Studies on Rheological Behaviors of Bismaleimide Resin System for Resin Transfer Molding

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Abstract: The rheological behavior of bismaleimide resin for resin transfer molding (RTM) was studied with DSC analysis and viscosity experiments. A rheological model based on the dual-Arrhenius equation was established and used to simulate the rheological behavior of the resin. The model predictions determined from the dual-Arrhenius equation were in good agreement with experimental data. The processing window of the resin system can be well determined based on the developed model. The rheological model is important for processing simulation and quality control of RTM processing for high performance composites.

Key words: composites; RTM; bismaleimide resin; rheological models; curing reaction kinetics
双马来酰亚胺树脂化学流变特性研究. 路遥, 段跃新, 梁志勇. 中国航空学报(英文版), 2002, 15(3): 181-185.

摘 要: 在粘度实验的基础上, 根据双阿累尼乌斯方程对用于 RTM 工艺的双马来酰亚胺树脂体系的化学流变特性进行了研究, 建立了树脂体系的流变模型。通过 DSC 热分析实验研究树脂体系的固化反应规律, 验证了双阿累尼乌斯模型。研究表明, 模型与实验结果具有良好的一致性。模型可揭示树脂体系在不同工艺条件下的粘度变化规律, 定量预报 RTM 工艺树脂的低粘度平台工艺窗口, 为合理制定 RTM 工艺参数、保证产品品质量和实现工艺参数的全局优化提供必要的科学依据。

关键词: 复合材料; RTM 工艺; 双马树脂; 流变模型; 固化反应动力学
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The RTM process has been recognized as a very high potential process for advanced composites manufacturing, and has been widely used in many industry fields such as aerospace, mobile and civil architecture. The RTM process must depend on the special low viscosity resin, whose rheological behavior contains a low viscosity area meeting the demand of the RTM. This means, the viscosity of the resin should maintain 50-200cP when injected in molding for complete fill and fiber wetting[1,2]. Therefore, through establishing the chemorheology model of the resin-viscosity function about temperature and time (or cure degree), the resin viscosity at any temperature and time (or cure degree) can be calculated, and the low viscosity area can be defined precisely. Hence, one can optimize the RTM process parameters and improve the quality of the products[3].

QY8911-4 BMI resin is a suitable resin for RTM. In order to optimize the RTM process parameters and improve the quality of the products, the chemorheological behavior of the QY8911-4 BMI resin is studied, its rheological model is established, and a processing window is predicted[4-8].

1 Viscosity Experiment

QY8911-4 BMI resin is prepared for determination of viscosity. Viscosity determinations are carried out at dynamic temperatures and selected

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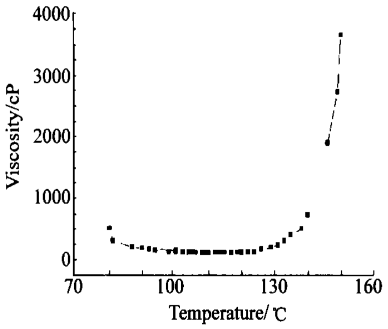
temperatures, using NDJ-1 rotating viscometer, according to GB7193. 1.

1. 1 Viscosity at heating condition

The viscosity curve of QY8911-4 BMI resin is shown as Fig. 1.



ig. 1 Viscosity-temperature curve of BMI resin system

For QY8911-4 BMI resin, its viscosity will descend with the heating condition. On the other hand, it will ascend because of resin cross-linking. During heating the resin, viscosity descending is primary at lower temperatures; otherwise ascending is primary at higher temperatures. The viscosity will be a minimum when the two effects keep balance. QY8911-4 BMI resin will be melted at 80°C. So viscosity measurement begins at 80°C. Viscosity maintains under 800cP between 80°C and 140°C. Therefore, isothermal viscosity measurement is selected in the range of 90-140°C.

1. 2 Isothermal viscosity measurement

According to the dynamic viscosity curve, isothermal viscosity measurements are carried out at 90°C, 126°C and 135°C. The curves of isothermal viscosity are shown as Fig. 2. The viscosity changing rate is improved with time and temperature.

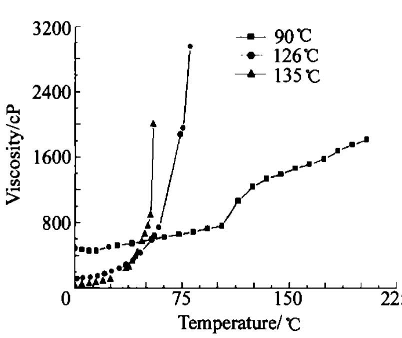


Fig. 2 Isothermal viscosity-time curves

2 Dual Arrhenius Model

In the case of isothermal cure, the viscosity, which is affected by time and temperature, can be described into the dual Arrhenius model given by[3]

$$\ln\eta(T,t) = \ln\eta_\infty + E_\eta/(RT) + k_\infty t\exp[E_k/(RT)] \qquad (1)$$

where η_∞ and k_∞ are the Arrhenius preexponential factors, respectively, while E_η and E_k are respectively the activation energies for the flow and the curing reaction. R is an ideal gas constant.

The model can be simplified

$$\ln A = \ln\eta_\infty + E_\eta/(RT) \qquad (2)$$

$$\ln B = \ln k_\infty + E_k/(RT) \qquad (3)$$

So the model can be described as

$$\ln\eta(T,t) = \ln A + Bt \qquad (4)$$

The curves of $\ln\eta$-t at the isothermal temperature are shown as Fig. 3.

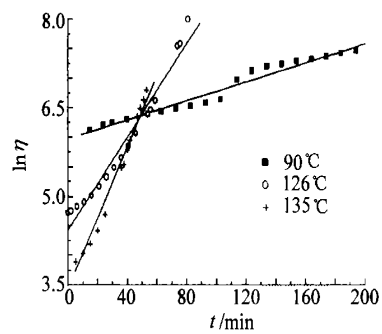


Fig. 3 $\ln\eta$ *vs* t curves at isothermal temperature

According to Fig. 3, the model parameters $\ln A$ and B can be calculated; the results are presented in Table 1.

Table 1 Parameters of the viscosity model

Temperature/°C	$\ln A$	B
90	5. 97	0. 008
126	4. 43	0. 039
135	3. 44	0. 060

The curves of $\ln A$-$1/T$ and $\ln B$-$1/T$ are presented in Fig. 4 and Fig. 5 respectively.

According to Fig. 4 and Fig. 5, one can obtain the following relation about the parameters $\ln A$ and $\ln B$

$$\ln A = -14.91 + 7603/T \qquad (5)$$

$$\ln B = 12.98 - 6465/T \qquad (6)$$

Note that the time unit should be changed

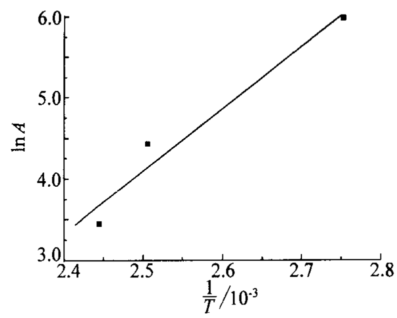


Fig. 4 ln$A$ *vs* 1/ T of the dual-Arrhenius equation

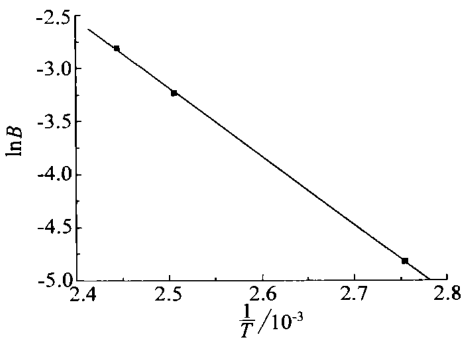


Fig. 5 ln$B$ *vs* 1/ T of the dual-Arrhenius equation

from minute to second, and the rheological model of QY8911-4 BMI resin can be presented as

$$\ln\eta = -14.91 + 7603/T + t\exp(17.07 - 6465/T) \quad (7)$$

For nonisothermal cure, where the resin temperature history is given by $T = f(t)$, the viscosity can be presented as an integral formation as

$$\ln\eta = -14.91 + \frac{7603}{T(t)} + \int \exp\left(17.07 - \frac{6465}{T(t)}\right) dt \quad (8)$$

3 Reaction Kinetics

The curing reaction kinetics of the resin is studied by DSC analysis[9-11]. In this paper, a kinetic model based on Kissinger function is established. The parameters in the kinetic model —— preexponential factor and the activation energy for the curing reaction —— are compared with the parameters in the dual Arrhenius model, so the rationality of the dual Arrhenius model and the physics definitions of the model parameters are verified.

3.1 DSC analysis

Differential Scanning Calorimetry (DSC) made in American Rheometric Scientific Company is used in this study. The resin samples are scanned at different heating rates as 5°C/min, 10°C/min and 20°C/min. And the results are shown in Fig. 6.

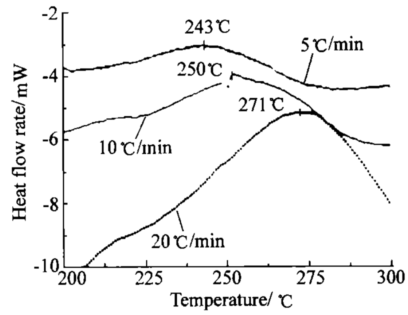


Fig. 6 Dynamic DSC curves at various heating rates

3.2 Data analysis

The Kissinger function is performed to describe the curing reaction kinetics of the thermalset resin. The relation between the temperature at maximum rate of the DSC curve and the constant heating rate is shown as follows[12]

$$\ln\left(\frac{\Phi}{T_m^2}\right) = (\ln A + \ln R - \ln E) - \frac{E}{RT_m} \quad (9)$$

where Φ is the constant heating rate; T_m is temperature at maximum rate; A is preexponential factor, and E is the activation energy of the curing reaction.

According to Eq. (9), plot $\ln(\Phi/T_m^2)$ *vs* $1/T_m$ as Fig. 7. The slope is $-E/R$, and the intercept is $\ln A + \ln R - \ln E$.

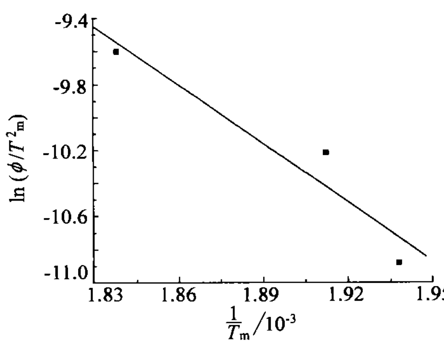


Fig. 7 $\ln(\Phi/T_m^2)$ *vs* $1/T_m$

The activation energy for QY8911-4 resin system is 98486J/mol, and the preexponential factor is 21.61.

The reaction order n can be determined by the peak shape factor S of the DSC curve. S is defined as the absolute ratio value of the tangent slopes at the curve inflection point. Therefore, n can be obtained as the following equation[13]

$$n \approx 1.26 S^{1/2} \quad (10)$$

The reaction order is 2.076 from Fig. 6.

So the curing reaction kinetic model of QY8911-4 resin system is shown as

$$\frac{d\alpha}{dt} = 21.61 e^{-11846/T}(1-\alpha)^{2.076} \quad (11)$$

Eq. 11 can be presented as an integral formation as

$$\alpha = 1 - [1 - (1 - 2.076) 21.61 t e^{(-11846/T)}]^{\frac{1}{1-2.076}} \quad (12)$$

The curing degree vs time at different isothermal temperatures is shown as Fig. 8.

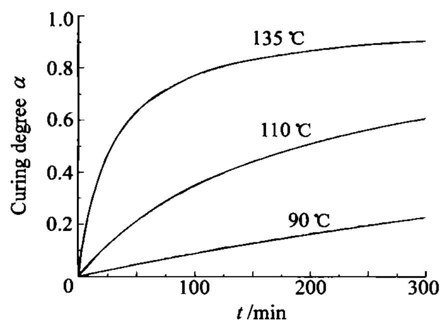


Fig. 8 Isothermal curing degree vs time curves

According to Fig. 8, the curing degree vs time shows the linear relation on the initial stage of the curing reaction, and the time maintaining the linear relation accords with the time maintaining the low viscosity in the dual Arrhenius model. It is certain that the assumption for the dual Arrhenius model (the curing degree vs time shows the linear relation in the low viscosity area) is right.

The parameter relationship between the dual Arrhenius model and the Kissinger equation is presented as the following experience equation

$$E = E_k^{n-1} \quad \text{and} \quad k = k_\infty^{n-1} \quad (13)$$

where E and k are the activation energy and the preexponential factor from the Kissinger equation; E_k and k_∞ are from the dual Arrhenius model; n is the reaction order.

The results of the parameters of the dual Arrhenius model compared with the parameters of the Kissinger equation are shown in Table 2.

Table 2 The parameters of the two models

para	dual Arrhenius	Kissinger	Calc.	error/%
k	17.07	21.61	21.18	1.96
E/R	6465	11846	12594	6.32

According to the DSC analysis, one can conclude that the resin viscosity at the low curing degree area can be calculated by the dual Arrhenius model, and the parameters in the dual Arrhenius model and in curing reaction kinetics have the corresponding relation.

4 Model Application

4.1 Prediction of processing window

The resin viscosity at a certain temperature and time can be calculated by the dual Arrhenius model. The viscosity map is shown as Fig. 9.

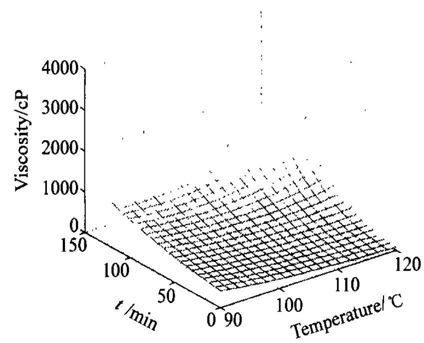


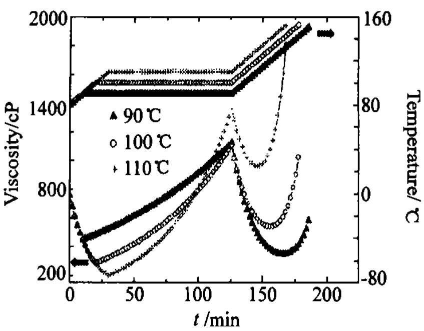
Fig. 9 Viscosity map

The temperatures, at which the resin viscosity is less than 800cP and the time maintaining the low viscosity is more than 40 minutes, are 90°C, 100°C, 110°C and 120°C. Therefore, the processing windows of the QY8911-4 BMI resin system for the RTM processing are the temperature range from 90 to 120°C.

4.2 Viscosity simulation

For nonisothermal cure, where the resin temperature history is given by $T = f(t)$, the viscosity can be presented as the integral formation as Eq. 8. So the viscosity can be simulated at the given condition of the temperature as a function of time, and the results are shown in Fig. 10.

The resin is heated at a constant rate, maintained at an assigned temperature for about 100 minutes, and then heated again to cure complete-



ig. 10 Calculated viscosity during processing procedure

ly. From Fig. 10, one can get the same trends at different conditions: At the first heating stage, the viscosity drops continually, at isothermal stage, the viscosity rises gradually, and at the second heating stage, the viscosity drops momently and rises quickly to a gel point.

Compared with different viscosity curves, at 110℃ the viscosity can maintain less than 300cP for 55 minutes. So the resin can be suitable to manufacture the medium or small sized structures as the RTM processing. One can confirm that the temperature at 110℃ is the suitable injection temperature. If the parts are relatively large and the injection time is long, the temperatures at 90-100℃ are the suitable injection temperature.

5 Conclusions

QY8911-4 BMI resin system is the suitable resin for the RTM processing. The dual Arrhenius model can be used to present the rheological behavior of the QY8911-4 BMI resin at low viscosity areas. And the model predictions are in good agreement with experimental data. The processing window for the RTM processing can be predicted precisely by the dual Arrhenius model, and the viscosity can be simulated during the processing procedure. The rheological model is important for processing optimization and quality control of RTM processing for high performance composites.

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