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The cure behavior of tetraglycidyl diaminodiphenyl methane with diaminodiphenyl sulfone

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Abstract

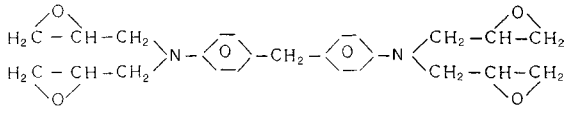
It is well known that the preparation of an high-performance composite product depends not only on raw materials (resin and fiber) but also on the curing technological condition, or rather, the determination of the curing technological parameters. In this study torsional braid analysis (TBA) is used to study the cure behavior of tetraglycidyl diaminodiphenyl methane (TGDDM or Ag-80) with diaminodiphenyl sulfone (DDS), providing theoretical data for determining the curing condition of this resin matrix composites. Isothermal TBA technique is used to obtain a time–temperature-transformation (TTT) cure diagram, according to which the three different types of cure behavior are discussed. The data for T_g for different cure temperatures and times provide and estimation of the time to full cure vs. isothermal cure temperature for the resin system. An empirical T_g–T_c–time (TTT) equation is also developed.

Keywords: Cure behavior; TBA; Epoxy resin; TTT diagram; TTT equation

1. Experimental

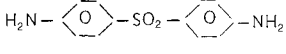
1.1. Material

(1) *Resin*. A commercial grade of TGDDM, i.e., Ag-80 supplied by Shanghai Institute of Synthetic Resins, is used as received. Its molecular formula is as follows:



It is a thick and tacky liquid with viscosity from 7000 to 10 000 cP. Its epoxy value of this resin is approximately 0.80.

(2) *Curing agent*. The curing agent used in this investigation is chemically pure DDS supplied by Shanghai No. 2 Chemical Pharmaceutical Factory. This is a white powder crystal with a melting point of 180°C and amino equivalent of 62. Its molecular formula is as follows:



1.2. Instrument

A NBY-1 TBA instrument made by the National Changkong Machinery Factory is used in this study.

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Details for the TBA apparatus have been described elsewhere [1].

1.3. Experimental procedure

(1) *Matrix formulation*. Stoichiometric mixtures (one epoxy group per amine hydrogen) of Ag-80 (epoxy value, 0.80) and DDS (amine equivalent, 62) are used as reactive systems in this investigation. Solutions of the reactive mixtures (50% in acetone, weight/volume) are used after being stored in a freezer for not more than a week, during which their viscosity does not change at room temperature.

(2) *Specimen preparation*. A multifilamented glass braid, after having been heat-cleaned at 450°C for 2 h, impregnated with the acetone solution of the reactants, and dried in vacuum at room temperature, to obtain a composite specimen.

(3) *TBA analyses*. The prepared specimen is mounted in the TBA specimen chamber. Changes in the dynamic viscoelasticity due to cure are monitored as a function of time or temperature by measuring relative rigidity and logarithmic decrement.

Two types of TBA techniques are employed in this investigation, they are:

1. Isothermal TBA — torsional braid analysis at the chosen constant temperatures.
2. Dynamic TBA — torsional braid analysis at the heating rates of 2°C/min.

2. Results and discussion

2.1. Dynamic scan for fully cured resin

According to the standard cure recommended, a fully cured specimen is prepared by heating it at 150°C for 2 h and then at 180°C for 3 h with a postcure at 200°C for 3 h. The dynamic scan for the fully cured resin is shown in Fig. 1. The value of T_g^{∞} is 263°C, located by maximum in the logarithmic decrement plot.

2.2. Isothermal TBA

The TBA curves for isothermal cure (Fig. 2) show that, depending on the curing temperature, there are three different type of dynamic behavior

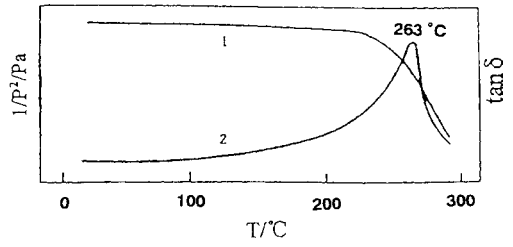

Fig. 1. Dynamic TBA scan for the fully cured specimen: (1) relative rigidity; (2) logarithmic decrement.

1. Fig. 2, curve (a) shows the first type of behavior at relatively low temperatures where a single logarithmic decrement peak A is accompanied by a slight increase in rigidity, because molecular chains are frozen at low temperatures and thus gelation does not occur, the epoxy system would convert from liquid state directly into glassy state.
2. In Fig. 2, curves (b)–(e) at higher temperatures, the relative rigidity plots show two distinct increases. Correspondingly, the two peaks A and B appear in the logarithmic decrement plots. It can be verified through DSC that, the first smaller peak B in logarithmic decrement is associated with gelation of the system, while the second larger peak is associated with vitrification (i.e., transition to the glassy state). Therefore, the times to gelation and to vitrification can be given in Table 1 by the times at the logarithmic decrement peak maxima.
3. Curve (f) in Fig. 2 shows further increase in the cure temperature is accompanied by the disappearing of peak A in the logarithmic decrement plots. The resin system changes into rubbery state and then into glassy state because of the violent motion of molecular chain segments at high temperatures.

Table 1
Values of t_g and t_v for isothermal cure temperatures (the extrapolated values are in brackets)

T (°C)	t_g (min)	t_v (min)	T (°C)	t_g (min)	t_v (min)
95	745	1258	148	73.0	144
107	522	710	158	48.7	96.6
115	(355)	497	164	34.8	75.6
126	212	(346)	172	25.0	55.8
136	127	257	178	20.9	40.1
138	119	222	199	9.6	23.8
142	92.4	179	210	(6.7)	16.4

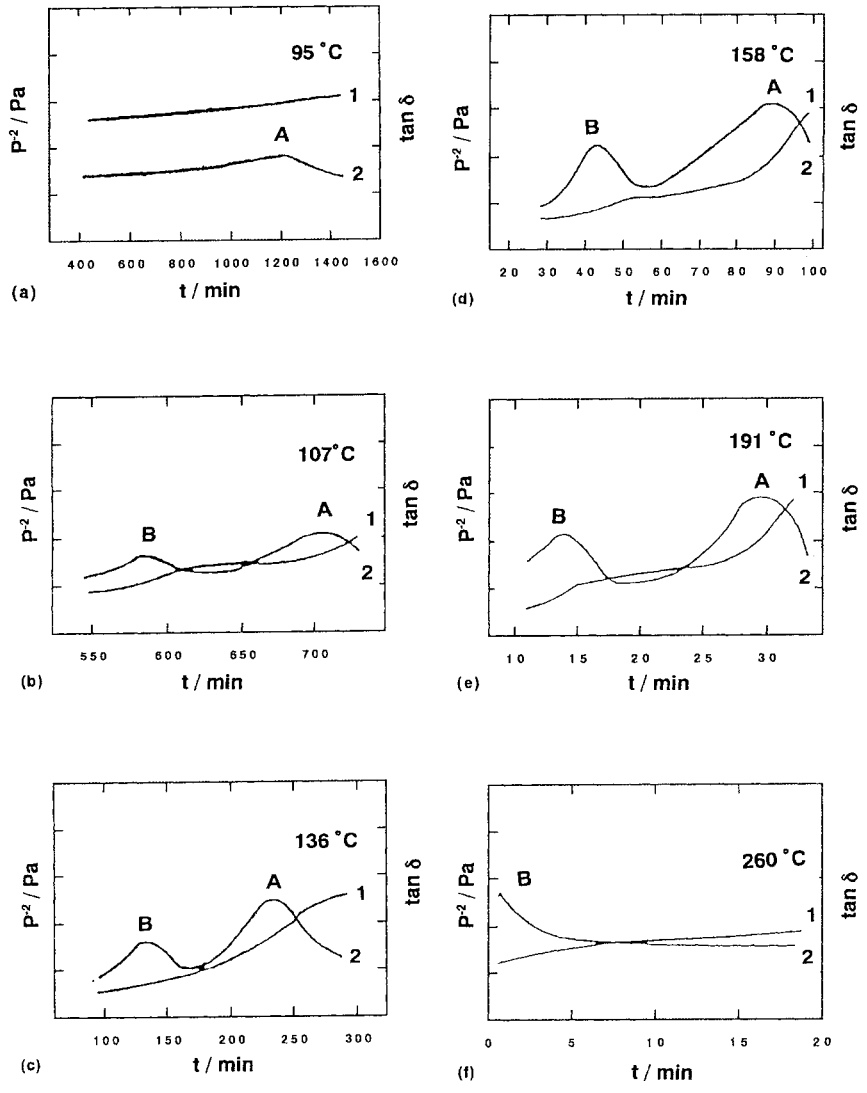

Fig. 2. Isothermal TBA curves at different temperatures: (1) relative rigidity; (A) vitrification; (2) logarithmic decrement; (B) gelation.

Combining the TBA estimate for the time to gelation with the DSC estimate of the percent conversion as a function of time leads to the estimate of conversion at the gel point between 0.55 and 0.80, as calculated from Flory's theory [2].

2.3. TTT diagram and three types of cure behavior

The so-called TTT diagram, i.e., time–temperature-transformation isothermal cure diagram, such as Fig. 3, is a useful tool for illustrating the phenomena during curing. The TTT diagram is taken after Gillham [3] and can be generated by either TBA or DMA measurements. The relevant glossary is shown in Table 2.

Fig. 4 is the TTT cure diagram for Ag-80/DDS resin system, where T_g^{∞} obtained from TBA heating scan for fully cured specimens is 263°C; the gelation and the vitrification lines are plotted in terms of the times to gelation and to vitrification vs. isothermal cure temperature given in Table 1; T_{gg} is 84°C, determined by the intersection of the two lines. The full cure line is obtained in the section of TTT equation.

Table 2
Glossary of TTT diagram

α	Extent of conversion, fraction reacted, degree of cure
α_{gel}	α at the gel point
t_g	Time to gelation (gel time)
t_v	Time of vitrification
T_{cure}	Cure temperature
T_{co}	T_c below which no significant reaction of the uncure resin mixture occurs, $\cong T_{go}$
T_{cg}	T_c at which vitrification and gelation occur simultaneously
T_c^{∞}	Minimum T_c at which ultimate conversion occurs
T_g	Glass transition temperature
T_{go}	T_g for thermoset with degree of conversion $\alpha = 0$
T_{gg}	T_g for thermoset with degree of conversion $\alpha = T_{gg}(T_{cg})$
T_g^{∞}	T_g for thermoset with degree of conversion $\alpha = 1$

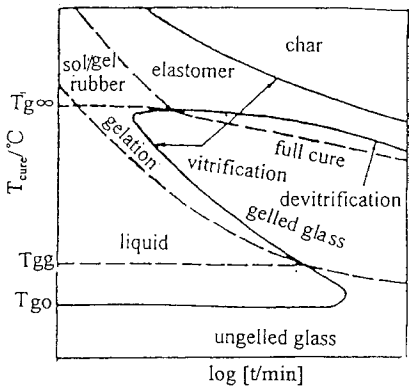

Fig. 3. A generalized time–temperatre-transformation isothermal cure diagram.

The TTT diagram (Fig. 3) displays the distinct states corresponding to different cure temperatures and times. These states are liquid, sol/gel rubber, elastomer, ungelled (sol) glass, gelled glass, and char. The diagram also displays the transition lines gelation, vitrification, devitrification, full cure and the critical temperatures T_{go}, T_{gg}, T_g^{∞}. Much of the behavior of a thermosetting system can be understood immediately in terms of the TTT diagram.

According to the TTT cure diagram, it is clear that, depending on the cure temperature T_{cure}, there are three types of cure behavior:

1. If $T_{go}<T_{cure}<T_{gg}$, molecular motion would be confined, gelation cannot occur, only vitrification can be observed, the system would convert directly from liquid into glass (the first type of cure behavior).
2. If $T_{gg}<T_{cure}<T_g^{\infty}$, both gelation and vitrification can be observed, and the system would convert from liquid into gelled rubber and then into gelled glass. This is the second type of cure behavior. In this temperature range, the gel time decreases with increased temperature, while the vitrification time first decreases, undergoing a minimum and then increases. This results from the joint actions of changes of the reaction rate and the crosslink density. Increasing cure temperature increases the reaction rate and rapidly increases the degree of cure and so decreases the gel time since gelation occurs at a constant conversion which is independent of temperature for a given reactive system

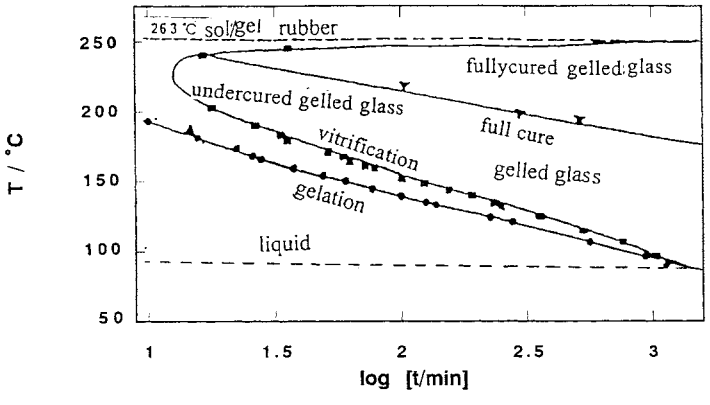

Fig. 4. TTT diagram for Ag-80/DDS resin system.

Table 3
T_g vs. T_{cure} for specified cure time

	Cure time (min)										
	100				300			500			
T_{cure} (°C)	170	180	190	200	170	190	200	160	180	190	200
T_g (°C)	252	253	256	258	255	260	262	254	259	261	263
T_{gcal} (°C)[a]	251	253	255	258	255	260	262	254	259	261	263

[a] T_{gcal}: calculated values.

(Flory's theory). However, at higher temperatures, the increased crosslink density confines and lowers the rate of cure. Since glass transition occurs at isofree volume, the competition between the reaction rate and the degree of cure leads to the changes of vitrification time mentioned above.

3. If $T_g^{\infty} < T_{cure} < T_{decomposition}$, molecules would be in active motion, only gelation can be observed, and the system would change into gelled rubbery state (the third type of cure behavior).

The three types of cure behavior above are distinguished by the difference in the two main structural transitions (i.e., gelation and vitrification) of the system at different cure temperatures.

2.4. TTT equation

The data for T_g vs. T_{cure} for the system for different times of isothermal cure are given in Table 3 and are plotted as T_g vs. T_{cure} in Fig. 5. A set of approximately parallel lines are obtained. Each line represents a linear relationship between T_g and T_{cure} for the same cure time (longer than the vitrification time). Therefore

$$T_g = c + dT_{cure}, \quad (1)$$

where c depends on the cure time, and d is independent of cure time. The values of c and d for different cure times are presented in Table 4.

Assuming that the system is fully cured when T_g reaches T_g^{∞}, the temperature for full cure to occur in a specified time, $T_{\infty}(t)$, as shown in Table 5, is determined by extrapolation of the $T_g - T_{cure}$ line for the same cure time to T_g^{∞} using Eq. (1).

If the data for T_{cure} vs. time to full cure are plotted as T_{cure} vs. log time of cure, a new line presents which is designated the full cure line on the TTT curve diagram (Fig. 4 or Fig. 6). The gelled glass region is divided into two parts by the full cure line in the absence of degradation (Fig. 3, devitrification and char formation), the top and lower parts can be designated fully cured gelled glass (gel glass) and under cured gelled glass (sol/gel glass) regions, respectively. The line appears to the linear, which can therefore be expressed by

$$T_{\infty} = a + b\log[t_{\infty}], \quad (2)$$

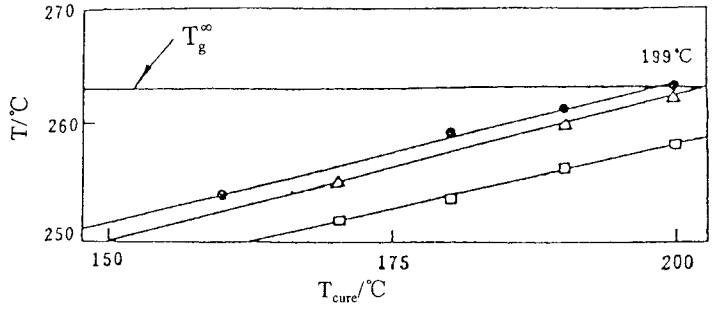

Fig. 5. T_g vs. T_{cure} for preselected times of cure (●) 500 min; (Δ) 300 min; (□) 100 min.

Table 4
Values of c and d (the average of d is 0.23, and r is the correlation coefficient)

	Cure time (min)		
	100	300	500
c	215.9	215.0	218.0
d	0.21	0.24	0.23
r	0.98	1.00	1.00

Table 5
Values of T_{cure} and t_∞

T_{cure} (°C)	199	204	224
t_∞ (min)	500	300	100

where T_∞ and t_∞ are the temperature and time to full cure, respectively. The intercept a=296.9, the slope b=−36.7 and the correlation coefficient is 0.99.

Following Peng Xinsheng and Gillham [4], an empirical T_g−T_{cure}-time equation can be derived from Eqs. (1) and (2) in the form of

$$T_g = T_g^\infty - da - db\log[t] + dT_{cure}. \quad (3)$$

The particular equation for Ag-80/DDS system is obtained by regression on the basis of the data given in Tables 3, i.e.,

$$T_g = 7.36\log[t] + 0.226\,T_{cure} + 198.4, \quad (4)$$

where t is in minutes, and T_{cure} and T_g are in °C.

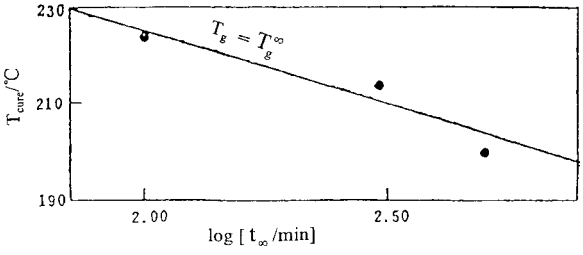

Fig. 6. Full cure line ($T_{cure} \sim \log[t_\infty]$).

The T_g calculated (T_{gcal}) by Eq. (4) are included in Table 3 together with the corresponding experimental values for T_g. The agreement is good. Therefore, the T_g of the material cured at temperature T_{cure} for time t can be calculated from this T_g−T_{cure}-time equation.

3. Conclusions

1. The TTT cure diagram and the TTT equation, which may provide theoretical data for curing resin matrix composites, are obtained by TBA. On the diagram, T_{go} and T_{gg} serve to define storage temperatures for unreacted resin and preimpregnated cloth; the temperature range for curing can be selected between T_{gg} and T_g^∞; the time for pressing can be obtained according to gel time vs. T_c; T_g^∞ also serves to determine the temperature for post-cure.
2. The TTT diagram and the TTT equation for Ag-80/DDS system shows that the system has long storage time at room temperature and high cure temperatures. The T_g for the fully cured resin is also high (263°C). Therefore, Ag-80/DDS system may be considered as heat-resisting composite matrixes and adhesives due to its high heat-resistance.
3. The TBA technique combined with the DSC technique is an effective method to monitor the cure behavior of a resin system. TBA and DSC can characterize the cure behavior by thermal property and mechanical property, respectively. Many DSC data, such T_{co}, T_c^∞ and cure activation energy, are omitted here as spaces is limited.

References

[1] US AD-734005.
[2] P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY, 1953, p. 350.
[3] J.K. Gillham, British Polym. J. 17 (1985) 224–226.
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