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Cure behavior of epoxy resin/CdS/2,4-EMI nanocomposites investigated by dynamic torsional vibration method(DTVM)

Yao Yuan, Chen Dazhu, He Pingsheng (✉), Yang Haiyang

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, Anhui, China
E-mail: hpsm@ustc.edu.cn

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Summary

Epoxy resin/CdS nanocomposite was prepared by a novel method and its cure behavior was investigated by the HLX-II Resin Curemeter based on the dynamic torsional vibration method (DTVM). The non-equilibrium thermodynamic fluctuation theory, the Avrami equation and the Flory's gelation theory have been used to analysis the cure behavior of the composite systems with different CdS and cure agent loadings at various temperatures. The results show that the addition of CdS nanoparticles reduces the gel time t_g, but has little effect on the mechanism of the cure reaction. The theoretical prediction is in good agreement with the experimental results. The Avrami exponent of n decreases a little when the temperature increases.

Introduction

The synthesis of nanoparticles embedded in polymeric matrixes has recently attracted considerable attention [1-5]. Because of their unique phase morphology and improved interfacial properties, nanocomposites usually exhibit improved properties, such as optics [6], molecular electronics [7] and magnetism [8] etc, compared with conventional composite materials. Polymers, normally exhibiting special physical and mechanical properties, such as long-term stability, flexible process abilities, can be used for preparing various functional nanocomposites. Epoxy resin, as one of the important thermosetting resins, has been of great current interest in the synthesis of nanocomposites [9-12]. The nature properties of epoxy resin make it possible to manufacture nanocomposite with nice characteristics.

CdS nanocrystals, as one of the most important II-VI group semiconductors, have critical applications in solar cells, quantum size effect semiconductors, non-linear optics, optoelectronic and electronic devices[13]. Due to the difficulties of dispersing nanoparticles with high specific energies into matrix polymer, it is important to prepare polymer/CdS nanocomposite with a simple method. In the present study, we introduced a novel approach of in situ synthesis of CdS nanoparticles and epoxy resin E51/CdS nanocomposite, and the reaction was taken place in epoxy resin/water emulsion. The resulting nanocomposite, cured with a normal curing agent, displayed

the mechanical strength and the optical transparence properties analogous with or even better than that of pure cured epoxy resin. The CdS particles in epoxy resin were proved to be in nano-size by XRD, UV reflective adsorption and TEM analysis.[14-16] As well known, the curing process of a resin system is the critical and productivity controlling step in the fabrication of thermosetting-based composites. As soon as the cross-linking forms, the resin will not be softened and melted. Traditionally, chemical analysis, Fourier transformed infrared spectroscopy [17] and differential scanning calorimetry [18] that detect the degree of the conversion of reactive groups were used to study the cure process. The sensitivity and function of these analysis techniques are much reduced at the last curing stage due to the increased consumption of reactive groups. Whereas, mechanical methods, such as the dynamic torsional vibration method (DTVM) used in the HLX-II Resin Curemeter, developed in our lab, shows a potential in monitoring the complicated cure process[19-26]. The application in epoxy resin and unsaturated polyester resin [19-22] has proved that the DTVM technique is considerably effective for cure study.

Experimental

Materials

The diglycidyl ether of biphenyl A, epoxy resin E51 with an epoxy value 0.48-0.54 and average epoxy equivalent 196 (Shanghai Resin Factory), 2-ethyl-4-methyl-imidazole (2,4-EMI), AR, used as curing agent (Development Center of Special Chemical Agents in Huabei Region) were commercial available. Other chemicals including methanol, acetone, $Cd(Ac)_2$ and Na_2S were all A.R. grade and used without any treatment.

Preparation of epoxy resin E51/CdS nanocomposites

0.5g $Cd(Ac)_2$ was dissolved in 4ml methanol, then 5g (10g) epoxy resin E51 and 10ml (20ml) acetone were added in and mixed with each other. After that, it was slowly added into aqueous solution of Na_2S, 1g in 75ml (2g in 150ml), with agitation. It was observed that emulsion was formed quickly and the color turned into yellow, and began to precipitate. The product was filtered and washed with water, dried in oven at 75°C for 2h with agitation every 10 min. Finally the homogenous viscous liquid of orange color was obtained, and the CdS loadings were 5phr and 10phr respectively. For the isothermal cure experiment, the epoxy resin E51/CdS nanocomposite was mixed with 2,4-EMI with loadings of 5, 10, 15 phr, respectively.

Dynamic torsional vibration method and experimental curve

Dynamic torsional vibration is a non-resonant forced vibration. The resin system with a different degree of cure has a different torque (or modulus, viscosity etc.). Therefore the change in the mechanical properties, i.e. the degree of cure of the resin system, can be monitored and determined by measuring the changes in torque during the cure process. The schematic diagram of a homemade experimental setup—HLX-II Resin Curemeter is shown in Fig.1. It has three parts: mechanical system, electric system and computer system. The mechanical system is the key part for the apparatus to realize its functions. The principle of this part will be introduced later. The electronic

system serves in amplifying the torque and temperature signals, collecting the state messages of the apparatus and proceeding the A/D transition, which makes it possible for the computer system to collect system states and data and thereby control the whole curemeter. Its hardcore is made up of amplifier A/D converter, temperature controller and interface control unit. The computer system is responsible for sending commands to control each operation of the curemeter. With the aid of a self-programming software, the recordation and treatment of data is completed efficiently through this part.

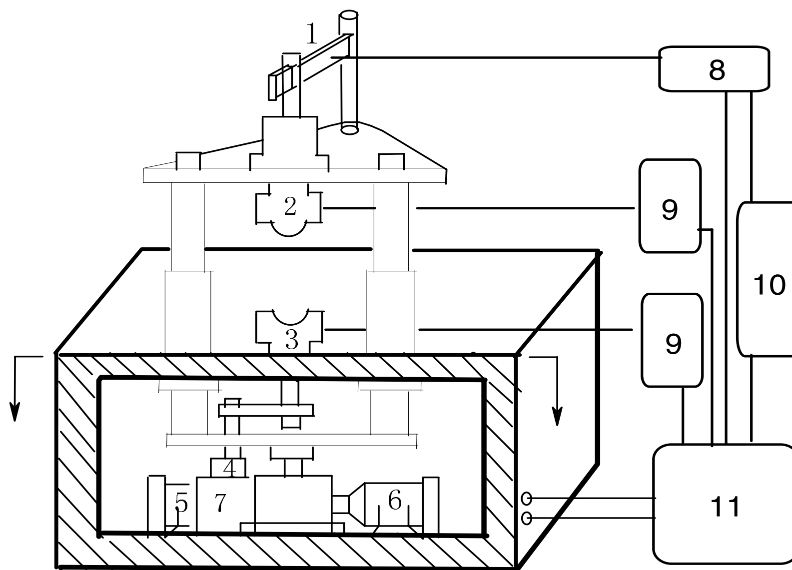

Figure 1 Schematic representation of the dynamic torsional vibration apparatus. 1 Strain gauge load cell; 2 upper mold; 3 lower mold; 4 eccentric disc; 5 motor for torsional vibration; 6 motor for closing molds; 7 speed change gear; 8 amplifier; 9 temperature control meter; 10 recorder; 11 power supporter

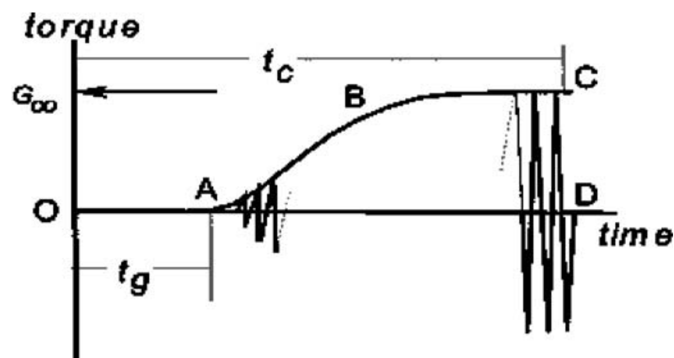

Figure 2 Illustration to the isothermal experimental cure curve

The resin mixture is placed in the lower mold 3. When the motor 6 is switched on, the upper mold 2 comes down, and the molds close with a gap that can be adjusted. Before this operation, the two molds are heated to an appointed temperature via the heater. The cure temperature is controlled by the thermistor. 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 an eccentric disc4 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.After amplified through the electronic system, the electric signals are recorded by the computer, and as the result, the resin cure process is timely monitored.
A typical experimental curve obtained by DTVM is shown in Fig.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 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 curing curve is a 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 completed enough) for the gelation in the resin system to occur, and the torque appears and the strain gauge load cell inputs some signal. Thus, the point A is the gel point and the time corresponding to OA is the gel time t_g for the system. After point A the torque increases with increasing curing time. The increasing amplitude of the torque (slope of the curve) reflects the rate of the curing reaction. The increasing trend of the torque tends to steady with increasing curing time, and the equilibrium torque G_∞ is thus reached (point B). In the meantime, the curing reaction is completed and a cup-like experimental curve is obtained. The time corresponding to OC is the full curing time. 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 the time axis, for convenience we can just take the upper-half of the envelope as the isothermal cure curve to analyze the cure process.

Results and Discussion

Isothermal cure curve of epoxy resin E51/2,4-EMI

The isothermal cure curves (G-t) of pure epoxy E51-2,4-EMI (2,4-EMI loading is 10 phr) system at 65, 70, 75 and 80°C obtained by DTVM are shown in Fig. 3. The curves at different temperatures are similar in shape, but obvious differences in their gel times t_g. The t_g is 33.10 min for the resin system cured at 65°C, and is down to 12.88 min for the resin system cured at 80°C. The initial torque G_0 is zero because the curve at the time period of 0-t_g is identical to abscissa. The torque appears after t_g and the increasing amplitude of torque rises with increasing of the temperature, indicating that the cure rate is improved at higher temperature. The dependence of cure rate on curing temperatures is quite consistent with the description in the documents. With raising cure temperature, more reactants arrive at the desired reactive state, and thus the cure rate increases. In the testing of DTVM, the time to reach the maximum or equilibrium torque G_∞ is determined as the completed cure time t_c and decreases with

increasing of the temperature, but the G_∞ is almost the same for these four temperatures. The values of t_g and t_c at four temperatures for the pure resin system are listed in Table 1. As mentioned above, the degree of cure of the resin system can be reflected from the changes of torque. After the gel point, the increase of the viscosity and torque illuminates a formation of the three-dimensional network of the epoxy. The improvement of cure temperature raises the crosslinking density, and the longer the curing time, the higher the crosslinking density.

Owing to the torque of the cure curve after the gel point is proportional to the degree of cure reaction of the resin system, it is convenient to introduce a new parameter of relative degree of cure α at any time as following:

$$\alpha = G(t) / G_\infty \quad (\mathbf{1})$$

Where $G(t)$ is the torque at time t. Based on the definition, therefore, the isothermal cure curve of (G - t) can be easily converted to the plot of (α - t) which directly reflects the relation between the relative cure degree and the cure time (Fig. 4).

The cure behavior of epoxy resin-based nanocomposite has an obviously temperature dependence in the same way. With increasing cure temperature, the cure reaction is accelerated and the slope of the cure curve is increased. As the result, the values of t_g and t_c decrease markedly. The t_g of the system decrease a little with increasing of the

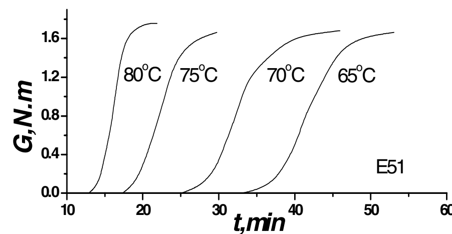

Figure 3 Plots of torque vs. time for epoxy resin E51/2,4-EMI nanocomposites

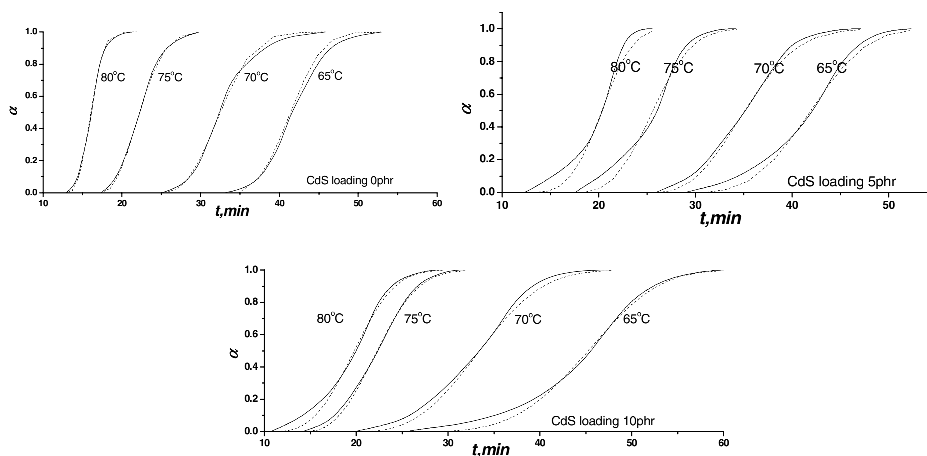

Figure 4 Plots of relative degree of cure vs. time for epoxy E51/CdS/2,4-EMI nanocomposite with varying loadings of 2,4-EMI。 —Experimental ; ------Theoretical

CdS loading in nanocomposite, indicating that the addition of CdS has some effect on enhancing the gelation. For example, the system with 5 phr CdS loading cured at 65°C has a decrease of 2.8 min in t_g comparing with the pure epoxy resin. Fig.5 shows the influence of CdS to the nanocomposites. As we all know, cure temperature and agent have active effect on the whole process. The higher of cure temperature and agent loadings, the sooner of the cure process. The addition of CdS has the same effect on cure process with agent. With the cure process carried on, the crosslinking density increased rapidly. Due to the obstructive effect of viscosity, the left reactive groups have difficulty to match each other. When this obstructive effect plays leading role, the reaction after t_g has been decelerated, and the t_c increased. The addition of CdS make this effect more apparent. If the temperature and 2,4-EMI loadings were not high enough, the accelerated effect and the decelerated effect of viscosity have equal influence on the system. We can see from Tab.1, for 5phr 2,4-EMI, the change in t_c was not clear, at 65°C the t_c even decreased a little when CdS loading increased. But for 15phr 2,4-EMI the t_c increased obviously with the increase of CdS loading. It can be concluded that although the addition of CdS decreases the gel time, it has obstructive effect on the whole reaction.
The isothermal cure curves of E51/CdS/2,4-EMI with the same CdS loading and the different 2,4-EMI loadings can be seen from Fig.6. It is evident from Fig.6 that with the increasing loadings of 2,4-EMI the t_g decreases, and the reaction rate increases in turn, but the 2,4-EMI has little influence on the cure mechanism of epoxy system.

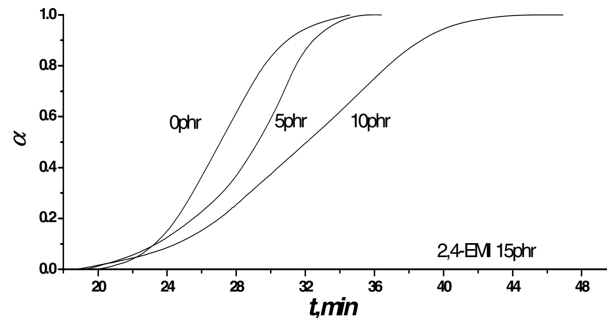

Figure 5 Plots of relative degree of cure vs. time for epoxy resin E51/CdS/2,4-EMI nanocomposites, CdS loadings are 0,5,10phr respectively, 80°C

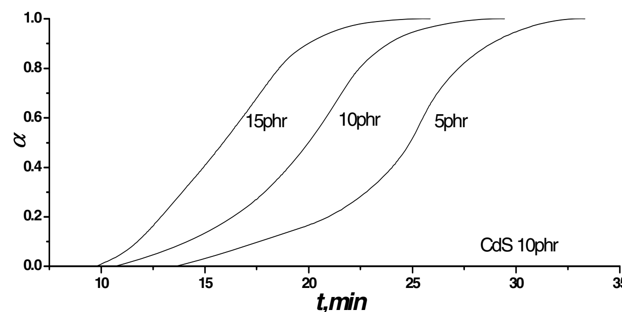

Figure 6 Plots of relative degree of cure vs. time for epoxy resin E51/CdS/2,4-EMI nanocomposites, 2,4-EMI loadings are 5,10,15phr respectively, 80°C

Tab.1 Isothermal cure data of epoxy resin E-51/CdS/2,4-EMI nanocomposites at different temperatures

2,4-EMI	T	CdS 0phr		CdS 5phr		CdS 10phr	
(phr)	(°C)	t_g (min)	t_c(min)	t_g (min)	t_c(min)	t_g (min)	t_c(min)
5	65	47.70	82.73	45.43	79.60	37.18	75.67
	70	35.95	61.45	32.28	56.60	29.24	61.45
	75	21.33	40.63	22.43	40.50	18.77	42.14
	80	17.32	30.40	16.50	31.88	13.59	32.32
10	65	33.10	52.73	28.88	51.40	25.40	58.33
	70	25.11	45.33	25.86	45.15	19.78	44.66
	75	17.33	29.80	17.55	32.50	14.16	30.25
	80	12.88	21.40	12.29	24.22	10.68	28.00
15	65	29.78	47.55	23.33	50.13	22.64	54.06
	70	19.88	34.30	19.26	34.50	18.73	43.83
	75	15.50	24.40	14.08	26.44	13.27	27.00
	80	10.17	17.75	10.42	19.18	9.73	23.82

Theoretical prediction of cure behavior

Hsich's non-equilibrium thermodynamic fluctuation theory [27] directly describes the changes of physical or mechanical properties of the curing system during cure. According to the theory, the physical or mechanical properties of the resin system during cure can be expressed as

$$\frac{G_\infty - G_{(t)}}{G_\infty - G_0} = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \quad (2)$$

Where G_0 and G_∞ are the initial and final physical and mechanical quantities (torque or modulus, viscosity etc.) during cure, respectively; $G(t)$, the property at time t; τ, the time parameter (relaxation time) of the reaction system; and β, the constant describing the width of the relaxation spectrum. In our experiment the mechanical quantity is torque. As seen from the isothermal cure curve in Fig.4, G_0 is zero, the torque beginning to appear only after the gel time t_g. Eq. (2) describing the curing curve after t_g would be

$$\frac{G_\infty - G_{(t)}}{G_\infty} = \exp\left[-\left(\frac{t - t_g}{\tau}\right)^\beta\right] \quad (3)$$

or

$$G_{(t)} = G_\infty \left\{1 - \exp\left[-\left(\frac{t - t_g}{\tau}\right)^\beta\right]\right\} \quad (4)$$

Eq.(4) describes the changes in torque of the resin system during cure in which t_g and G_∞ can be read directly from the isothermal cure curve.

In order to obtain the relaxation time τ, let $t = t_g + \tau$, thus

$$G\,(t_g + \tau) = G_\infty\,(1 - e^{-1}) = 0.63\,G_\infty \quad (5)$$

From a measurement of the time corresponding to $0.63G_\infty$ in the experimental curing curve, the relaxation time τ can be obtained according to $\tau = t - t_g$.
Having determined τ, Eq(4) is reduced to an equation with a single parameter only. A non-linear regression is used to fit Eq(4) to all experimental cure curves. The values of β at various temperatures or CdS loadings can be determined using the line of best fit, as seen in Table 2. With this β value, the torque $G(t)$ at any time, i.e., the theoretically predicted value can be calculated according to Eq.(4) provided that the gel time t_g and the relaxation time τ are already known. The theoretical curing curves are also plotted in Fig.4 as a dot line. The theoretical prediction shows a good agreement with the experimental curves for various curing temperatures.

Tab.2 Cure data of epoxy resin E-51/CdS/2,4-EMI nanocomposites at different temperatures

2,4-EMI	T	CdS 0phr		CdS 5phr		CdS 10phr	
(phr)	(°C)	τ(min)	β	τ(min)	β	τ(min)	β
5	65	18.70	2.06	20.40	2.31	25.15	2.73
	70	12.79	2.49	15.13	2.40	20.98	2.90
	75	8.77	1.96	12.53	2.35	15.30	2.40
	80	6.56	2.39	8.98	2.71	12.06	3.49
10	65	9.40	2.95	14.62	3.28	21.90	3.72
	70	8.53	2.52	10.74	2.48	15.48	2.91
	75	5.76	2.27	9.15	2.91	9.32	2.65
	80	3.63	2.79	8.89	3.62	10.29	3.00
15	65	10.56	3.57	15.93	3.73	21.04	2.87
	70	8.18	2.73	10.98	3.40	15.47	2.69
	75	4.79	2.71	7.39	2.85	7.84	2.64
	80	3.73	2.70	4.40	2.56	7.32	2.06

The application of Avrami model

The Avrami equation has a classical form [28]

$$\alpha = 1\text{-}\exp[-k' t^n] \quad \textbf{(6)}$$

where α is the relative degree of cure; t the cure time; t_g the gel time; n the Avrami exponent that is a reflection of nucleation and growth mechanism; and k a temperature dependent kinetic constant.
Due to the cure curve being the same as the abscissa before gelation time t_g, the isothermal cure data obtained by the DTVM can be analyzed using the following modified Avrami equation [29]:

$$\alpha = 1\text{-}\exp[-k(t - t_g)^n] \quad \textbf{(7)}$$

or

$$\ln[-\ln(1\text{-}\alpha)] = \ln k + n\ln(t - t_g) \quad \textbf{(8)}$$

Eq. (8) can be used to get the kinetic parameters from the cure curves at different temperatures. The units of k and t or t_g are $(\text{min})^{-n}$ and min, respectively. A best fit line

of the plot of ln[-ln(1-α)] vs. ln(t-t_g) will provide parameter n from the slope and k from the intercept. Fig. 7 is a typical plot of the above equation for the cure process of the epoxy resin E51/CdS/2,4- EMI. The kinetic parameters obtained by the Avrami theory are listed in Table 3. The good linearity indicates that it is valid to illustrate the cure process after the gel point.

The apparent rate constant k determines the rates of the nucleation and growth processes that control the curing rate. As seen from Table 3, the apparent rate constant k retains a remarkable sensitivity to the cure temperature. Values of k rise with increasing cure temperature, that is, the higher the temperature, the faster the cure rate. The values of Avrami exponent n, describing the isothermal cure, depend on the cure temperatures for E51/CdS/2,4-EMI systems. Similar results are obtained in E51/2,4-EMI systems without CdS. As we have known, the Avrami exponent provides qualitative information on the nature of the nucleation and the growth process in the crystallization of a polymer and can change. The fact of change in n may imply that a change occurs in the cure mechanism when using a lower cure temperature, although the formation and growth of microgels (i.e. molecular aggregates) is essentially different from those of crystals. After the gel point, the cure reaction is predominantly diffusion-controlled, as the retardation of viscosity and a mass dispersion limitation eventually sets in, the microgel particles are forced to impinge on one another, and phase inversion may occur. From Table 3 we can see that as the temperature increased, n values decrease in turn, and E51/2,4-EMI systems without CdS always have higher n values. According to the discussion above, we may conclude that it is less of a mass transfer limitation at lower cure temperatures or with less CdS loadings that leads to the relatively higher values of n. At any curing temperature, the case of E51/CdS/2,4-EMI nanocomposites has a smaller value of n than that of E51/2,4-EMI system without CdS. This phenomenon may exist because the CdS particles play a role of speeding up the heterogeneous nucleation during curing.

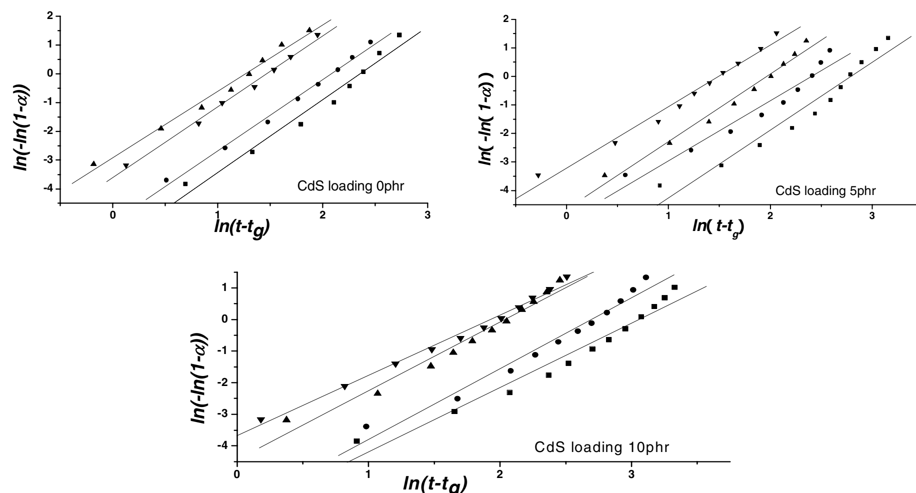

Figure 7 Plots of ln(-ln(1-α)) vs.ln(t-t_g) for epoxy resin E51/CdS/2,4-EMI nanocomposites, 2,4-EMI loading 15phr, ■65°C, ●70°C, ▲75°C, ▼80°C

Tab.3 The kinetic parameters of cure for the epoxy resin E51/CdS/2,4-EMI system

Kinetic parameters	T(°C)	k(10^{-3})	n
	65	2.58	2.53
CdS 0phr	70	5.74	2.48
	75	27.05	2.70
	80	53.93	2.32
	65	1.31	2.38
CdS 5phr	70	6.22	2.11
	75	9.47	2.37
	80	39.96	2.16
	65	2.0	2.04
CdS 10phr	70	2.4	2.24
	75	11.9	2.16
	80	25.50	2.20

Apparent activation energy

According to the Flory's gelation theory [30], the chemical conversion at the gel point of the resin system is constant and is not related to the reaction temperature and experimental conditions. As a result, the apparent activation energy of the cure reaction Ea can be obtained from the gel time t_g

$$\ln t_g = C + E_a/RT \qquad (\mathbf{9})$$

where T is the curing temperature (K); R, the gas constant, and C, a constant. Fig.8 shows a plot of ln t_g vs. $1/T$ for various CdS loadings of 0, 5, 10 phr, and 2,4-EMI loadings of 5phr. The apparent activation energy E_a can be calculated from the slope of the lines.

The activation energy can also be estimated by the Avrami method. An empirical approach can be used to describe the temperature dependence of the kinetic constant k. Assuming that k is thermally activated:

$$k^{1/n} = k_0 \exp(-E_a/RT) \qquad (\mathbf{10})$$

where E_a is an activation energy associated with the cure process and k_0, a pre-exponential constant. The logarithmic plots of $(1/n)\ln k$ as a function of $1/T$ are shown in Fig.9 for E51/CdS/2,4-EMI systems. The fit to linearity allows calculation of the activation energy from the slope of the straight line. The values of activation energy obtained by the above methods are listed in Table 4. We can see from the Table 4 that the activation energies of cure E51 system obtained by Eq.9 and Eq.10 are close to each other. The activation energies decrease with the addition of CdS loadings, indicating that the addition of CdS accelerates the gelation process, which is accordant with the variety of t_g discussed above.

Tab.4 Activation energy of epoxy resin E51/CdS/2,4-EMI nanocomposites

CdS(phr)	E_{a1}(kJ/mol)(Eq.9)	E_{a2}(kJ/mol)(Eq.10)
0	71.3	68.3
5	67.5	50.0
10	68.6	46.8

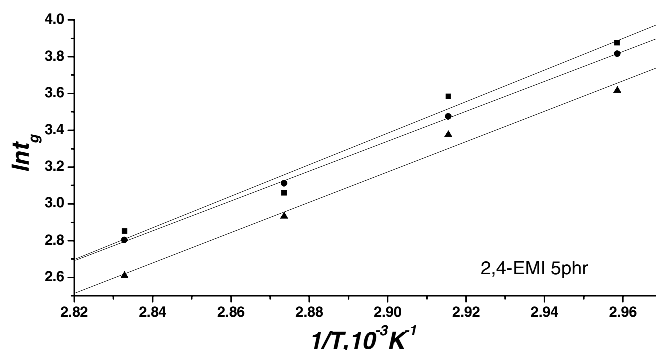

Figure 8 Plots of lnt_g vs. 1/T of epoxy resin E51/CdS/2,4-EMI nanocomposites, CdS loading ■0phr●5phr▲10phr

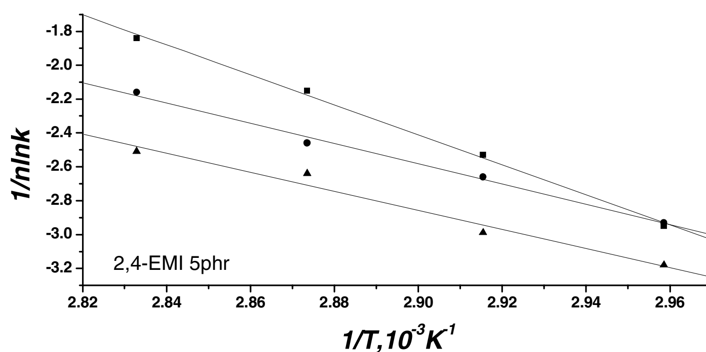

Figure 9 Plots of 1/nlnk vs. 1/T of epoxy resin E51/CdS/2,4-EMI nanocomposites, CdS loading ■0phr●5phr▲10phr

Conclusions

The HLX-II Resin Curemeter based on the dynamic torsional vibration method (DTVM) has successfully been applied to monitor cure behavior of epoxy resin/CdS/2,4-EMI nanocomposite. The influence of cure temperature, CdS loading and EMI curing agent loading on cure behavior could be investigated by the DTVM as well. The apparent kinetic parameters of cure reaction, including apparent activation energies E_a, gelation time t_g of cure systems with varying cure conditions and composes have been obtained. The results show that the addition of CdS nanoparticles reduces the gel time t_g, but has little effect on the mechanism of the cure reaction. The theoretical prediction of cure behavior based on the non-equilibrium thermodynamic fluctuation theory is in good agreement with the experimental results for different cure conditions here. Also Avrami theory used to study phase change of crystallization behavior could be used to describe the cure behavior.

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