第 17 卷 第 2 期 化 学 物 理 学 报 Vol. 17, No. 2
2004 年 4 月 CHINESE JOURNAL OF CHEMICAL PHYSICS Apr. 2004

1003-7713/2004/02-219-6

碳纤维/双马树脂预浸料体系的固化动力学

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摘 要： 给出了以等温固化航空航天工业用预浸料和纯树脂的固化动力学模型的研究. 树脂基体是改性的 BMI 树脂，增强相是碳纤维（T700-12S）. 用 n 级反应模型分析了一系列差示扫描量热法（DSC）的试验数据. 无论是纯树脂或是预浸料，固化温度越高，固化速率就越大. 达到峰值以后，固化速率降低比较快，导致预浸料体系的总反应热低. 纤维的存在明显影响树脂的固化反应，预浸料体系固化动力学参数和纯树脂的参数有显著差异. 增强纤维约束了树脂基体固化过程中的分子运动能力，降低了体系的固化程度，但没有改变树脂的固化机理.

关键词： 固化动力学；纯双马树脂；预浸料；DSC
中图分类号： O631 **文献标识码：** A

Cure Kinetics of Carbon Fiber/Bismaleimide Prepreg

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Abstract A new isothermally based cure kinetic model for the prepreg was presented using an industrially supplied prepreg rather than neat resin. The matrix resin was bismaleimide (BMI) resin, and the reinforcement was carbon fiber T700-12S. A series of isothermal Differential Scanning Calorimetry (DSC) tests were performed and analyzed by the proposed nth-order reaction model. An increase in the cure rate was observed at the higher temperature in both neat and prepreg. After reaching the peak value, the cure rate of resin dropped off faster in prepreg, resulting in a lower average value of the ultimate heat of reaction. The presence of carbon fiber was found to significantly impact the curing behavior of the resin, leading to significant changes from the neat resin kinetic parameters. The carbon fibers imposed restrictions on the molecular mobility of reactive species, reduced the extent of polymerization within the system and did not change the cure mechanism of resin.

Keywords Cure kinetics, Neat BMI, Prepreg, DSC

1 Introduction

Information on the kinetics of cure allows a proper design of the cure and post-cure cycles, which play a crucial role in the optimization of processing parameters and the quality of the final product. There are many literatures for studying the cure kinetic of resin[1-18]. As it is known, the resin usually flows through the fiber reinforcements when used in aeronautical or other in-

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Received 30 June 2003；in final form 15 October 2003.

dustries. These fibers may be sized, and they may change the kinetics. There is no consensus, however, with respect to the influence of fillers or reinforced materials on the cure kinetics[10-16]. For example, Dutta and Ryan studied the kinetic effects of carbon black and silica fillers on the cure of an epoxy-amine system[10], concluding that the heat of reaction is independent of the filler content but dependent on the type of filler. Han *et al.* found that the curing rate of a resin is greatly influenced by the presence of fibers and the type of fibers employed[11]. The cure rate of prepreg system can be very different from that of neat resin, after a 10min cure. Mijovic and Wang found that the presence of graphite fiber in a tetraglycidyl 4,4-diaminodiphenylmethane (TGDDM)/diaminodiphenyl sulfone (DDS) composite caused a slight increase in the cure rate but had no effect on the degree of cure[12]. Kaelble *et al.* found that differing surface treatments of a graphite fiber did not substantially alter the cure kinetic or degree of cure of an epoxy resin[13]. Grenier-Loustalot and Grenier investigated the curing mechanism of similar TGDDM/DDS systems in the presence of glass and carbon fibers[14]. They concluded that the presence of fibers did not change the reaction mechanism or network structure, but did lead to notable differences in the cure rate, especially at low temperature. Michaud *et al.* studied the cure kinetic of resin transfer molding (RTM) resin[15], and found that the fiber impacted the cure behavior significant, and reduced the extent of polymerization within the system. Wang *et al.* studied the isothermal cure of the commercial epoxy prepreg SPX 8800[16], containing diglycidyl ether of bisphenol A, dicyanodiamide, diuron, and reinforcing glass fibers, under two conditions by near-infrared spectroscopy (NIR).

There are several experimental techniques to characterization of thermosetting resin and prepreg, such as differential scanning calorimetry (DSC)[1-19], NIR[16,20], and Fourier Transform Infra-Red (FT-IR)[13,21-24]. DSC is the widest utilized experimental technique to obtain the degree and cure rate of cure of thermosetting resins.

As a continuation of our comprehensive research program in the area of processing-structure-property-cost relationship in neat thermoset resin and composites, we have undertaken a study of cure kinetics of neat BMI resins[2]. In this study, cure kinetic model is established for a benchmark prepreg system: T700/bismaleimide(BMI), a carbon fiber reinforced BMI resin.

2 Experimental

2.1 Materials

The material used in this study was carbon fiber/bismaleimide (T700/BMI) prepreg, which is commonly used as the polymeric matrix in high-performance composites employed in the aircraft, spacecraft and other industries. The BMI matrix resins consisted of 4, 4′-bismaleimidodiphenylmethane (BMIM, BMPM) and 0,0′-diallyl bisphenol A (DABPA, DABA). BMIM was well mixed with both 87 phr of bisphenol A and other materials at 130℃, where the unit phr was an abbreviation of" part per one hundred mass base resin ", and here BMIM was a base resin. The reinforcement material was carbon fiber (T700-12S). The prepreg was prepared at the room temperature by the wet impregnated method. Reactions during mixing were negligible, as confirmed by 4 h isothermal (60℃) DSC thermogram. The prepreg was then either tested immediately or stored in the refrigerator. If prepreg isn't used in one month, it should be discarded and a fresh one prepared.

2.2 Procedure

Samples were removed from the refrigerator and allowed to warm to 25℃. Small sample quantities (15 ~30 mg) were then placed in sealed aluminum pans. The calorimetric measurements were made with Perkin Elmer Pyris 1 DSC. An inter-cooler was used to stabilize the system. Nitrogen with a flow rate of 20 ~ 30 mL/min was used as a purge gas to minimize oxidation of the sample during the measurements. Before the measurements on the BMI, two standard materials, indium (99.999% pure) and zinc (99.999% pure), were used to calibrate the temperature and energy axis of the Pyris 1 DSC following the manufacturer's manual. Thermal equilibrium was regained within 1 minute

after sample insertion and the exothermic reaction was considered complete when the recorder signal leveled off to the baseline. The heat of reaction was determined by carrying the reaction isothermally to completion at the following temperatures：170，180，190，200，210，220℃. The total area under the exotherm curve，based on the extrapolated baseline at the end of the reaction，was used to calculate the isothermal heat of cure，H_T at a given temperature.

After the isothermal cure was completed，the sample was cooled down to 50℃ rapidly in the DSC. It was then heated at 10℃/min from 50 to 350℃ in order to determine the residual heat of reaction，H_{res}. The sum of the isothermal heat（H_T）and the residual heat（H_{res}）were taken to represent the ultimate heat of cure（H_u）. Finally，the samples were weighted again and compared to the initial weight. Weight losses were negligible in all cases.

3　Results and discussion

A series of isothermal DSC thermograms of prepreg systems are obtained and shown in Fig. 1. The cure rate，which is proportional to the rate of heat generation，passes through a maximum and then decreases as a function of curing time. Also，with a decrease of the cure temperature，the cure reaction shifts to a longer curing time. The maximum cure rate（peak value）curves appearing at about $t=0$ mean that the cure reaction follows an nth-order reaction. Such behavior is typical of the nth-order reactions and is analogous to that observed and reported in the neat resin[2]. After reaching the peak value，the cure rate falls off to the baseline quickly. The cure rate equation used to describe the cure kinetics is：

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

where $d\alpha/dt$ is the cure rate，and α is the degree of cure；$k(T)$ is the rate constant，defined by an Arrhenius type of relationship，and $f(\alpha)$ is the function of cure mechanism，usually determined by experimental data；n is the reaction order，R is the universal gas constant，A is the frequency factor or pre-exponential constant，E is the activation energy，and T is the processing temperature expressed in Kelvin. The cure rate is determined from the DSC trace，the expression as follow：

$$\frac{d\alpha}{dt} = \frac{1}{H_u}\frac{dH}{dt} \qquad (2)$$

where H_u，the ultimate heat of cure，is the sum of the isothermal heat of cure（H_T）and the residual heat（H_{res}）obtained in the subsequently dynamic DSC run. To calculate the degree of cure，the DSC curves are integrated and normalized with respect to H_u and sample weight. We also note that the calculations of heats of reaction（H_T and H_{res}）in reinforced systems are normalized with respect to the mass of BMI.

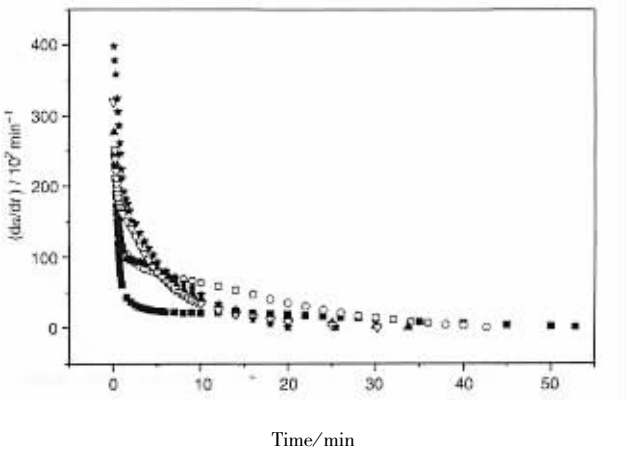

Fig. 1　Cure rate as a function of time at different temperatures
■ 170℃，○180℃，▲ 200℃，▽210℃，★ 220℃.

Values of the ultimate heat of cure，for both neat resin and prepreg system cured at different temperatures，are summarized in Table 1. The average value of H_u is higher for neat resin than that for reinforced resin. It appears then that the presence of carbon fiber contributes to a decrease in the overall number of chemical reactions and hence a lower value of H_u.

Plot of the degree of cure as a function of time for prepreg is shown in Fig. 2. The degree of cure increases with increasing temperatures. At a given time，the higher cure temperature，the higher degree of cure. The degree of cure increases quickly at the beginning of the cure stage，and becomes low in the latter cure stage. In the later cure stage，the cure is not controlled

by chemical reaction but by diffusion.

Table 1 The ultimate heat of cure as a function of cure temperature

Temperature/℃	Neat BMI resin/(J/g)	Prepreg (J/g)
170	86.53	71.22
180	161.5	135.71
190	180.2	149.83
200	212.4	184.45
210	264.6	206.43
220	288.44	221.93

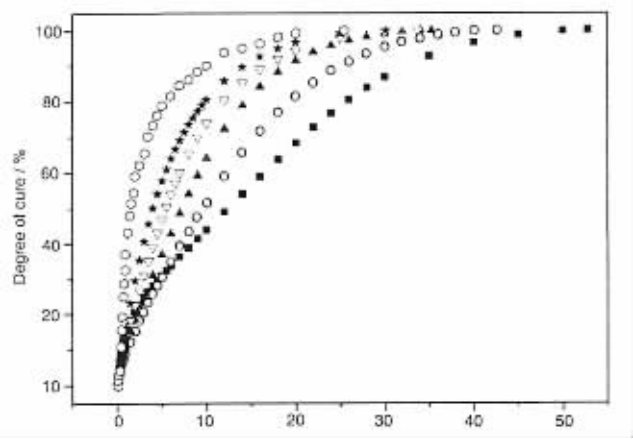

Fig. 2 Degree of cure as a function of time at different temperatures
■ 170℃, ○180℃, ▲ 190℃, ▽200℃, ★ 210℃, ⬡ 220℃.

A direct comparison between neat resin and prepreg system is shown in Fig. 3. The behavior difference is slight at lower cure temperatures, but significant at higher cure temperatures. The curves for prepreg are somewhat below the corresponding isotherms for neat resin. At the same temperature, the cure time for neat resin is shorter than that for the prepreg system. This may be caused by the fibers and viscosity increasing which impose restrictions on the molecular mobility of reactive species.

Cure rate as a function of degree of cure, with the temperature as a parameter, is shown in Fig. 4. Once again, the observed dependence is very similar to that reported for the neat resin[2]. It is seen in the Fig. 4 that the maximum cure rate occurs between 0 ~ 0.04% degree of cure. The *n*th-order reaction is generally characterized by the maximum rate at zero conversion[1]. By analyzing all isothermal cure temperatures

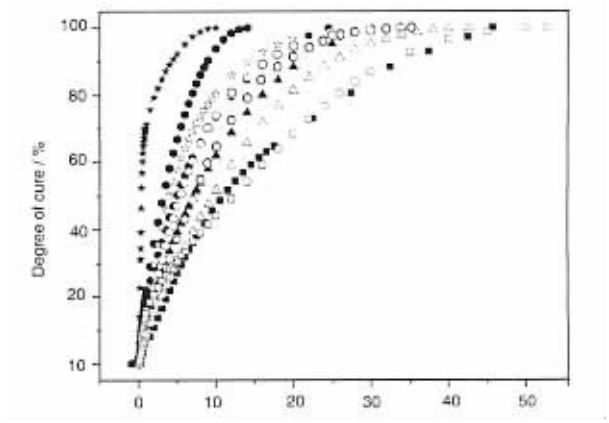

Fig. 3 Degree of cure vs. time for neat resin and prepreg system at different temperatures
■ BMI-170℃, ▲ BMI-180℃, ● BMI-190℃, ⬠ BMI-200℃, ★ BMI-210℃, ☆ Prepreg-210℃, ⬡ Prepreg-200℃, ⬠ Prepreg-190℃, △ Prepreg-180℃, □ Prepreg-170℃.

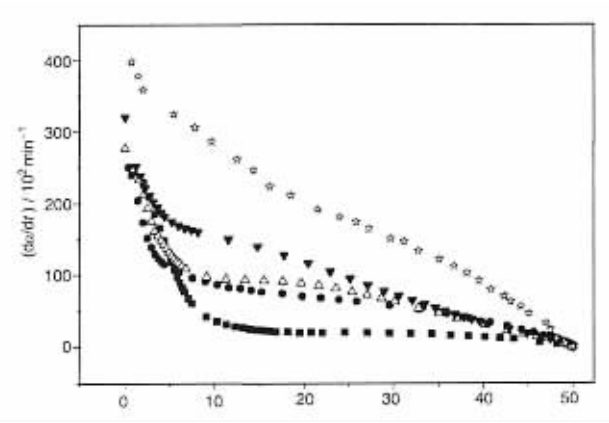

Fig. 4 Cure rate as a function of degree of cure at various temperatures
■ 170℃, ● 180℃, △ 200℃, ▼ 210℃, ☆ 220℃.

DSC curves, it is found that the time required to reach the maximum cure rate is approximately identical to zero. It is the same as neat resin.

Now we will determine the function of cure mechanism by the reduced time method, which is also called Sharp method[25]. For this prepreg system, Fig. 5 is the result when experimental data are compared with theoretical data where $G(\alpha) = \ln(1-\alpha)$. It is clear that they agree very well. This means that the conversion function $f(\alpha)$ is equal to $(1-\alpha)$.

As expected, the time required to reach the peak

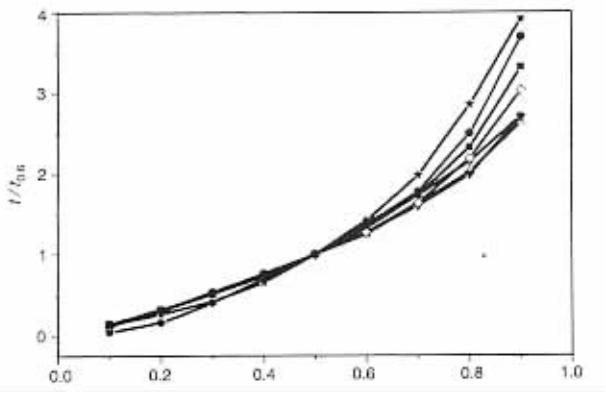

Fig. 5　The comparison experimental data and theoretical data for BMI resin

■ Sharp *et al.* theoretical curve, ● 170℃, ▼ 190℃, ◇ 200℃, △ 180℃, ○ 210℃, ★ 220℃.

(t_p) is found to decrease with increasing temperatures, in a linear fashion, as shown in Fig. 6. It is interesting to note, however, that the curves for the prepreg lie above those of neat resin. Hence at a given temperature, it takes a little longer to reach the maximum rate peak (t_p) in the presence of reinforcement.

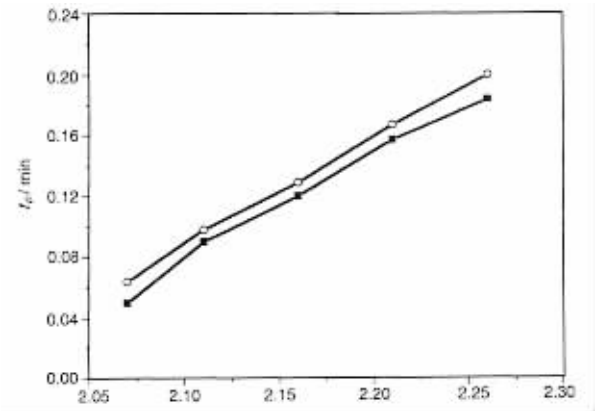

Fig. 6　Time to reach peak vs. cure temperature for neat resin and prepreg

■ BMI resin, ○ Prepreg.

The kinetic rate constant k is read off the original DSC trace and normalized with respect to the sample weight. The temperature dependence of cure rate constant k for both neat resin and prepreg can be presented by the Arrhenius equation. But the k values are slightly lower values for the prepreg than that for neat resin. A summary of the corresponding kinetic parameters is given in Table 2.

Table 2　Summary of kinetic parameters ($n = 1$)

	Neat resin	Prepreg
A/min^{-1}	4.95×10^8	4.11×10^5
E/(kJ/mol)	83.3	59.35

Although the effect of the reinforcement on cure kinetics is not only very pronounced, there are several points that should be emphasized. As one would expect, a higher cure temperature results in an increase in the cure rate in both neat and prepreg. The lower value of H_u in prepreg suggests the role of carbon fiber in restricting the molecular mobility of reactive species. As the diffusion control becomes progressively more important, the molecules in the vicinity of reinforcement are "shielded" (by carbon fiber) and hence increasingly less likely to encounter reactive species than the molecules in the bulk. That could be the reason why the cure rate, after going through the maximum, falls off to the baseline noticeably faster in the prepreg.

4　Conslusion

A new isothermally-based, cure kinetic model for the carbon fiber/BMI prepreg is presented using an industrially supplied prepreg rather than neat BMI resin. The DSC measurement of BMI prepreg is very useful in elucidating the curing process and in determining the kinetic parameters for the model. Its results can be used to optimize the curing process of BMI prepreg in its applications to aircraft and aerospace structures. The BMI prepreg is measured isothermally from 170 to 220℃. The isothermal cure reaction heat increases with the increment of cure temperature. The maximum reaction heat of isothermal cure can be achieved at 220℃. The degree of cure at isothermal cure temperatures below 220℃ is less than 1. In the earlier stage of isothermal cure reaction where the cure rate at the higher temperatures is faster than that at the lower temperatures, the cure reaction is controlled by chemical reaction, whereas in the latter cure stage, the cure reaction is controlled by diffusion.

Experimental results are described well by an *n*th-order reaction model. In all cases, higher cure temperature leads to an increase in cure rate. The degree of cure at the maximum rate of reaction is independent of temperature but takes a longer time to attain in prepreg. Values of the cure rate constant, k, are slightly lower for the prepreg. Also, the values of H_u are lower for prepreg. An explanation is offered in terms of the restrictions to molecular mobility imposed by the carbon fiber. The fibers act as heat sinks, reducing the peak exotherm, reducing the degree of cure within the system, and unchanging the cure mechanism.

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