

STUDY OF GELATION USING DIFFERENTIAL SCANNING CALORIMETRY (DSC)

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Abstract

A new method for determining the degree of conversion of gelation (α_{gel}) and gel time (t_{gel}) at gel point using a single technology, DSC, is discussed in this work. Four kinds of thermoset resins are evaluated. It is found that the mutation points of reduced reaction rate (V_r) vs. reaction conversion (α) curves, corresponding with the changes of reaction mechanism, represents the gelation of the reaction. The α at the mutation point is defined as α_{gel} . From isothermal DSC curves, the point at α_{gel} is defined as t_{gel} . Traditional techniques (ASTM D3532 and DSC method) are also used to determine α_{gel} and t_{gel} in order to demonstrate this new method. We have found that the results obtained from this new method are very consistent with the results obtained from traditional methods.

Keywords: curing, DSC, epoxy, gel time, gelation

Introduction

Gelation is one of the most important properties of thermoset polymers and has direct influence on storage and shelf life as well as processing parameters. During gelation, resin changes from a viscous liquid to an elastic gel. After this stage, resin does not possess favorable properties for flow, primary processing and storage.

The degree of conversion of gelation (α_{gel}) and gel time (t_{gel}) at gel point are the most important parameters normally used for determining gelation of polymer resins. Traditional methods for determining gelation use a significant change of some physical phenomena, such as modulus, viscosity, dielectric properties, occurring at the gel point, to quantify gelation. Two technologies have to be used for measuring α_{gel} and t_{gel} . First, mechanical techniques, which are sensitive to physical or mechanical property changes which are used to determine the t_{gel} at a series of constant temperatures. Then, a second technique, such as DSC or IR, which is sensitive to chemical changes, is used to measure the α_{gel} of resin at its gel point [1-5].

A new method for determining α_{gel} and t_{gel} using a single technology, DSC, is discussed in this work. Four kinds of thermoset resins are evaluated. Two of the resins are autocatalyzed reactions, and the remaining two are N th order reactions.

From isothermal DSC scans, a series of reduced reaction rate (V_r) vs. reaction conversion (α) curves can be obtained according to the related isothermal kinetics reaction modes. During a chemical-reaction the viscosity and chemical structure of a resin are changed. These changes may cause the mutation of reaction speed ($d\alpha/dt$). The reaction speed is determined by its reaction mechanism and the relative concentration of reactants. The dramatic change of reaction speed is normally due to changes of reaction mechanism. Although gel point and vitrification point of thermoset polymer represent different physical status, they are all related to the change of reaction mechanism and relative concentration of reactants. The gel point and related parameters, such as gel time and reaction extent at gel point, are focused in this work. It is found that change of reaction mechanism will change the slope of V_r vs. α curves dramatically. Therefore, the point of mutation or onset is the transition of reaction mechanism, which is in agreement with the gel point. Before the mutation point, the reaction is chemically controlled and dependent upon the concentration and reaction/energy rate of the reactants. After this point, the diffusion controlled reaction takes place. It is evident that the reaction rates of chemical controlled and diffusion controlled reactions are different because of the different reaction mechanisms [6, 7]. Therefore, the transition point of reaction is defined as the gel point in this work. At the mutation point of V_r vs. α curve, the point of X axis (α) is defined as α_{gel} . From isothermal DSC curves, the correspond of the points at α_{gel} is defined as t_{gel} . In order to prove this new measuring method, traditional techniques (ASTM D3532 and DSC method) are used to determine α_{gel} and t_{gel} . It is found that the results obtained from this new method are very consistent with the data obtained from traditional methods. In addition, a detailed mathematical model is discussed.

Samples and experiments

Samples

Four kinds of thermoset resins, modified Bismaleimide (4501A), Epoxy 913C, Epoxy HD03, and Epoxy E-51/DDM, were used for this evaluation. These resins are mainly used in high performance composite materials.

4501A, provided by the Composite Materials Research Institute of Aircraft Special Structures, China, is a modified Bismaleimide resin pre-polymerized by 4,4'-Bismaleimide diphenylmethane and 0,0'-Diallyl bisphenol A.

913C and HD03 epoxy resins were provided by Beijing Institute of Aeronautic Materials and Xian Aircraft Corporation, respectively.

E-51/DDM epoxy resin, provided by Wuxi Resin Plant (E-51) and Shanghai No. 6 Chemicals Plant (DDM), is polymerized product of E-51 epoxy resin and 4,4-Dimandiphenylmethane (DDM) at the weight ratio of 100:27.75.

DSC measurement

A Perkin-Elmer Differential Scanning Calorimetry DSC 7 was used for measuring heat flow and energy change during chemical reaction of the resins. Isothermal

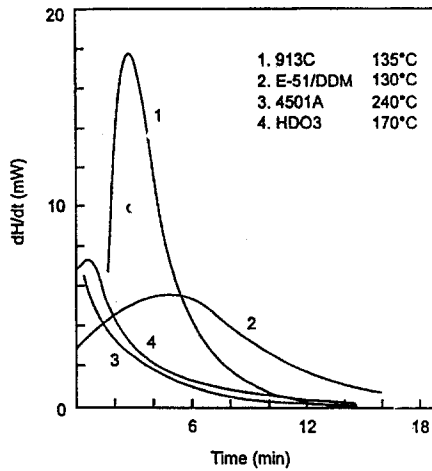


Fig. 1 The typical DSC isothermal scan curves of the four kinds of resin

and temperature scan methods were used for these measurements. The typical isothermal DSC curves of these resins are shown in Fig. 1.

The reaction rate, $d\alpha/dt$, and reaction extent, α , at time, t , can be calculated using equations below:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_{ult}} \tag{1}$$

$$\alpha = \frac{1}{\Delta H_{ult}} \int_0^t \frac{dH}{dt} dt \tag{2}$$

where the dH/dt is the heat flow rate, and ΔH_{ult} is the ultimate reaction heat calculated from the DSC temperature scan curve at $10^\circ\text{C min}^{-1}$.

Gel point measurement

A standard testing method, ASTM D3532, was used for determining the gel time of epoxies. A small probe was used to draw the resin to form strings as the glass tube, contained 2–3 gram sample, was dipped into an oil-bath at controlled temperatures. The time was recorded from the beginning. When the sample reached the point at which strings could not be formed, the time was defined as the gel time, t_{gel} .

The resin at the gel point was quenched to room temperature. A DSC was used for determining the residual curing heat, ΔH_{ris} , at temperature rate of $10^\circ\text{C min}^{-1}$. The α_{gel} was calculated from:

$$\alpha_{gel} = 1 - \frac{\Delta H_{ris}}{\Delta H_{ult}} \tag{3}$$

Table 1 The t_{gel} and α_{gel} measured by DSC and String drawing methods at different isothermal temperatures

Samples	$T/$ °C	DSC method		String drawing method	
		$t_{gel}/$ min	$\alpha_{gel}/$ %	$t_{gel}/$ min	$\alpha_{gel}/$ %
913C	115	12.70	54.93	8.17	
	125	6.72	51.55	5.83	
	130	4.75	50.48	4.16	53.10
	135	3.47	52.04	2.83	
E-51/DDM	100	30.53	60.24	22.67	
	110	18.79	63.53	17.40	
	120	13.15	65.87	11.33	68.50
HD03	140	5.28	64.58	5.28	
	160	11.24	60.00	10.00	
	170	8.05	62.01	5.01	65.87
4501A	180	3.21	61.50	2.50	
	200	10.50	36.50	10.00	
	220	4.60	40.00	1.67	
	240	2.25	37.01	0.91	36.50
	260	0.91	37.00	0.45	

The measured gel times and the calculated degrees of conversion at the gel point are listed in Table 1.

Results and discussion

Isothermal DSC heat flow curves of these four kinds of resins are shown in Fig. 1. It can be found that the reaction rates of Epoxy 913C and E-51/DDM resins increased to maximum at certain time, and then decreased with the continuation of the reaction. Whereas, the heat flow curves of Bismaleimide 4501A and Epoxy HD03 resins have different shapes with 913C and E-51/DDM. The reaction speeds were almost maximum at the beginning of the reaction and then decreased along with the reaction time. This main difference is because of the distinction in reaction mechanism [1]. According to the shape of heat flow curves showed in Fig. 1, the reaction mechanism of these four kinds of epoxy can be determined. The 913C and E-51/DDM follow autocatalyzed reaction mode, whereas the 4501A and HD03 are N th order reaction mode.

For autocatalyzed chemical-controlled reaction, the kinetic equation can be expressed as below [1, 6, 7]:

$$\frac{d\alpha}{dt} = (k_1\alpha + k_2)(1 - \alpha)(B - \alpha) \quad (4)$$

where k_1 and k_2 are constants of autocatalyzed and catalyzed chemical reaction, B is the mole ratio of catalyst to epoxide equivalent.

When $d\alpha/dt$ reaches maximum, α_p , the calculated B , using the equation below, are 0.8 and 1.24 for 913C and E-51/DDM, respectively.

$$3\alpha_p^2 - 2\alpha_p(1 + B) + B \cong 0 \quad (5)$$

Based on Eq. (4), the reduced reaction rate, V_r , is defined as:

$$V_r = \frac{d\alpha/dt}{(1 - \alpha)(B - \alpha)} = K_2 + K_1\alpha \quad (6)$$

Figures 2 and 3 are the plots of V_r vs. α of 913C and E-51/DDM resins at various isothermal temperatures. The plots of V_r vs. α would be straight lines with slopes of K_1 and interceptions at K_2 at different temperatures if the reactions were purely chemical-controlled [6, 7]. From Figs 2 and 3, it is observed that curves of V_r vs. α have good linear relationship when the α are small (lines 1, 2, 3, $\alpha < 40\%$; lines 4,5, $\alpha < 50\%$). However, the slopes of the curve change dramatically when the α is higher than 50% ($\alpha > 50\%$) This is because of the more extensive three-dimensional polymer structure formed during the reaction, which largely limits the chemical-reaction rate. Thereby, the chemical-controlled reaction change into the diffusion-controlled reaction mechanism. The point of the maximum curvature is considered as the transition of reaction mechanisms.

Normally, there are two reasons to make the change of reaction mechanism. One is the gelation which occurs at the same reaction extent at various temperatures, and does not affect the curing reaction. Another is the vitrification that occurs at various reaction extents and increases with the reaction temperature till reaching the ultimate glass transition temperature, $T_{g\infty}$ [1, 5, 8-10]. From Figs 2 and 3, it can be seen that the transitions of reaction mechanism would not vary with different isothermal temperatures. They maintained nearly the same reaction ex-

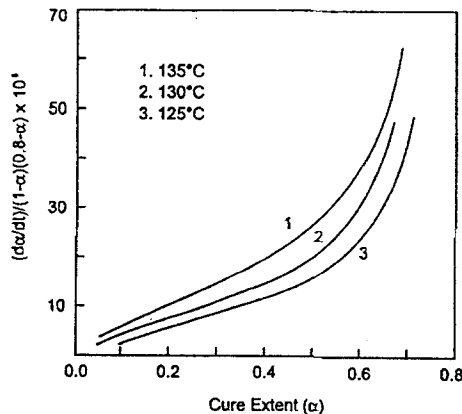


Fig. 2 The reduced reaction rate (V_r) vs. reaction conversion (α) curve of Epoxy 913C at different isothermal temperatures

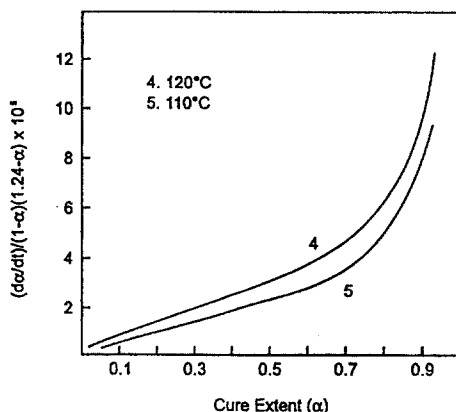


Fig. 3 The reduced reaction rate (V_r) vs. reaction conversion (α) curve of Epoxy E-51/DDM resin at different isothermal temperatures

tents. At this point, the α complies with the α_{gel} measured by string-drawing method (ASTM D3532). Comparing the transition α measured by DSC and α_{gel} measured by string-drawing method listed in Table 1, it is indicated that the transition α at mechanism change is very consistent with the α_{gel} measured by string-drawing method. Therefore, the corresponding transition point of V_r vs. α curve is defined as the gel point. The corresponding α and t are called α_{gel} and t_{gel} , respectively. The DSC data of α_{gel} in Table 1 is obtained at the point of tangent onset of V_r vs. α curve. The t_{gel} is the corresponding point of time at α_{gel} .

For N th order chemical reaction, such as 4501A and HD03 resin systems, the reaction mechanism can be described as [1, 6, 7]:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (7)$$

where k and n are reaction constant and reaction order, respectively. According to Eq. (6), the reduced reaction rate, V_r , can be defined as:

$$V_r = \frac{d\alpha/dt}{(1 - \alpha)^n} = k \quad (8)$$

The reaction order, n , can be any number of 0.5, 1.0, 1.5, 2.0, etc.. Theoretically, when n is proper to fit a typical reaction, the plot of V_r vs. α should be a horizontal line intercepting at k for a real N th order reaction. The mutation points of V_r vs. α , plotted in Fig. 4, of HD03 resin system also indicated the mechanism changes of the reaction. For 4501A system, the break points of V_r vs. α plots shown in Fig. 5 were also observed. At these points, the overall concave shape of the curves changed when the α passed through the reaction mechanism transition. The corresponding α , therefore, is also consistent with the data obtained from string-drawing method. All results are also listed in Table 1.

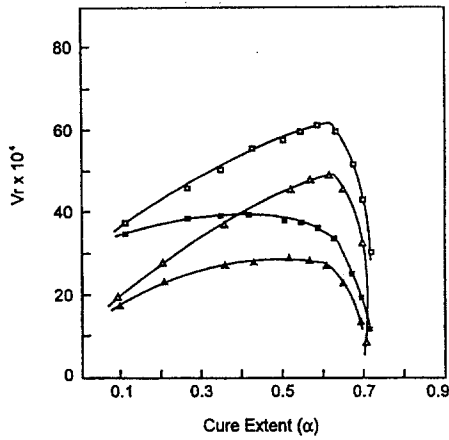


Fig. 4 The reduced reaction rate (V_r) vs. reaction conversion (α) curve of Epoxy HD03 resin when $n=1.5$ (\square) and $n=1.0$ (\blacksquare) at 170°C , and when $n=1.5$ (Δ), $n=1.0$ (\blacktriangle) at 160°C

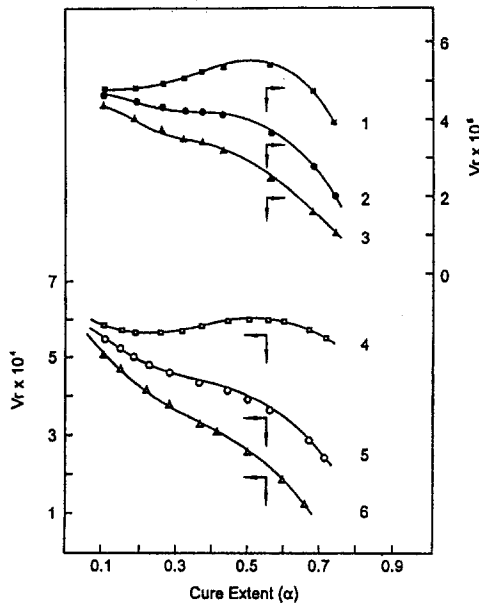


Fig. 5 The reduced reaction rate (V_r) vs. reaction conversion (α) curve of Bismaleimide 4501A resin when $n=1.0$ (curve 1), 0.5 (curve 2), and 2.0 (curve 3) at 240°C , and when $n=0.5$ (curve 4), 1.0 (curve 5), and 1.5 (curve 6) at 200°C

A small difference of α_{gel} and t_{gel} measured by string-drawing method and DSC has been found. This is mainly because of the difference of two experimental methods. String-drawing method uses change of physical property to determine the gel point. DSC measures the change of chemical reactions. In addition, the sample

temperature in DSC is well controlled and much uniform than the temperature at the sample tube in string-drawing method. Therefore, using DSC can provide a more accurate results.

Since curing reaction of thermosetting epoxies is non-uniform system, the diffusion-controlled reaction can happen at any time of the reaction. Normally, chemical-controlled reaction is considered at the beginning of curing. With the increase of viscosity of epoxy during curing, the reaction mechanism can be changed. At high viscosity, diffusion-controlled mechanism will play an important role. The reaction modeling and mechanism have been well addressed by Gillham and Prime [3, 5, 11, 12]. A simple and fast method for determining α_{gel} and t_{gel} , which is useful for industry process control, is only discussed in this work. The related kinetics and reaction mechanism are not focused.

Conclusion

DSC technique can be effectively used for determining the occurrence of gelation in thermoset polymer curing. Because of the changes of reaction mechanism from chemical-controlled to diffusion-controlled, the mutation points of V_r vs. α plots can be defined as the gel point. The results obtained from DSC are consistent with the data obtained from the traditional string-drawing method.

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