

Polyamidoamine Dendrimers as Curing Agents: The Optimum Polyamidoamine Concentration Selected by Dynamic Torsional Vibration Method and Thermogravimetric Analyses

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ABSTRACT: Polyamidoamine (PAMAM) dendrimers were investigated as curing agents in bisphenol A epoxy resin systems. The cure behavior of epoxy resin/PAMAM at varying components was investigated by a dynamic torsional vibration method (DTVM); the thermal behavior of the materials was characterized by means of thermogravimetric (TGA) analyses. The DTVM results show that 10/100 parts of the resin (phr) PAMAM was the optimum concentration for 1.0,

3.0, and 5.0 G PAMAM dendrimers/resin systems in our experiment. Also, the TGA results agreed with the conclusions made by the DTVM. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1430–1434, 2007

Key words: polyamidoamine; dendrimers; epoxy resin; optimum concentration; dynamic torsional vibration method; thermogravimetric analyses

INTRODUCTION

Dendrimers are hyperbranched, monodisperse, and three-dimensional macromolecules, having defined molecular weight and host–guest entrapment properties. They allow the precise control of size, shape, and placement of functional groups, and combine typical characteristics of small organic molecules and polymers that result in special physical and chemical properties.^{1–6} These special structures differ from typical polymers in possessing well-defined architectures. Accordingly, dendrimers have attracted increasing attention for their applications in many fields. Among them, the use of dendrimers in resin systems are at early stages of development and data on them are limited.^{7–9} In this study, the cure behavior of epoxy resin E-51/PAMAM/imidazole system was investigated by dynamic torsional vibration method (DTVM), and the thermal behavior of the material was characterized by means of thermogravimetric (TGA) analyses.

EXPERIMENTAL

Materials

The diglycidyl ether of biphenyl A, epoxy resin E-51 with the epoxy value 0.48–0.54 and average epoxy equivalent 196, was provided by the Shanghai Resin Factory. 2-Ethyl-4-methyl-imidazole (2,4-EMI), supported by the Development Center of Special Chemical Agents in Huabei region, was used as the curing promoter. Ethylenediamine and methyl acrylate were obtained from Shanghai Chemical and were used as supplied.

Synthesis of PAMAM dendrimers

PAMAM dendrimers were synthesized according to a literature procedure.¹ Ethylenediamine (10.0 g, 0.166 mol) was dissolved in 100 mL of methanol in a 1-L round-bottomed flask. To the solution of ethylenediamine, methyl acrylate (94.6 g, 0.751 mol) was added at 40°C and left stirring for 24 h under nitrogen atmosphere. The excess methyl acrylate was removed by vacuum distillation at room temperature. Michael addition of the amine to the acrylate yielded a product bearing four terminal methyl ester groups, which was defined as 0.5 G PAMAM. Subsequently, ethylenediamine (120 g, 2.00 mol) was dissolved in

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TABLE I
The Characteristic Data of PAMAM Dendrimers

Generation	Molecular formula	Molecular weight	Number of primary amino groups	Number of total amino groups	Radius from SAXS (Å)
G1	C ₂₂ H ₄₈ O ₄ N ₁₀	516	4	10	–
G2	C ₆₂ H ₁₂₈ O ₁₂ N ₂₆	1,428	8	26	–
G3	C ₁₄₂ H ₂₈₈ O ₂₈ N ₅₈	3,252	16	58	15.8
G4	C ₃₀₂ H ₆₀₈ O ₆₀ N ₁₂₂	6,900	32	122	17.1
G5	C ₆₂₂ H ₁₂₄₈ O ₁₂₄ N ₂₅₀	14,215	64	250	24.1

methanol and added to 0.5 G PAMAM. After stirring for 48 h under nitrogen atmosphere and removing excess reactants by vacuum distillation, the product bearing terminal amino groups were obtained and defined as 1.0 G PAMAM. By repeating the above cycle, PAMAM dendrimers of higher generations (up to 5.0 G) were synthesized. For sample preparation, 1–2 wt % PAMAM/ethyl acetate solution was repeatedly filtrated through a 0.1 mm nylon filter. Purity of the amine-terminated PAMAM dendrimers was characterized using FTIR (MAGNA-IR 750, Nicolet Instrument, U.S.A), ¹H and ¹³C NMR (DMX-500, German), mass spectral analysis (BIFI EXTM 3, German), and element analysis (VARIO EL 3, Elementar Instrument, German). The characteristic data of different generations of PAMAM are listed in Table I.

Isothermal cure experiment by DTVM

Epoxy resin E-51 and 2,4-EMI were mixed in the stoichiometric ratio of 100/1 (by weight). Then the mixture was mixed with various generations of PAMAM with the ratio of 0, 5, 10, 20, and 40 parts per hundred parts of the resin (phr), respectively.

Dynamic torsional vibration is a nonresonant forced vibration.¹⁰ The schematic diagram of a homemade experimental setup—HLX-I Resin Curemeter—is shown in Figure 1. The lower mold 3 having a heater within it and used as the torsional vibrator is filled with the resin materials. When the motor 6 is switched on, the upper mold 2 having a heater within it too comes down, and the molds close with a gap that can be adjusted. The cure temperature is controlled using thermistors. Thus, the isothermal cure process can be performed. As soon as the upper and lower molds close, the motor 5 is on, and the lower mold starts a torsional vibration with a frequency of 0.05 Hz at an angle below 1°, which also can be adjusted according to the hardness of cured resin materials, by means of eccentric disc 4 on the speed change gear 7. The torque amplitude of the torsional vibration is transformed into electric signals by means of the strain gauge load cell 1, amplified through the amplifier 10, and recorded by the re-

corider 11. The operating principle of the equipment was described in Ref. 11.

The typical experimental curve obtained by the dynamic torsional vibration apparatus is shown in Figure 2. The abscissa is the curing time and the ordinate is the torque required to turn the resin system by a small angle, which corresponds to the modulus or viscosity of the resin system, and can be thought of as a relative parameter of the degree of cure. The time of closure of the molds is taken as the starting time of cure point O. In the range of OA of the curing time, the network structure formed during the cure reaction is not enough to cause forced vibration of the upper mold. As a result, the strain gauge load cell will not have any signal to input, so that the experimental curve is linear line corresponding to the abscissa. At the point A, the viscosity of the resin system is high enough (i.e., the network formed is complete enough) for the gelation in the resin system to occur, and the torque appears and the strain gauge load cell inputs some signal. Thus, point A is the gel time t_g for the resin system. After point A, the torque increases with increase in curing time. The increasing amplitude of the torque (slope of the curve) reflects the rate of the curing reaction. The increasing trend of torque tends to steady with increase in curing time, and the equi-

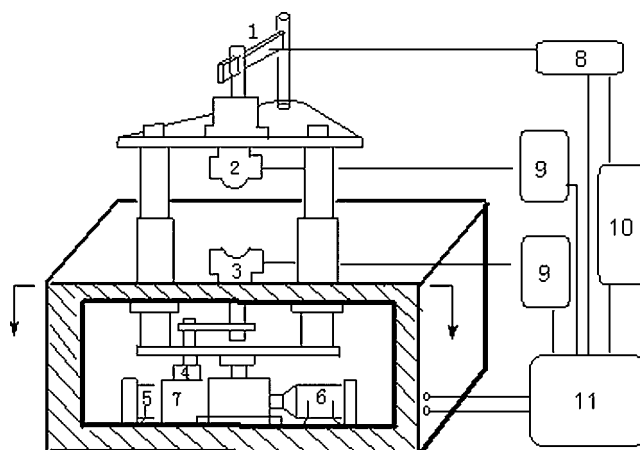


Figure 1 Schematic representation of the dynamic torsional vibration apparatus.

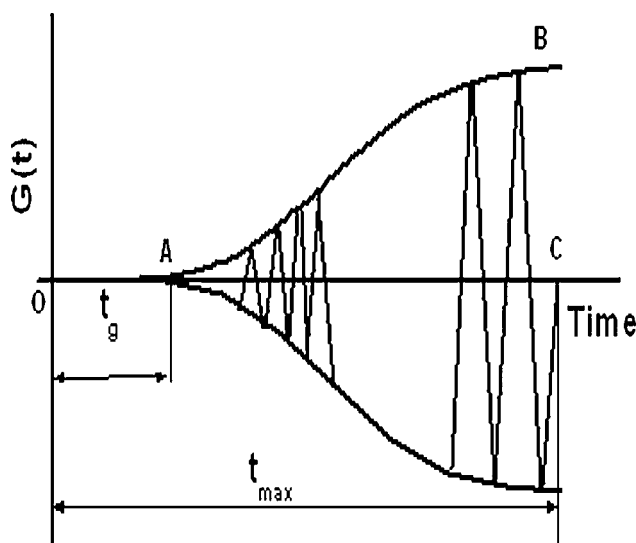


Figure 2 Isothermal cure curve obtained by dynamic torsional vibration method.

librium torque G_{∞} is thus reached (point C). $G(t)$ is the physical and mechanical quantities (torque or modulus, viscosity, etc.) at time t during cure. In the meantime, the curing reaction is completed and a cup-like experimental curve is obtained. The envelope of the experimental curve corresponds to the change of mechanical behavior of the resin system during cure. Since the cup-like experimental curve is symmetric to time axis, for convenience, we can just take the upper-half of the envelope as the isothermal cure curve to analyze the cure process.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) measurements were carried out using 5–10 mg of the cured E51/PAMAM/2,4-EMI at a heating rate of $10^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere, using a TGA analyzer (Shimadzu TGA-50H). The samples were subjected to TGA in high purity nitrogen under a constant flow rate of $10\text{ mL}/\text{min}$. Thermal decomposition of each sample occurred in a programmed temperature range of $20\text{--}800^{\circ}\text{C}$. The continuous records of weight loss and temperature were determined and analyzed to determine the following TGA indices: thermal degradation rate (% weight loss/min), initial degradation temperature, and residual weight.

RESULTS AND DISCUSSION

Analysis of isothermal cure behavior by DTVM

Figure 3 shows the isothermal cure curves of the epoxy resin E-51/imidazole using PAMAM dendrimers of different generations as curing agents. The effects of various generations and concentrations of PAMAM on

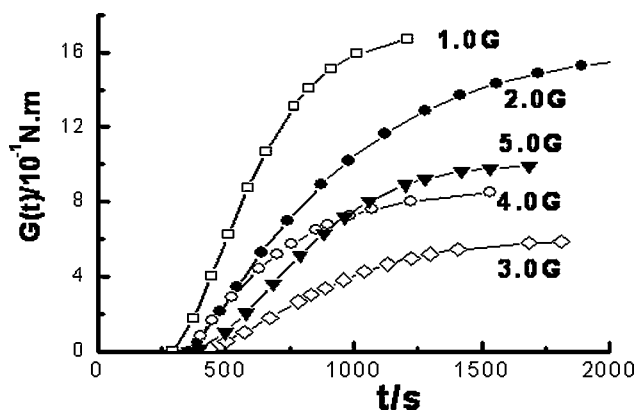


Figure 3 Isothermal cure curves using PAMAMs as curing agent with an epoxy/PAMAM ratio of 10 phr at 110°C .

gelation time t_g are quite complicated. At a fixed PAMAM concentration, there is no simple monotone relationship between the gelation time t_g and the generations of PAMAM. The 1.0 G PAMAM dendrimer shows the shortest gelation time while 3.0 G PAMAM shows the longest. Beyond 3.0 G, the gelation time decreased with the generation of PAMAM dendrimers. Table I shows some important characteristic data of different generations of PAMAM dendrimers. The 1.0 G PAMAM dendrimer has the most number of primary amines per diagram of PAMAM in the outer shell of the dendrimers when compared with the other generations of dendrimers (G2–G5), so the epoxy resin system with the same diagrams of 1.0 G PAMAM shows the shortest gelation time (Fig. 3). Furthermore, the G3 PAMAM dendrimer has the lowest density of primary amines per volume of PAMAM dendrimers in contrast with other generations that can be calculated from the data listed in Table I. As a result, the gelation time decreased with the generation of PAMAM dendrimers beyond 3.0 G. Figures 4–6 show the isothermal cure curves in the presence of PAMAM dendrimers (generations 1.0, 3.0, and 5.0 G) with different ratios of 5, 10,

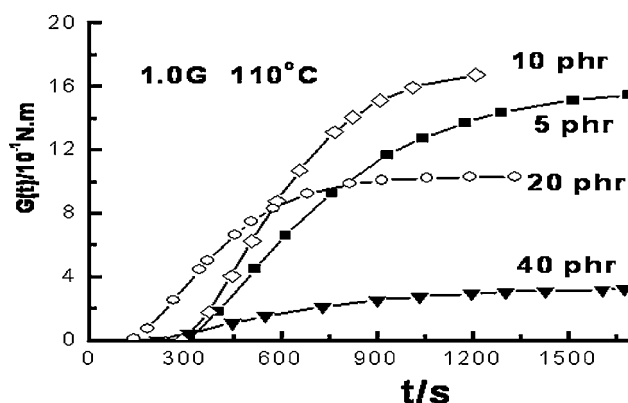


Figure 4 Isothermal cure curves using 1.0 G PAMAM as curing agent with different epoxy/PAMAM ratios (5 to 40 phr) at 110°C .

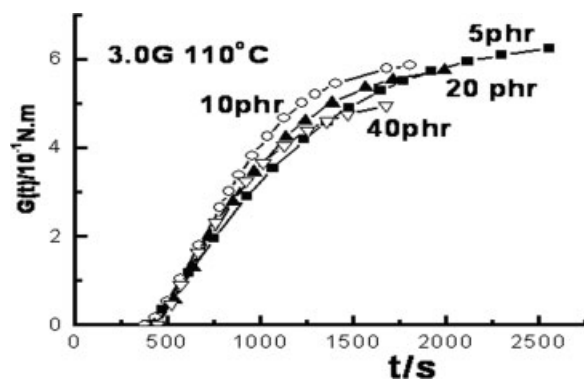


Figure 5 Isothermal cure curves using 3.0 G PAMAM as curing agent with different epoxy/PAMAM ratios (5 to 40 phr) at 110°C.

20, and 40 phr. The relationship between the gelation time t_g and the concentration of PAMAM become even more complicated in contrast to the one between gelation time t_g and the generation of PAMAM dendrimers. However, the cure rate after gelation time (calculated by the slope of the curves) is fastest, and the physical and mechanical quantities $G(t)$ is the largest when the PAMAM ratio is 10 phr for 1.0, 3.0, and 5.0 G. This experimental result could be explained by the competition and compromise of the two effects: the density of reactive amino groups and the steric hindrance effect of the dendrimers after it was saturated for the resin systems. The DTVM results show that 10 phr PAMAM was the optimum concentration for 1.0, 3.0, and 5.0 G PAMAM dendrimers/resin systems in our experiment.

Analysis of thermal behavior by TGA

Weight loss of a material as function of time or temperature is commonly determined using TGA and it is an irreversible process because of the thermal degradation. TGA curves of E51/1.0 G PAMAM and

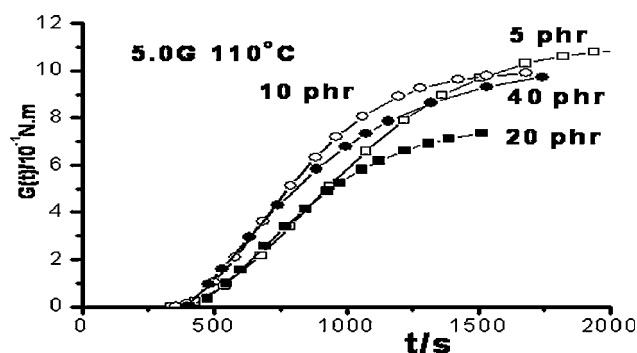


Figure 6 Isothermal cure curves using 5.0 G PAMAM as curing agent with different epoxy/PAMAM ratios (5 to 40 phr) at 110°C.

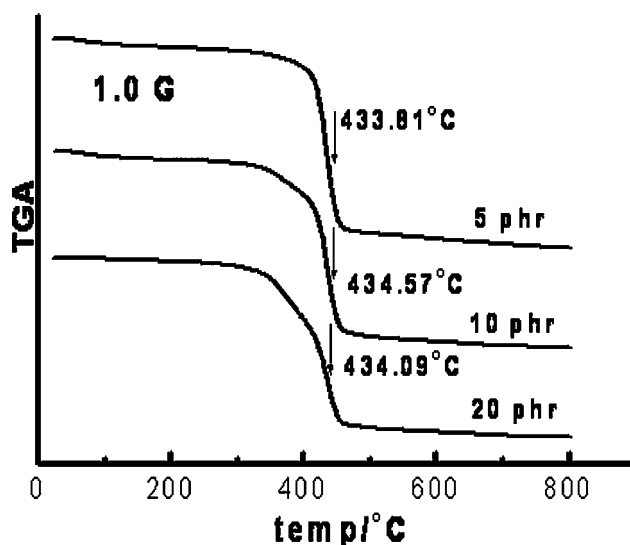


Figure 7 The TGA curves of material using 1.0 G PAMAM as curing agent with different epoxy/PAMAM ratios (5, 10, and 20 phr).

E51/5.0 G PAMAM are shown in Figures 7 and 8. For 1.0 G PAMAM, the maximum weight loss rate of the material using 5 phr PAMAM as curing agent occurs at 433.81°C, while for the material using 10 phr PAMAM at 434.57°C. However, it is not a simple monotone relationship between the maximum weight loss rate temperature and the concentrations of PAMAM. The maximum weight loss rate of the material using 20 phr PAMAM as curing agent occurs at 434.09°C. The results of these materials show the similar rule for both 1.0 G PAMAM and 5.0 G PAMAM. TGA curves of the material using different generations of PAMAM as curing agents were also shown in Figure 9. It can be deduced that the presence of PAMAM enhances the thermal stability of the resin according to the com-

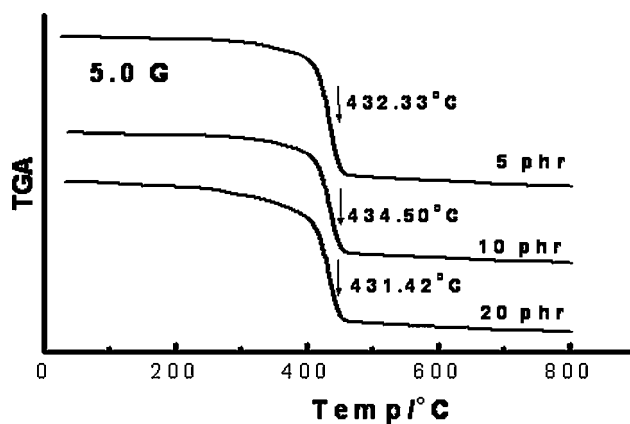


Figure 8 The TGA curves of material using 5.0 G PAMAM as curing agent with different epoxy/PAMAM ratios (5, 10, and 20 phr).

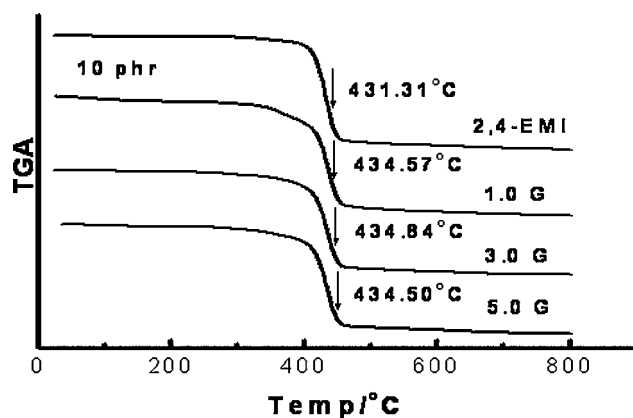


Figure 9 The TGA curves of material using different generations of PAMAM as curing agents with the epoxy/PAMAM ratio 10 phr.

parison made with the same concentration of 2,4-EMI. However, when the concentration of PAMAM dendrimers reached the saturated concentration (10 phr for PAMAM dendrimers in this experiment) for the epoxy resin systems, the excess dendrimers play roles as hindrance effect in crosslinking structures of resin systems. This means that the excess dendrimers would decrease the maximum weight loss rate temperature of the material. The TGA results are in agreement with the conclusions that the optimum PAMAM concentration for 1.0, 3.0, and 5.0 G

PAMAM dendrimers/resin systems was 10 phr in our experiment made by the DTVM.

CONCLUSIONS

The DTVM results show that 10 phr PAMAM was the optimum concentration for 1.0, 3.0, and 5.0 G PAMAM dendrimers/resin systems in our experiment. Also, the TGA results are in agreement with the conclusions made from the DTVM. Although dendrimer as curing agents is in its infancy, it offers several attractive features. Our future work will focus on evaluating the properties of the cured resin products with dendrimers, discussing the advantages and disadvantages of PAMAM dendrimers as curing agents in the resin systems in comparison with conventional aliphatic and aromatic amines.

References

1. Tomalia, D. A.; Baker, H.; Dewald, J. *Polymer J* 1985, 17, 117.
2. Tomalia, D. A.; Baker, H.; Dewald, J. *Macromolecules* 1986, 19, 2466.
3. Tomalia, D. A.; Dewald, J. U.S. Pat. 4,507,466 (1985).
4. Tomalia, D. A.; Dewald, J. U.S. Pat. 4,558,120 (1985).
5. Tomalia, D. A.; Dewald, J. U.S. Pat. 4,568,737 (1986).
6. Tomalia, D. A.; Frechet, J. M. *J Polym Sci A* 2002, 40, 2719.
7. Boogh, L.; Pettersson, B.; Manson, J. A. E. *Polymer* 1999, 40, 2249.
8. Ratna, D.; Simon, G. P. *Polymer* 2001, 42, 8833.
9. Cheng, Y. Y.; Chen, D. Z.; Fu, R. Q. *Polym Int* 2005, 54, 495.
10. He, P. S.; Li, C. E. *J Appl Polym Sci* 1991, 43, 1011.
11. Cheng, Y. Y.; Chen, D. Z.; Wang, C. L. *J Appl Polym Sci* 2005, 97, 1.