Curing Behavior of a Novel Polytriazole Resin

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ABSTRACT: The curing behavior of a novel low temperature curing polytriazole resin, prepared from *p*-xylylene diazide and *N,N,N′,N′*-tetrapropargyl-*p,p′*-diaminodiphenylmethane, was investigated by DSC and rheological analyses. The kinetics of the curing of the resin was studied by nonisothermal and isothermal DSC measurements and the kinetics parameters were obtained. The values of apparent activation energy E_a of the curing reaction obtained by nonisothermal and isothermal DSC are 80.7 and 75.3 kJ/mol, respectively. The curing of the resin was traced by the isothermal rheological analysis. The gelation times of the resin at 70, 75, 80, and 85°C are about 200, 150, 110, and 75 min, respectively. The viscosity equation for the resin was found as follows: $\ln \eta = -107 + \frac{33.5 \times 10^3}{T} + t \exp\left(26.3 + \frac{9.87 \times 10^3}{T}\right)$. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2111–2116, 2007

Key words: polytriazole resin; DSC; kinetics; rheological behavior

INTRODUCTION

In recent years, there has been a growing interest in the application of polymer matrix composites for the manufacture of structural components. Compared with traditional structural materials, the polymer matrix composites exhibit much better properties such as high specific strength and modulus, corrosion resistance, good fatigue and fracture properties, relative ease of fabrication into complex shapes, and ease of repair.[1–3] However, the high cost of polymer matrix composites, especially for advanced composites, limits their wide applications. Thus, it is necessary to develop advanced composites with low cost. One approach is to develop low temperature curing (LTC) composites, which would have low manufacturing cost by employing cheaper molds and other processing materials. LTC technology of a polymer matrix composite would greatly not only reduce the cost of the manufacture but also results in low inner stress and heat expansion due to high temperature curing in the composite so as to raise the properties and the size precision of a composite part. Furthermore, LTC technique is more suitable for the manufacture of large dimension composite parts.[4–8] In 1970s, the ACG Corporation (UK) and the Air Tech Corporation (USA) started the exploration of low temperature molding (LTM) materials and now had developed a series of LTM products.[9–13] Recently, our laboratory has reported the preparation and properties of a new kind of thermosetting polytriazole resins, which can be cured at temperature lower than 80°C and exhibit good mechanical and thermal properties.[14–17] A polytriazole resin prepared from *p*-xylylene diazide (XDA) and *N,N,N′,N′*-tetrapropargyl-*p,p′*-diaminodiphenylmethane (TPDDM) can be cured at 70°C. The glass transition temperature and thermal decomposition temperature of the cured resin are 218 and 350°C, respectively. The tensile and flexural strengths of the cured resin achieve 99.0 and 200 MPa, respectively.[17] The polytriazole resin is greatly potentially used as a low cost and easy processing thermal stable resin matrix for advanced composite applications. The curing behavior of the polytriazole resin is investigated by DSC and rheological analyses in this article.

EXPERIMENTAL

Materials

The syntheses of XDA and TPDDM were described in the Ref. 17. The monomers XDA and TPDDM (the molar ratio [XDA]/[TPPDM] = 2.0 : 1.0) were mixed in a three-neck bottom flask equipped with a stirrer, a cooling condenser, and a thermometer. The monomer mixture was heated with an oil bath to 50°C, and stirred continuously at 50°C for 10 min. A clear

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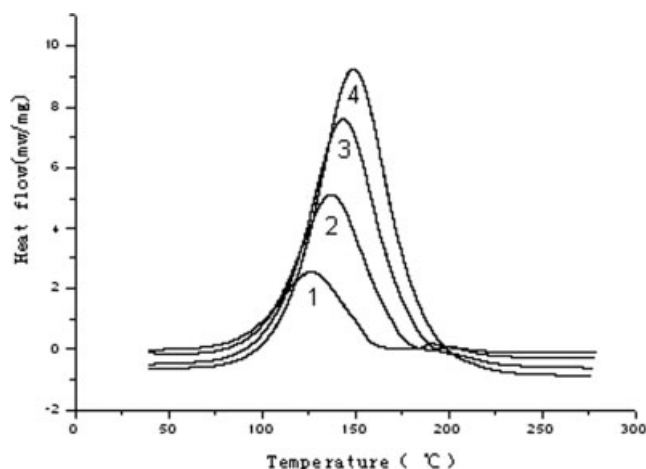
Figure 1 DSC scans of the polytriazole resin at various heating rates (1 : 5; 2 : 10; 3 : 15; 4 : 20°C/min).

and light yellow viscous liquid polytriazole resin was obtained and used for the curing investigation.

Characterization

Differential scanning calorimetric measurements was carried out on a universal V2.3 TA 2910 differential scanning calorimeter under nitrogen. Nonisothermal DSC experiments were conducted at heating rates of 5, 10, 15, and 20°C/min from room temperature to 300°C. Isothermal DSC experiments were performed at 90, 95, 100, and 105°C. Rheological behavior was traced on a RheoStress RS600 Rheometer with a shear rate of 0.1 s^{-1} at 70, 75, 80, and 85°C.

RESULTS AND DISCUSSION

Thermal curing behavior and kinetics of the polytriazole resin[18,19]

Nonisothermal DSC

Nonisothermal DSC technique can be used to investigate the kinetics of the curing reaction of the polytriazole resin. Kissinger and Ozawa methods are used to calculate the kinetic parameters of the curing reaction. The apparent activation energy for the curing reaction can be obtained by the following equations:

The Kissinger equation[20]:

$$d\left[\ln(\phi/T_p{}^2)\right]/d\left[(1/T_p)\right] = -E_a/R \tag{1}$$

The Ozawa equation[21]:

$$d\left[\ln(\phi)\right]/d\left[(1/T_p)\right] = -1.052\, E_a/R \tag{2}$$

where ϕ is the heating rate (K/min), T_p is the exothermic peak temperature (K), E_a is the apparent

TABLE I
Nonisothermal DSC Analysis of the Polytriazole Resin at Different Heating Rates

Φ (K/min)	T_p (K)	$1/T_p$ (10^3)	$\ln(\phi/T_p{}^2)$	ΔH (J/g)
5	399.8	2.501	-10.37	1305
10	410.4	2.437	-9.73	1396
15	416.7	2.400	-9.36	1405
20	422.2	2.369	-9.10	1463

activation energy (kJ/mol), and R is the universal gas constant (8.314 J/mol).

Figure 1 shows the nonisothermal DSC curves of the curing reaction of the polytriazole resin at different heating rates and the results were tabulated in Table I. As shown in Figure 1, the curing reaction starts at about 70°C and ends at about 200°C. The plots of $\ln(\phi/T_p^2)$ versus $(1000/T_p)$ by Kissinger's method and $\ln(\phi)$ versus $(1000/T_p)$ by Ozawa's method are drawn and shown in Figure 2. The apparent activation energy E_a can be calculated from the slopes of lines and E_a values obtained by Kissinger's and Ozawa's equations methods are 80.7 and 83.7 kJ/mol, respectively. The E_a values obtained by the two ways are close. This illustrates the obtained E_a is creditable.

When $E_a/nR \gg 2T_p$, the apparent reaction order of the curing reaction can be calculated by Crane equation[22]:

$$d\left[\ln(\phi)\right]/d\left[(1/T_p)\right] \approx -E_a/nR \tag{3}$$

where n is the apparent reaction order. The value of n obtained from the slope of the plots of $(\ln \phi)$ versus $(1/T_p)$ is 0.93.

Isothermal DSC analysis

The isothermal DSC analysis can also be used to investigate the kinetics of the curing reaction of the polytriazole resin. Figure 3 shows the isothermal
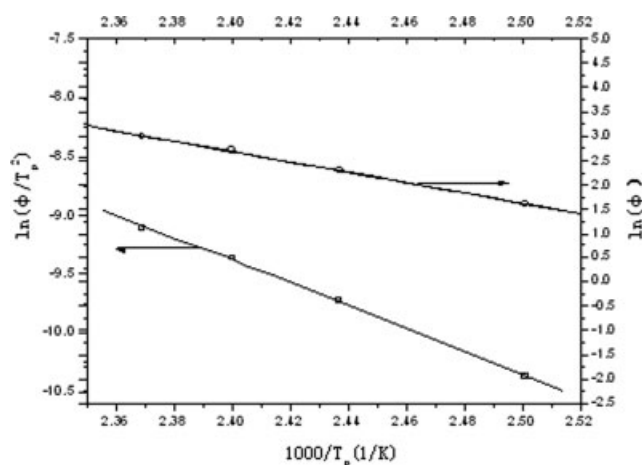
Figure 2 Plots of $\ln(\phi/T_p^2)$ versus $1000/T_p$ and $\ln(\phi)$ versus $1000/T_p$ of the polytriazole resin.
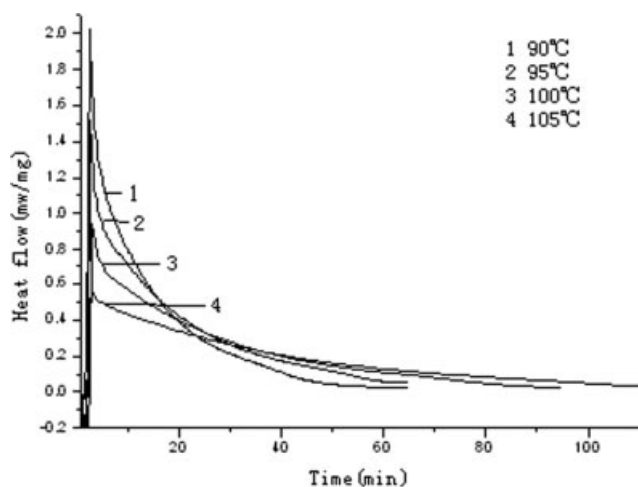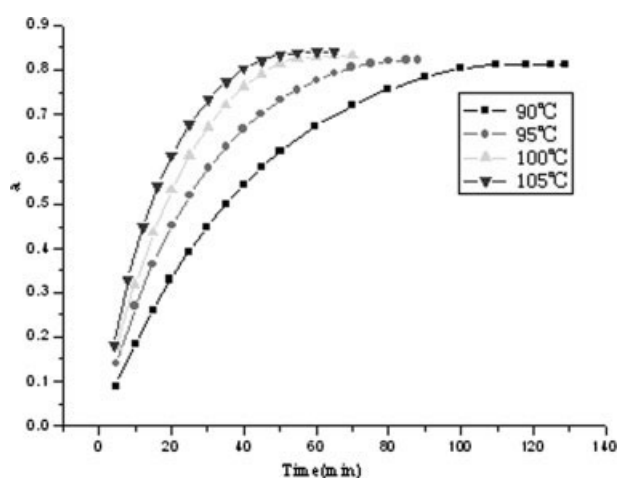
Figure 3 Isothermal DSC curves of polytriazole resin at 90, 95, 100, and 105°C.

Figure 5 The plots of ln(1 − α) versus time for the curing of polytriazole resin at different temperatures.

DSC curves of the polytriazole resin at 90, 95, 100, and 105°C. As shown in Figure 3, the intensity of peaks increases and the width of exothermal peaks decreases with the increase in temperature. This illustrates that the curing reaction of the resin speeds up with the increase in the temperature for the test.

From Figure 3, $H(t)$, which is the accumulative exothermic heat of the curing reaction up to curing time t, can be obtained by integrating the area below the DSC curve and above the base line in Figure 3. Thereby, the extent of curing reaction a can be calculated by eq. (4):

$$\alpha = H(t)/H_0 \qquad (4)$$

where H_0 is the total exothermic heat of the whole curing reaction, which could be given by the average of the exothermic heat of curing reaction measured
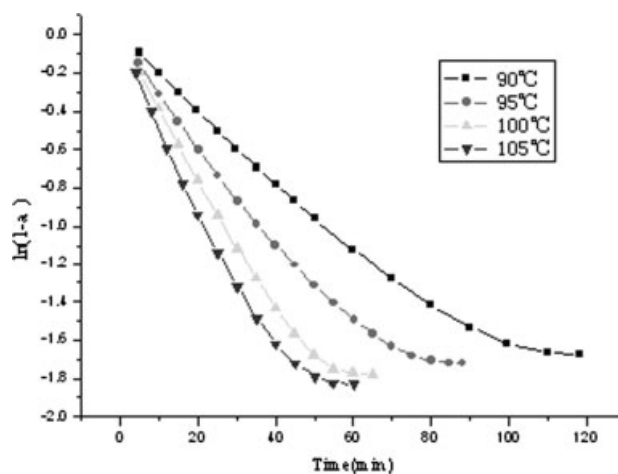
by the nonisothermal DSC analysis at different heating rates.[23] The H_0 value is 1401 kJ/mol, which is calculated from the data in Table I.

As usual, if ln(1 − α) is linear with the curing time, t, the curing reaction is considered by first-order reaction. If 1/α is linear with t the curing reaction is considered by second-order reaction. Figures 4–6 show the plots of α, ln(1 − α), and 1/α versus t at different temperatures. As shown in the figures, ln(1 − α) is linear with t at the prophase of the curing reaction, but 1/α is not linear with t. This indicates that the curing reaction follows first order in the prophase of the curing. However, in the anaphase of the curing reaction, the relationship between ln(1 − α) and t departs from the line. This probably results from the curing reaction process. As the curing reaction of the resin progresses, the viscosity of resin increases and the motion of the reaction groups
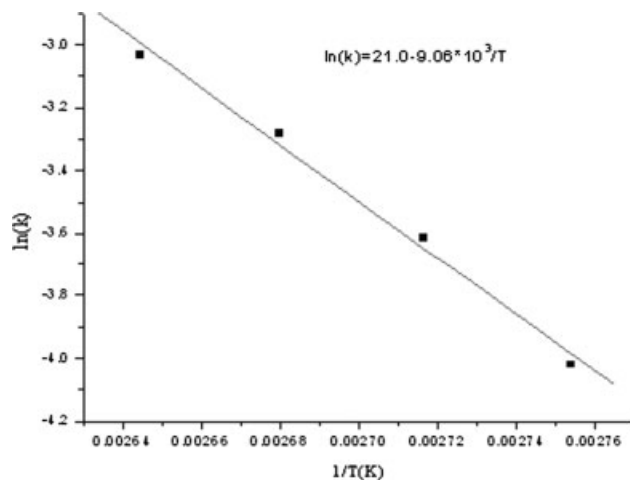

Figure 4 The plots of α versus time for the curing of poly triazole resin at different temperatures.
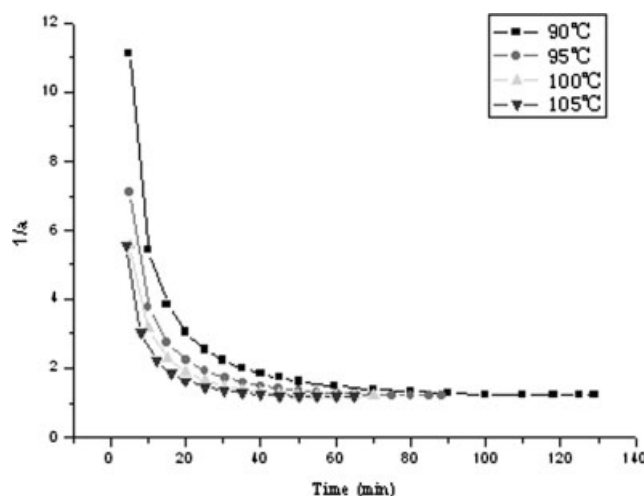
Figure 6 The plots of 1/α versus time for the curing of polytriazole resin at different temperatures.

TABLE II
Values of Curing Reaction Rate Constant (k) of the Polytriazole Resin at Different Temperatures
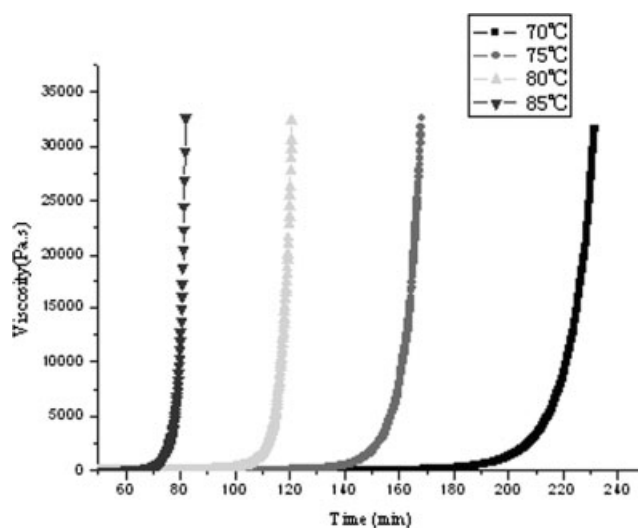
Temperature (°C)	k
90	0.01793
95	0.02697
100	0.03757
105	0.04815

in the resin becomes difficult. The curing reaction process changes from a process controlled by chemistry to one controlled by diffusion. In the chemistry-controlled process, the curing reaction agrees with first-order kinetics model. The value of the curing reaction rate constant (k) can be obtained by the linear fitting of $\ln(1 - \alpha)$ with t at the prophase of the curing. The result is listed in Table II.

Assuming that the curing reaction follows the equation $k = Ae^{-E_a/RT}$, the plots of $\ln k$ versus $1/T$ are shown in Figure 7. The apparent activation energy (E_a), 75.3 kJ/mol, can be obtained from the slope. The value of the apparent activation energy (E_a) for the curing of polytriazole resin is lower than that of other high-performance resins such as BMI resin (E_a = 108 kJ/mol for pure BMI resin[24] and E_a = 110 kJ/mol for allyl compounds modified BMI resin[25]) and cyanate ester resin (E_a = 106.7 kJ/mol).[26] This implies that the curing reaction is easy to take place. The E_a value is a little lower than that obtained from nonisothermal DSC analysis. The main reason is that the kinetics treated by nonisothermal DSC analysis deals with the overall reaction, but that treated by isothermal DSC analysis only do with prophase of the curing reaction. In addition, the different treatment methods will result in different kinetics parameters value.


Figure 8 The viscosity of the resin versus time at a fixed temperature.

Rheological behavior of polytriazole resin

Isothermal rheological behavior of the resin

Figures 8 and 9 show the viscosity and modulus of the polytriazole resin versus curing time at 70, 75, 80, and 85°C. The viscosity of the polytriazole resin is low before gelation occurs, which benefits for processability of the resin. The viscosity increases as the curing reaction goes along and then increases rapidly when the curing reaction progresses further and approaches the gelation point of the resin.

The gelation time (t_g) is one of the most important kinetic characteristics of curing process for a thermosetting resin since it describes the attainment of a certain critical conversion responsible for the transition from the first to second stage. The gelation time

Figure 7 The plots of $\ln(k)$ versus $1/T$ for the curing of the polytriazole resin.

$$\ln(k) = 21.0 - 9.06 \times 10^3/T$$
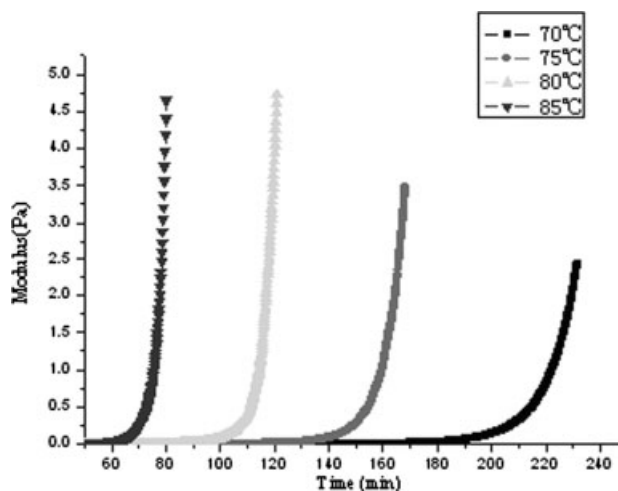
Figure 9 The modulus of the resin versus time at a fixed temperature.

TABLE III
Gelation Time of the Polytriazole Resin in Different Temperatures

Temperature (°C)	Gelation time on the criteria of modulus (min)	Gelation time on the criteria of viscosity (min)		
		1000 (Pa s)	2000 (Pa s)	5000 (Pa s)
70	222.5	197.4	204.9	214.5
75	159.8	146.1	151.0	157.1
80	114.3	107.3	111.0	114.7
85	75.6	73.7	75.6	78.1

could be determined according to the following criteria[27]:

  Criteria of viscosity: at the point the viscosity reaches several determined values (1000, 2000, and 5000 Pa s).
 Criteria of modulus: at the point the modulus reaches 1 Pa.

Table III shows the gelation time values obtained according to the aforementioned criterions. The gelation time decreases when the cure temperature increases because an increase of temperature implies an increase in the mobility of the active chains, leading to a faster cure reaction. As shown in the Table III, the gelation time for the polytriazole resin at 70, 75, 80, and 85°C are about 200, 150, 110, and 75 min, respectively.

Viscosity model equation of the polytriazole resin

For isothermal curing of a thermosetting resin, the predominant empirical model of viscosity is as follows[28]:

$$\ln \eta = \ln \eta_\infty + (E_\eta/RT) + At \, \exp(E_a/RT) \quad (5)$$
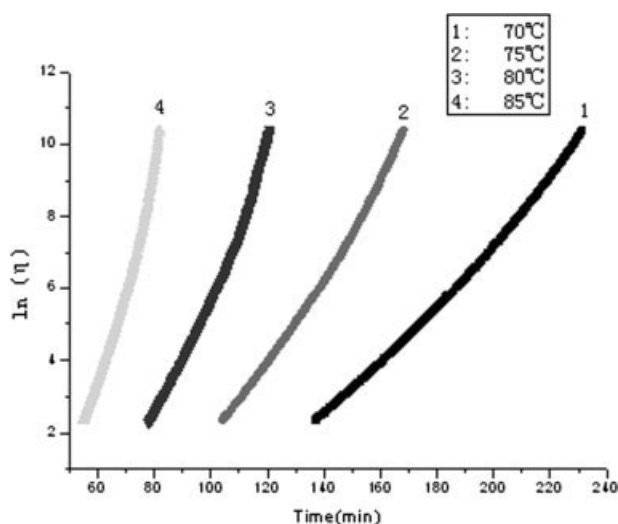
Figure 10 The plots of ln(η) versus time for the polytriazole resin at different temperatures.

where η is the viscosity (Pa s), T is the absolute temperature (K), t is the curing time (min), η_∞ is the reference viscosity at "infinite temperature" (Pa s), E_η is the Arrhenius activation energy for viscosity (kJ/mol), E_a is the Arrhenius activation energy of the curing reaction (kJ/mol), and A is the frequency factor (min^{-1}).

Equation (5) can be simplified as follows:

$$\ln \eta(T, t) = \ln C + Dt \quad (6)$$

where $\ln C = \ln \eta_\infty + E_\eta/RT$, $\ln D = \ln A + E_a/RT$.

As shown in eq. (6), there is a linear relationship between $\ln \eta(T, t)$ and t at a fixed temperature. Figure 10 shows the plots of $\ln \eta(T, t)$ versus time at different temperatures. There is a good linear relationship between $\ln \eta(T, t)$ and t. The values of $\ln C$ and D at different temperatures can be obtained from the slope and intercept of the lines. The results are listed in Table IV.

Furthermore, η_∞ and E_η can be obtained by the linear fitting of $\ln C$ with $1/T$. In the same way, E_a and A can be obtained by the linear fitting between $\ln D$ and $1/T$. The values of η_∞, E_η, E_a, and A are 3.40×10^{-47} Pa s, 279 kJ/mol, 82.0 kJ/mol, and 2.64×10^{11} min^{-1}, respectively. After the parameters are put into the eq. (5), the viscosity equation for the polytriazole resin is obtained as follows:

$$\ln \eta = -107 + \frac{33.5 \times 10^3}{T} + t \, \exp\left(26.3 + \frac{9.87 \times 10^3}{T}\right) \quad (7)$$

The viscosity of the polytriazole resin at different curing time at a fixed curing procedure can be pre-

TABLE IV
Parameters of the Viscosity Equation for the Polytriazole Resin

Temperature (°C)	ln C	D
70	9.48	0.0838
75	10.8	0.123
80	12.3	0.181
85	13.5	0.281
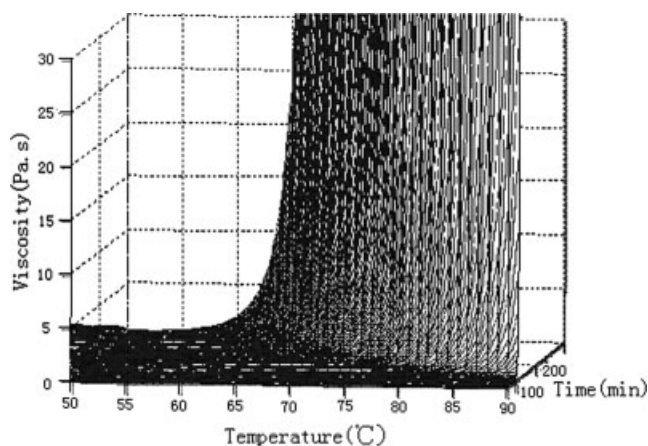
Figure 11 The curve of the relationship of viscosity–temperature–time for the polytriazole resin.

dicted through the eq. (7). The three dimensional curve of $\ln \eta \sim T \sim t$ is shown in Figure 11. This graph could be used for the reference for the preparation of the polytriazole resin matrix composite.

CONCLUSIONS

The kinetics of the curing reaction of the polytriazole resin prepared from XDA and TPDDM is investigated by nonisothermal and isothermal DSC analyses. The apparent activation energy E_a obtained by nonisothermal and isothermal DSC analyses are 80.7 and 75.3 kJ/mol, respectively. The curing reaction of the polytriazole resin is first-order reaction. In addition, the isothermal rheological behavior of the polytriazole resin is investigated. The gelation times of the resin at 70, 75, 80, and 85°C are about 200, 150, 110, and 75 min, respectively. And the viscosity of the resin follows the equation:

$$\ln \eta = -107 + \frac{33.5 \times 10^3}{T} + t \, \exp\left(26.3 + \frac{9.87 \times 10^3}{T}\right)$$

References

1. Lin, S. C.; Pearce, E. M. High Performance Thermosets; Hanser/Gardner: New York, 1994.
2. Serafini, T. T. High Temperature Polymer Matrix Composites; Noyes Data Corporation: New Jersey, 1987.
3. Chen, X. B. Low Cost Technology of Advanced Composites; Chemical Industry Press: Beijing, 2004.
4. Jackson, K. Int SAMPE Symp 1998, 43, 1.
5. Jackson, K. Int SAMPE Symp 1998, 43, 23.
6. Dodiuk, H.; Kenig, S.; Liran, I. Composite 1991, 22, 319.
7. Frank, L. Int SAMPE Symp 1998, 43, 9.
8. Martin, P. S. Low temperature curing epoxy. U.S. Pat. 4,297,254 (1981).
9. Hermanson, R. D. Low exotherm, low temperature curing, epoxy impregnants. U.S. Pat. 5,350,779 (1994).
10. Meador, M. A. In Proceedings of the 40th SAMPE Symposium, Anaheim: CA, 1995; p 268.
11. Doerner, F. J.; Smith, R. M. In Proceedings of the 41st International SAMPE Symposium and Exhibition, Covina: CA, 1996; p 35.
12. Ridgard, C. In Proceedings of the 42nd International SAMPE Symposium and Exhibition, Anaheim: CA, 1996; p 147.
13. Ridgard, C. In Proceedings of the Eighth International Conference of the Society for the Advancement of Material and Process Engineering, Covina: CA, 1987; p 18.
14. Wan, L. Q.; Hu, Y. H.; Luo, Y. H.; Rong, Z. X.; Zhou, W.; Huang, F. R.; Qi, H. M.; Du, L. In Proceedings of the 13th National Conference on Composite Materials in China, Chengdu, China, 2004; p 327.
15. Luo, Y. H.; Hu, Y. H.; Wan, L. Q.; Zhou, W.; Huang, F. R. In Proceedings of the 13th National Conference on Composite Materials in China, Chengdu, China, 2004; p 355.
16. Hu, Y. H.; Luo, Y. H.; Wan, L. Q.; Qi, H. M.; Huang, F. R. Acta Polym Sin 2005, 4, 560.
17. Wan, L. Q.; Luo, Y. H.; Xue, L.; Tian, J. J.; Hu, Y. H.; Qi, H. M.; Shen X. N.; Huang F. R.; Du, L. J Appl Polym Sci 2007, 104, 1038.
18. Luo, Y. H.; Hu, Y. H.; Wan, L. Q.; Xue, L.; Huang, F. R.; Shen, X. N.; Qi, H. M.; Du, L. Chem J Chin Univ 2006, 27, 170.
19. Zhang, Y. Q.; Gao, J. Y.; Shen, X. N.; Huang, F. R. J Appl Polym Sci 2006, 99, 1705.
20. Kissinger, H. E. Annu Chem 1957, 29, 2702.
21. Ozawa, T. J. Therm Anal 1970, 2, 301.
22. Crane, L. W. J Polym Sci Polym Lett Ed 1973, 11, 533.
23. Zhang, X. H.; Min, Y. Q.; Zhao, H.; et al. J Appl Polym Sci 2006, 5, 3483.
24. Liu, X. Y.; Yu, Y. F.; Li, S. J. Polymer 2006, 47, 3767.
25. Ma, X. Y.; Yan, H. X.; Ning, R. C. J Appl Polym Sci 2001, 80, 2518.
26. Gómez, C. M.; Recalde, I. B.; Mondragon, I. Eur Polym J 2005, 41, 2734.
27. Laza, J. M.; Julian, C. A.; Larrauri, E. Polymer 1999, 40, 35.
28. Kiuna, N.; Lawrence, C. J.; Fontan, Q. P. V.; Lee, P. D.; Selerland, T.; Spelt, P. D. M. Compos A 2002, 33, 1497.