

EFFECT OF NANOSILICA ON THE KINETICS OF CURE REACTION AND THERMAL DEGRADATION OF EPOXY RESIN

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Abstract Nanocomposites from nanoscale silica particles (NS), diglycidylether of bisphenol-A based epoxy (DGEBA), and 3,5-diamino-*N*-(4-(quinolin-8-yloxy) phenyl) benzamide (DQPB) as curing agent were obtained from direct blending of these materials. The effect of nanosilica (NS) particles as catalyst on the cure reaction of DGEBA/DQPB system was studied by using non-isothermal DSC technique. The activation energy (E_a) was obtained by using Kissinger and Ozawa equations. The E_a value of curing of DGEBA/DQPB/10% NS system showed a decrease of about 10 kJ/mol indicating the catalytic effect of NS particles on the cure reaction. The E_a values of thermal degradation of the cured samples of both systems were 148 kJ/mol and 160 kJ/mol, respectively. The addition of 10% of NS to the curing mixture did not have much effect on the initial decomposition temperature (T_i) but increased the char residues from 20% to 28% at 650°C.

Keywords: Thermosets; Resins; Curing of polymers; Thermal properties; DSC.

INTRODUCTION

Epoxy thermosets have been widely used as high performance adhesives, barrier films in food packing and matrix resins in fiber-reinforced compositions due to their outstanding mechanical and thermal properties. The properties of a thermosetting polymer depend on the extent of chemical reactions that take place during cure and the resin morphology. To predict the morphology developed by the phase separation of rubber-rich phase during polymerization of epoxy resin with amines, it is necessary to know the reaction kinetics of the crosslinked polymer system. DSC in both isothermal and dynamic modes has been used extensively in studying kinetics of cure reaction of epoxy with different curing agent systems^[1–9]. Silica particles are widely used as reinforcing fillers for epoxy molding compounds and encapsulants in the modern electronic industrials. Mixing the nanoscale particles with polymeric materials provides a convenient approach to form organic-inorganic hybrid materials. Hybrid materials, also known as nanocomposites, are interesting substances from the standpoint of their potentially increased performance capabilities relative to those either of their nonhybrid species^[10–18].

Silicon-containing polymers are described that can degrade, forming thermally stable silica, which have the tendency to migrate to the char surface serving as a protection layer to prevent further degradation of char at high temperatures^[19]. It was also reported^[16] that nanoscale colloidal silica particles can act as curing agent for epoxy without adding metal salts as catalyst and also in the presence of different metal salts. In our previous article we reported the synthesis and characterization of a novel diamine 3,5-diamino-*N*-(4-(quinolin-8-yloxy) phenyl) benzamide (DQPB)^[20]. In this paper, we report this diamine as thermal curing agent for diglycidylether of bisphenol-A based epoxy (DGEBA). The kinetics of cure reaction of DGEBA with the prepared diamine

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(DQPB) and in the presence of nanosilica particles was investigated by using non-isothermal DSC technique. Thermal degradation of the cured samples was also determined by using TGA.

EXPERIMENTAL

Apparatus

Differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK). Scanning electron microscopic images were taken from the free surface of free films which was sputter coated with a thin conducting layer of gold using a CAMScan-MV2300 instrument (England).

Materials

The epoxy compound used in the study was a DGEBA-based epoxy, Ep. 5: Epoxide equivalent of 196–208, clear yellow liquid, viscosity of 25000 mPa s (at 25°C), provided by Iran Petrochemical Industry (Khuzestan, Iran). Nanosilica with 12.6 nm average particle size and a silanol density of 2.5/nm² was purchased from Nissan Chemical (Tokyo, Japan). Other chemicals were purchased either from Merck or Fluka Chemical Co.

Preparation of DGEBA/DQPB/NS Mixtures

The stoichiometric amount of the curing agent (DQPB) was calculated through the number of active amino hydrogen atoms. DQPB with a molar mass of 370 g/mol and four active hydrogen atoms in the molecule represents 92.5 g for one mole of active hydrogen. This figure is in the stoichiometric equivalent of the eew (epoxy equivalent) and, hence, for every about 200 g of DGEBA, 92.5 g DQPB was used as curing agent. 10% of nanosilica particles (NS) based on the weight of DGEBA was used. Therefore, samples of DGEBA containing the required amount of NS particles were mixed at 50°C to reduce the viscosity of the mixture and to be stirred thoroughly for 30 min to give a homogeneous and uniform mixture. Then, stiochiometric amount of curing agent was added to the mixture at room temperature and mixed completely before using for DSC, TGA and SEM tests.

DSC Analysis

A 10 mg of the uniform viscous mixture was put into a DSC sample pan and covered with an aluminum lid and closed tightly under pressure. The sample pan was placed in the DSC sample cell at ambient temperature, and an empty pan was also placed in the DSC reference cell, and it was heated according to the program of a constant heating rate (5, 10, 15 and 20 K/min) from room temperature to 300°C under nitrogen purge gas.

TGA Analysis

Thermal stability of the epoxy-silica hybrid material was measured with TGA. Heating scans were carried out at 10 K/min. Samples were prepared by pouring the uniform viscous hybrid into aluminum cells and curing it in an oven at 145°C for 2 h. The cured samples were cut into small discs with a certain weight for TGA, and also used for SEM tests.

RESULTS AND DISCUSSION

Curing of DGEBA Nanocomposites

Figure 1 shows dynamic DSC curves for DGEBA/DQPB mixtures at different heating rates. The exothermic peak shifted from 200°C at the heating rate of 20 K/min to less than 158°C at the heating rate of 5 K/min. Slower heating rates give the sample more time to cure, and the exothermic peak shifts toward lower temperatures. There is small exothermic peak at 120°C which is more pronounced at the higher heating rates. The first peak is attributed to the formation of adduct from the catalytic reaction of the epoxide group with the tertiary amine of quinoline ring and the second large exothermic peak is due to the cure reaction. There has been extensive work on the cure reaction of epoxy group with the unsubstituted and 1-substituted imidazoles which has shown the formation of a 1:1 adduct between epoxy group and 1-substituted imidazole through the attack on the epoxy group by the more basic pyridine-type nitrogen^[21, 22].

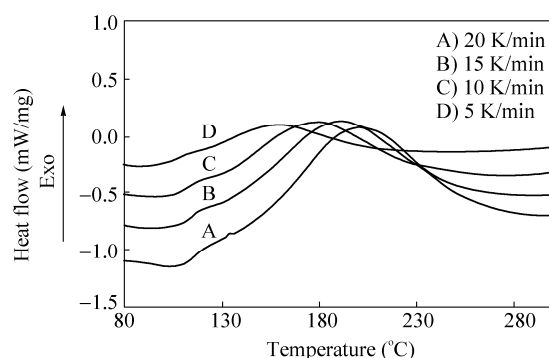


Fig. 1 DSC curves of DGEBA/DQPB at different heating rates

The exothermic peak temperature (T_p) for DGEBA/DQPB system containing 10% of NS shifted towards lower temperature, as shown in Fig. 2 and Table 1. In comparison with the T_p of DGEBA/DQPB system, the decrease in the T_p of DGEBA/DQPB/10% NS system is attributed to the increased rate of the cure reaction.

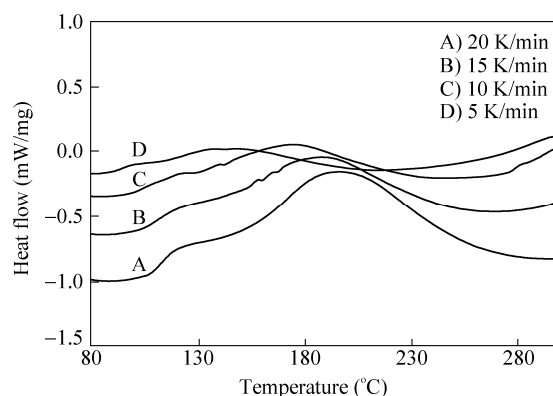


Fig. 2 DSC curves of DGEBA/DQPB/10% NS at different heating rates

Table 1. DSC scanning data for the curing of DGEBA at different heating rates

Sample	q (K/min)	T_p (K)	$1/T_p \times 10^3$ (K ⁻¹)	$\ln q$	$-\ln(q/T_p^2)$	Exo. heat (J/g)
DGEBA/DQPB	5	431	2.32	1.6	10.52	228
	10	451	2.21	2.3	9.92	247
	15	464	2.11	2.7	9.57	252
	20	475	2.10	3.0	9.33	236
DGEBA/DQPB/10% NS	5	416	2.40	1.6	10.45	193
	10	445	2.24	2.3	9.89	151
	15	458	2.18	2.7	9.45	167
	20	468	2.13	3.0	9.30	201

The exothermic curing of both systems DGEBA/DQPB and DGEBA/DQPB/10% NS started at almost 100°C, and samples containing NS reached to the maximum rate at the lower temperature. In general, the exothermic heat of the samples containing NS is lower than the exothermic heat of the samples without NS, as shown in Table 1, and also reported by other researchers^[23].

This can be suggested to be due to the absorption of some of the exothermic heat of cure reaction by the nanosilica particles. The exothermic peaks of both systems showed a very steep slope, meaning that the cure reaction took place rapidly in a short temperature range. The chemical kinetics in the region near vitrification, transition of low molecular weight in liquid or rubbery state to an amorphous glassy state with infinite molecular

weight, is often complicated by diffusion and/or mobility control. In principal, the reaction can proceed to a point ($T_g > T_{cure}$) where all chain movement ceases and the reaction arrests due to the complete absence of mobility. The ultimate conversion can also be lower due to the fact that the remaining reactive groups can not meet and react even in the absence of any diffusion hindrance. The exothermic peak of DSC curves is mainly caused by the sum of the reactions: (a) Non catalytic and catalytic reactions between primary and secondary amines with epoxide groups which yield secondary and tertiary amines and hydroxyl groups. The catalytic reaction between amine and epoxide groups can be carried out by the catalytic action of hydroxyl groups present in the NS particles and produced during epoxide ring opening reaction. (b) The etherification reaction, which may be neglected for stoichiometric mixtures of epoxy with diamines since the reactivity of the diamines to the epoxide rings is much higher than the hydroxyl groups, can be significant when diamine is lower than stoichiometric value and at temperatures above 200°C. However, many equations were developed to investigate the cure kinetics of the epoxy system. All kinetic models start with the following basic equation:

$$d\alpha/dt = k f(\alpha) \quad (1)$$

where $d\alpha/dt$ is the instant cure rate, α is the fractional conversion at a time t , k is the Arrhenius rate constant, and $f(\alpha)$ is a function form of α that depends on the reaction mechanism. Kissinger derived the following equation^[24, 25] for which the temperature varies with time at a constant heating rate, $q = dT/dt$:

$$-\ln(q/T_p^2) = E_a/RT_p - \ln(AR/E_a) \quad (2)$$

where q is the heating rate, T_p is the temperature at which $d\alpha/dt$ is maximum, E_a is the activation energy, R is the gas constant and A is the pre-exponential factor. This method gives a relatively accurate values of E_a and A by calculating the relationship between $-\ln(q/T_p^2)$ and $1/T_p$. The data of the fourth and sixth columns, in Table 1, were introduced to the Kissinger equation, and $-\ln(q/T_p^2)$ versus $1/T_p$ is plotted in Fig. 3.

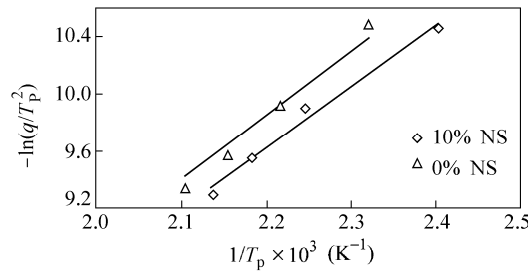


Fig. 3 Kissinger plots for DGEBA/DAPB systems

The E_a and A values, calculated from the slope and the y intersect, respectively, are listed in Table 2. To compare the cure rate for the two systems at a selected temperature (415 K), A and E_a values were introduced to the Arrhenius equation and the results are shown in Table 2.

Table 2. Values of kinetic parameters of cure reaction of DGEBA

Sample	E_a (kJ/mol) ^a	E_a (kJ/mol) ^b	A (min ⁻¹)	K (min ⁻¹) ^c
DGEBA/DQPB	46.5	51.3	6.4×10^4	0.091
DGEBA/DQPB/NS	35.4	40.6	5.4×10^3	0.19

^a Kissinger method; ^b Ozawa method; ^c Arrhenius rate constant at 415 K

The rate constant for the cure reaction of DGEBA/DQPB/NS system increased in comparison with the rate constant of DGEBA/DQPB system. Ozawa-Flynn-Wall method based on Doyle's approximation^[26, 27] is an alternative method for the calculation of E_a and is expressed as follows:

$$\ln q_i = \text{Const.} - 1.052E_a/RT_p \quad (3)$$

A plot of $\ln q_i$ versus $1/T_p$ from Table 1, should give a straight line with a slope of $1.052E_a/R$, as shown in Fig. 4.

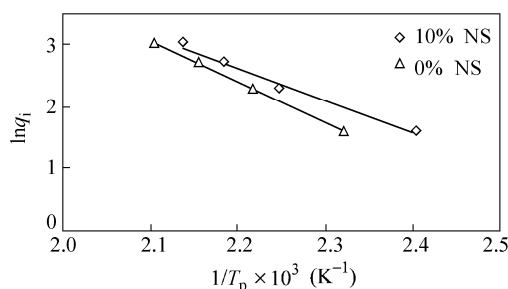


Fig. 4 Ozawa plots for DGEBA/DQPB systems

The E_a values from Ozawa equation are given in Table 2. The E_a values obtained from both equations of (1) and (2) showed a decrease when the cure reaction of epoxy resin proceeded in the presence of nanosilica particles. Therefore, it is concluded that the NS particles acted as catalyst in reaction between epoxide and amine groups. Introducing a catalyst increases the speed of a reaction by lowering the activation energy for the reaction, and acting as a facilitator bringing the reactive species together more effectively. Reducing catalytic substances to nanometers in size greatly increases the surface area available per gram, which in turn boosts the level of catalytic activity. By comparing the kinetic parameters for the epoxy resin cured with neat nanosilica and in the presence of high loaded metal salt promoters^[16] and also for the epoxy-amine system catalyzed with nanoclay particles^[28], it can be suggested that NS as catalyst, as listed in Table 2, improved the cure reaction and decreased E_a in a greater extent.

Scanning electron microscopy was used to study the structure of the produced composite surface. When studying composite structure, the surface is cleaned and coated with a conducting gold layer. Figure 5 shows SEM images of cured epoxy filled with 10% of NS particles. The dispersion of the nanosilica particles is clearly seen from the images. Comparing the primary particle size and the size of nano-particles at the surface of the films, it is seen that the nano-silica particles show some degree of aggregation and are relatively homogeneous at the applied magnification.

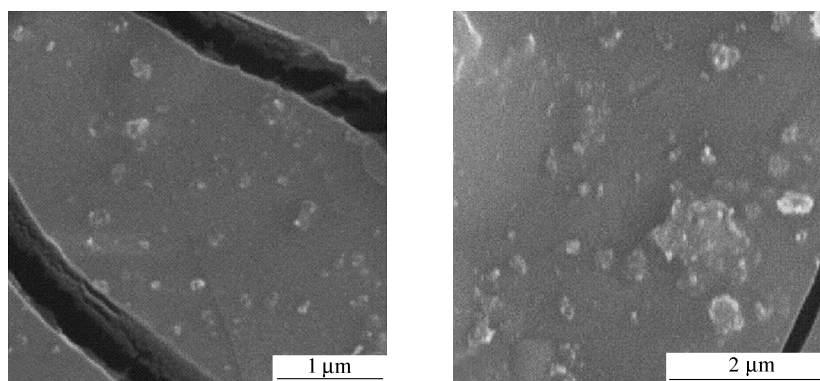


Fig. 5 SEM images of cured epoxy filled with 10% of NS particles

Thermal Stability of Nanocomposite

TGA curves of the cured samples provide their thermal stability and thermal degradation behaviors. Figure 6 shows TGA curves of the cured DGEBA/DQPB and DGEBA/DQPB/NS systems under nitrogen atmosphere. The patterns of the thermogravimetric curves of the epoxy resins hybrid with silica were similar to the patterns of the silica-free resins under nitrogen. The relative thermal stability of the cured samples was compared by noting the initial decomposition temperature (T_i), the temperature of maximum rate of weight loss (T_{max}) and the percent of char yield (Ch.Y.).

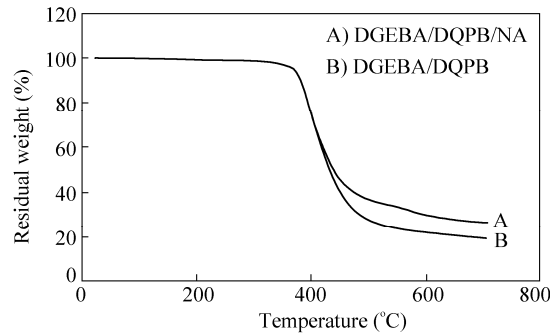


Fig. 6 TGA curves of cured DGEBA nanocomposites

The results are summarized in Table 3. T_i indicates the apparent thermal stability of the cured epoxy resins, *i.e.*, the failure temperatures of the resins in processing and molding. T_i for the cured sample of DGEBA/DQPB and DGEBA/DQPB/10% NS is almost identical of about 375°C, because the thermal weight loss of the hybrid resins comes from the organic phase of epoxy resin. Thermal decomposition of cured epoxy resin involves simultaneous dehydration and C—C bond scission leading to many volatile products such as water, acetone, carbon dioxide, hydrogen cyanide, aliphatic hydrocarbons, *etc.*, at different temperatures^[29–33]. The thermal decomposition of secondary alcohol groups (generated during curing) with elimination of water (dehydration) is the first step of degradation of the epoxy network, which precedes chain scission. Calculation of the E_a value for decomposition of the cured epoxy resin can be carried out from the data of TGA curves, through the integral method based on the Horowitz-Metzger equation^[32]:

$$\ln[\ln(1 - \alpha)^{-1}] = E_a \theta / RT_{\max}^2 \quad (4)$$

where α is the decomposition ratio, θ is the difference between T and $T_{\max}$, $T_{\max}$ is the temperature of maximum rate weight loss, and R is the ideal gas constant. E_a is given by the straight line corresponding to the plot of $\ln[\ln(1 - \alpha)^{-1}]$ versus θ shown in Fig. 7.

Table 3. Thermal degradation data of the cured samples of DGEBA

Sample	IDT (°C) ^a	T (°C) ^b	$T_{\max}$ (°C) ^c	E_a (kJ/mol)	Chr.Y (%), 650°C
DQPB/DGEBA	375	390	430	148	20
DQPB/DGEBA/NS	375	390	436	160	28

^a Initial decomposition temperature (°C); ^b Temperature (°C) for 10% weight loss;

^c Temperature (°C) of maximum weight loss

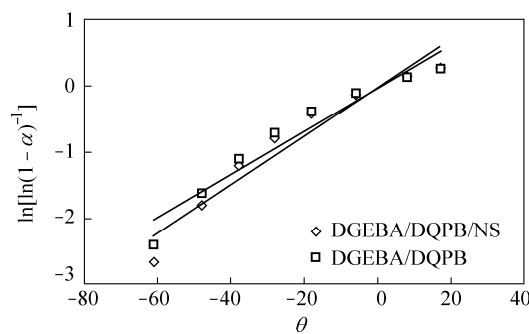


Fig. 7 Plots of $\ln[\ln(1 - \alpha)^{-1}]$ versus θ (Eq. (4))

The E_a values of both systems were calculated from the slope of the straight lines and the values are almost identical of 148 and 160 kJ/mol for thermal degradation of DGEBA/DQPB and DGEBA/DQPB/10% NS systems, respectively, under N_2 atmosphere. Identical pattern of changes in the E_a values for the thermal stability

of the epoxy-silica hybrid materials has been reported by Liu *et al.*^[15]. These results indicate that there is no synergism effect between epoxy resin network and silica filler. The silica particles can function as thermal insulating materials to the residual, and only at high temperatures the thermal insulation effect of the silica can act effectively^[33]. As shown in Table 3, the char yields at 650°C increased from 20% to 28% with the addition of 10% of NS to the curing mixture of DGEBA/DQPB system.

This increase in the char-yield (28%) is just due to the thermal inert of the silica and is based on the rule-of-the-mixture. The char residues from the cured sample of DGEBA/DQPB/NS are the total residue of the epoxy resin and the silica.

CONCLUSIONS

Kinetics of cure reaction of DGEBA with an aromatic diamine and in the presence of 10% nanosilica was studied by non isothermal DSC technique, and by using Ozawa and Kissinger equations. The E_a value of cure reaction of DGEBA/DQPB system decreased about 10 kJ/mol when 10% nanosilica particles were present in the mixture. It is suggested that nanosilica particles acted as catalyst in reaction between the epoxide and amine groups. The E_a value of thermal degradation was calculated from Horowitz-Metzger method. The presence of 10% of NS in the cured sample of epoxy resin did not increase the initial decomposition temperature (T_i), but improved thermal stability and weight loss rate at the high temperatures with increasing E_a value.

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