up to 70-percentage conversion. Goodwin explored the curing kinetics of BMI and a bisphenol A derivative in the temperature range 180–200°C (8). He also used the *n*th-order model to fit his experimental data. Mijovic and Andjelie studied the isothermal BMI cure by remote fiber optic near infra-red spectroscopy in the 140–250°C range (9, 10). They reported the relative rates of allyl and maleimide consumption and that essentially complete conversion of these groups occurs at 200°C. Also, they observed the onset of dehydration at low temperature, 140°C, over a period of hours.

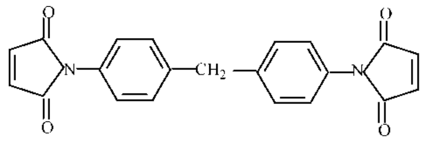
As a continuation of our comprehensive research program in the area of processing-structure-property-cost relationships in neat thermosets and composites (11–13), we describe a study of the cure characterization of the neat BMI resins in this paper. A variety of experimental techniques have been employed to study the kinetics of thermosetting reactions, including DSC, (2–8, 11–16) and Fourier transform infrared spectroscopy (FTIR) (9, 17–19). DSC is by far the widest utilized experimental technique to obtain the degree and reaction rate of cure of thermosetting resins.

The objective of this study was to utilize isothermal DSC to evaluate the mechanism of cure of BMI resins in the range of 170–220°C, by obtaining complete cure information of this neat BMI in the continuous temperature range. When combined with carbon fibers, the resins studied here become promising candidates for high performance composite structures in aerospace applications. The search for a mathematical description of the DSC data is usually sought in terms of a "kinetic triplet" (i.e., Arrhenius parameters *A*, activation energy *E*, and the reaction model, $f(\alpha)$).

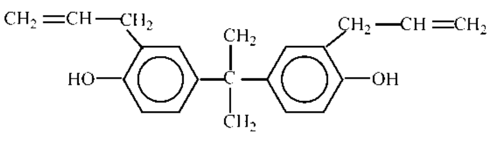
Experimental

Materials

The BMI resin was 4,4′-bismaleimidodiphenylmethane (BMIM) and 0,0′-diallyl bisphenol A (DABPA). BMIM was well mixed with 87 phr of bisphenol A at 130°C;



4, 4'-biamaleimidodiphenylmethane (BMI)



0, 0'-diallylbisphenol A (DABPA)

Figure 1. Chemical structures of an aromatic bismaleimide.

here BMIM is the base resin. They were stored at -18°C to prevent the cure reaction during the storage. A general scheme for the synthesis of a typical aromatic BMI is given in Figure 1.

Techniques

The DSC can operate under isothermal or non-isothermal (dynamic) conditions. To measure the total heat evolved during the complete cure, dynamic DSC analysis was carried out from 50 to 350°C at a heating rate of 10°C/min and to measure the cumulative heat for a given time of reaction, isothermal DSC analyses were performed at, 10°C intervals from 170°C to 220°C.

The heat of reaction of BMI was measured using a Perkin-Elmer (PE) Pyris 1 DSC.

The sample was weighed before and after each experiment to determine any mass loss during the measurements: an electronic balance with 0.005 mg accuracy was used for the measurements. In all cases for these experiments, the mass loss was found to be negligible.

Results and Discussion

The mechanism for crosslinking of thermosetting resins is very complex because of the relative interaction between the chemical kinetics and the physical properties, and it is still not perfectly understood. Two distinct approaches can be used: phenomenological (2–8) and mechanistic (9, 17–19). The former is related to an overall reaction (only one reaction representing the entire process), the latter to a kinetic mechanism for each elementary reaction occurring during the process.

The phenomenological models are semi-empirical and hence do not provide a clear description of the curing process and its chemistry. This study is focused on phenomenological models and is based on equation (1).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is a fractional conversion of the reactive group, called degree of cure, t is the reaction time, $f(\alpha)$ is a reaction model, also called the conversion function, which is determined for each system, and k is a rate constant, defined by an Arrhenius type of relationship:

$$k(T) = A\exp\left(\frac{-E}{RT}\right) \tag{2}$$

where A is the frequency factor or pre-exponential constant, E is the activation energy, R is the universal gas constant, and T is the processing temperature expressed in Kelvin. The search for a mathematical description of the DSC data is usually sought in terms of a "kinetic triplet" (i.e., Arrhenius parameters A, activation energy E, and the reaction model, $f(\alpha)$). Variations of $f(\alpha)$ can be found depending on the type of thermosetting resin and experimental conditions. A few functions for $f(\alpha)$ have been proposed in the literature (20), with the most common being equation (3).

$$f(\alpha) = (1-\alpha)^n \tag{3}$$

corresponding to a nth-order reaction and equation (4).

$$f(\alpha) = (k_1 + k_2\alpha^m)(1 - \alpha)^n \tag{4}$$

Because the cure of thermosetting resins is an exothermic process, with the reaction being the only thermal event that exists, the degree of cure, α, can be related to heat released during the reaction of the components. Thus, we have:

$$\alpha = \frac{H_t}{H_u} \tag{5}$$

where H_t is the heat of reaction at a specific time and H_u is the total heat of reaction at the end of the curing process when $\alpha = 1$. The cure rate is then:

$$\dot{\alpha} = \frac{d\alpha}{dt} = \frac{1}{H_u}\frac{dH}{dt} \tag{6}$$

because the total heat of reaction is a constant for a particular resin (20).

After the isothermal cure was completed, the isothermally cured sample was cooled rapidly in the DSC to 50°C. It was then analyzed using dynamic DSC at a heating rate of 10°C/min from 50 to 350°C in order to obtain the residual heat of reaction. Table 1 gives the total heat evolved per unit mass of the sample at all isothermal temperatures. From the dynamic DSC experiment we know the total heat was 288.44J/g. These measurements indicate that complete cure is never achieved when the cure temperature is below 220°C.

A series of isothermal reaction rate curves for BMI at six different temperatures are shown in Figure 2. With a decrease in cure temperature a decrease in the peak value of the reaction rate and its shift to longer times are observed. The maximum in the cure rate curves appear at about $t = 0$ means that the cure reaction follows an nth-order reaction; therefore, cure kinetics should be investigated using equation (7) in this system.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A\exp\left(\frac{-E}{RT}\right)(1 - \alpha)^n \tag{7}$$

Plots of degree of cure vs. curing time for BMI resin are shown in Figure 3. At any given time, the degree of cure is seen to increase as the temperature is increased. An increase in reaction rate was observed at a higher cure temperature. At the beginning, the reaction rate increases rapidly and reaches its maximum (Figure 3). After this point, it starts to decrease and gradually dies out because of diffusion-controlled reactions. Further study will be focused on this respect.

The rate constant k exhibits Arrhenius behavior, as shown in Figure 4. From equation (2), a plot of ln k vs. T^{-1} should be linear. Values for frequency factor A and activation energy E can be obtained from the intercept and slope, respectively. The frequency factor is $4.95 \times 10^8\ \mathrm{min}^{-1}$ and activation energy is 83.31 kJ/mol. They are consistent with the literature (9–13).

Table 1

Total heat of reaction for BMI samples cured at different temperature

Temperature (°C)	170	180	190	200	210	220
H_u (J/g)	68.4	128.5	180.2	212.4	264.6	288.44

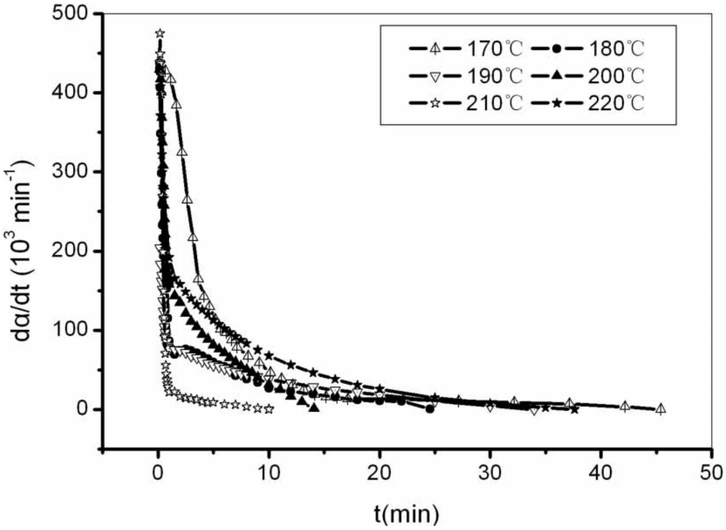


Figure 2. Cure rate vs. time at temperatures.

The reaction model can be determined by the reduced time method, which is called the Sharp method (also called induced-time method) (20). Sharp defined

$$G(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = kt = \frac{G(\alpha)_{\alpha=0.5}}{G(\alpha)_{\alpha=1.0}}\left(\frac{t}{t_{0.5}}\right) \tag{8}$$

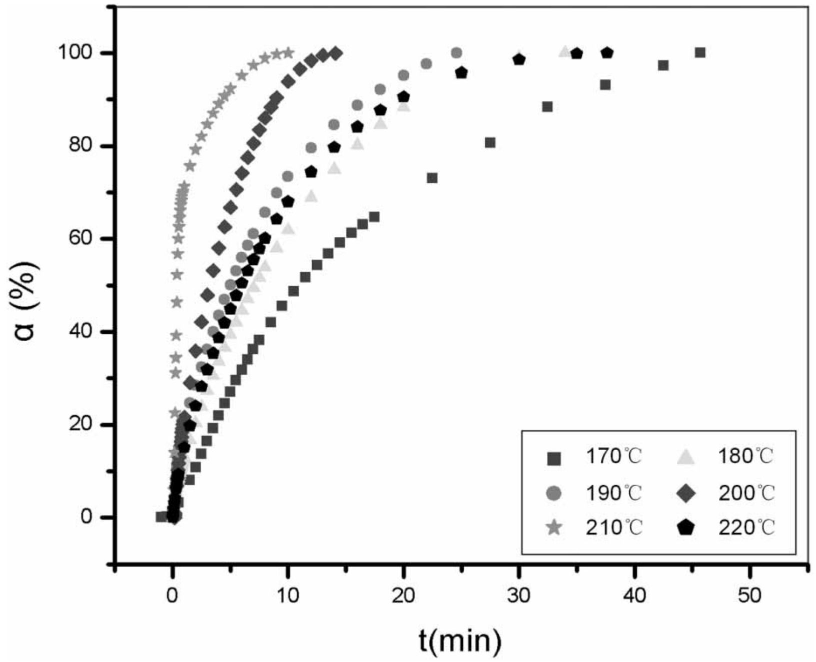


Figure 3. Degree of cure vs. time at temperatures.

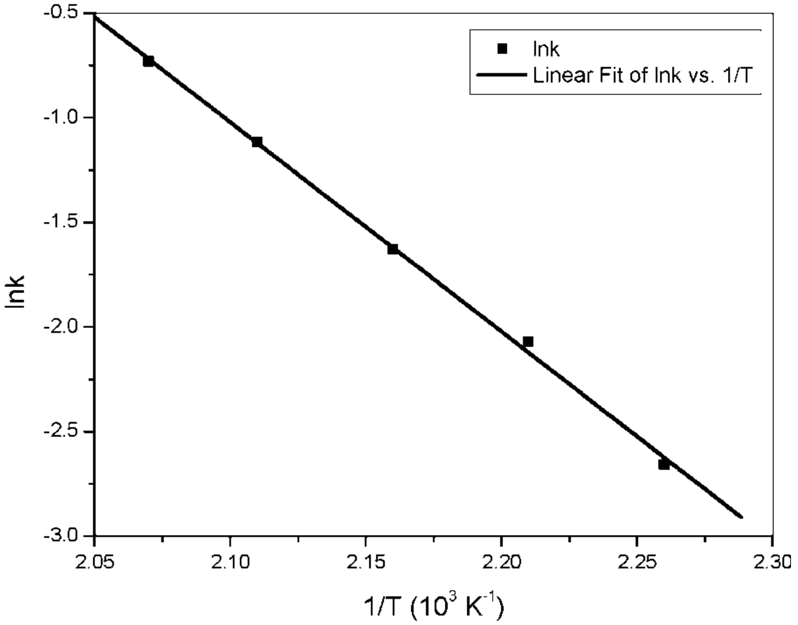


Figure 4. Kinetic constant vs. cure temperatures.

where $G(\alpha)$ is the integral conversion function, $G(\alpha)_{\alpha=0.5}$ and $G(\alpha)_{\alpha=1.0}$ are values when the degree of cure $\alpha = 0.5$, $\alpha = 1.0$, respectively. $t_{0.5}$ is the time when the degree of cure reached $\alpha = 0.5$. For a first-order reaction, the integral conversion function is:

$$G(\alpha) = F_1(\alpha) = \ln(1-\alpha) = -kt = -0.6931(t/t_{0.5}) \tag{9}$$

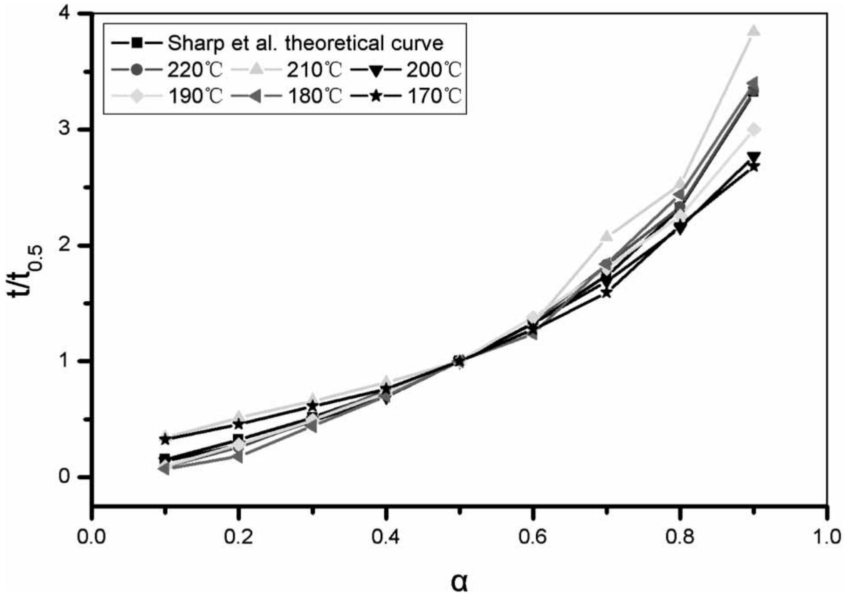


Figure 5. Comparison experimental data and theoretical data.

If the curve of experimental data α_i vs. $t_i/t_{0.5}$ ($i = 1, 2, \ldots, L$) agrees with one of the kinds of $G(\alpha)$ theoretical curves, this $G(\alpha)$ is the integral conversion function of the studied resin. For this BMI resin, Figure 5 is the result when the experimental data were compared with theoretical data where $G(\alpha) = \ln(1 - \alpha)$. It is clear they agreed very well.

Conclusions

The results of this study suggest the presence of a single mechanism during cure of this new bismaleimide. Kinetic parameters were calculated and the reaction model was determined by the method proposed by Sharp. From the isothermal DSC data, it was found that the first-order kinetic expression was correct to analyze the cure characterization of this new material system. An increase in degree of cure was observed at a higher cure temperature. When the cure processed, the reaction rate starts to decrease and gradually dies out because of diffusion-controlled reactions.

References

1. Boyd, J. (1999) *SAMPE J.*, 35: 13–22.
2. Boey, F.Y.C., Song, X. L., Rath, S.K., and Yue, C.Y. (2002) *J. Appl. Polym. Sci.*, 85: 227–235.
3. Boey, F.Y.C., Song, X.L., Yue, C.Y., and Zhao, Q. (2000) *J. Polym. Sci. Part A: Polymer Chemistry*, 38: 907–913.
4. Xiong, Y., Boey, F.Y.C., and Rath, S.K. (2003) *J. Appl. Polym. Sci.*, 90: 2229–2240.
5. Morgan, R.J., Shin, E.E., Rosenberg, B., and Jurek, A. (1997) *Polymer*, 38: 639–646.
6. Rozenberg, B.A., Dzhavadyan, E.A., Morgan, R., and Shin, E. (2002) *Polymers for Advanced Technologies*, 13: 837–844.
7. Abbate, M., Martuscelli, E., Musto, P., and Ragosta, G. (1997) *J. Appl. Polym. Sci.*, 65: 979–990.
8. Goodwin, A.A. (1993) *Polym. Int.*, 32: 87–92.
9. Mijovic, J. and Andjolic, S. (1996) *Macromolecules*, 29: 239–246.
10. Mijovic, J. and Schafran, B. (1990) *SAMPE J.*, 26: 51–59.
11. Du, S., Guo, Z.-S., Zhang, B., and Wu, Z. (2004) *Polym. Int.*, 53: 1343–1347.
12. Guo, Z.-S., Du, S., Zhang, B., and Wu, Z. (2005) *J. Appl. Polym. Sci.*, 97: 2238–2241.
13. Guo, Z.-S., Du, S., Zhang, B., and Wu, Z. (2004) *J. Appl. Polym. Sci.*, 92: 3338–3342.
14. Sourour, S. and Kamal, M.R. (1976) *Thermochimica Acta*, 14: 41–48.
15. Rosu, D., Mustata, F., and Cascaval, C.N. (2002) *Thermochimica Acta*, 383: 119–127.
16. Um, M.-K., Daniel, I.M., and Hwang, B.-S. (2002) *Compos. Sci. Tech.*, 62: 29–40.
17. Phelan, J.C. and Sung, C.S.P. (1997) *Macromolecules*, 30: 6845–6851.
18. Hopewell, J.L., George, G.A., and Hill, D.J.T. (2000) *Polymer*, 41: 8221–8229.
19. Hopewell, J.L., George, G.A., and Hill, D.J.T. (2000) *Polymer*, 41: 8231–8239.
20. Turi, E.A. (1998) *Thermal Characterization of Polymeric Materials*; Academic Press: New York, 1379.