

Effect of Silica Nanoparticles on the Curing Kinetics of Epoxy Vinyl Ester Resin

V. Arabli*, A. Aghili†

Department of Polymer Engineering, Shiraz Branch, Islamic Azad University, Shiraz, Iran

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A nanocomposite was synthesized using silica nanoparticles (SN) and Epoxy Vinyl Ester Resin (VE671). Nanoparticles were dispersed in the mixture by ultrasonic equipment to prevent the agglomeration. Transmission electron microscopy (TEM) was used to investigate the dispersion of the silica nanoparticles in the mixture. Non-isothermal differential scanning calorimetry (DSC) technique was used to study the cure kinetics of VE671 resin with and without adding silica nanoparticles. The activation energy (E_a) was determined by using Kissinger and Ozawa equations. The E_a values of curing for VE671 / 4% SN system showed a decrease with respect to the neat resin. It means that there is a catalytic effect of silica nanoparticles in the cure reaction. A dynamic kinetic model was obtained to predict the degree of cure and cure rate of resin. The results showed a good agreement between the model and the experimental data for different heating rates. The char yields increased with the addition of 4% of SN to the epoxy resin and improved the polymer flame retardancy and thermal resistance at high temperatures.

Keywords: Silica Nanoparticles, Epoxy Vinyl Ester Resin, Nanocomposite, Curing Kinetics, Modeling.

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1. INTRODUCTION

The thermoset resins have many applications, because of their highly desirable properties such as stiffness, suitable chemical resistance, wear resistance, excellent adhesion and low shrinkage after curing. It is important to study the cure kinetics and the correlation between the degree of cure and the thermal and mechanical properties to design the optimum curing conditions [1-6]. To provide organic-inorganic hybrid materials, we can mix the silica nanoparticles with polymeric materials. The hybrid materials are also known as nanocomposites [5, 7]. Silica nanoparticles can be widely used in paints, plastics, color rubbers, reinforce fillers in epoxy molding compounds, adhesives and many other fields [5-8]. Liu et al have reported that nanoscale colloidal silica particles act as a curing agent in the curing state of epoxy-silica nanocomposite formation [7]. It was showed an interesting reactivity of silica nanoparticles toward epoxy resins without the need of adding other catalyst in cure reaction.

In this research, an epoxy-silica nanocomposite was synthesized and the cure kinetics of reaction for neat epoxy and nanocomposite was investigated by using non-isothermal DSC technique and a kinetic model was obtained. Thermal degradation of nanocomposite by using thermo gravimetric analysis (TGA) technique was studied and discussed.

2. EXPERIMENTAL

2.1 Materials

Crystic® VE671 vinyl ester resin using bisphenol A epoxy, with viscosity of 430 ± 50 mPa @ 25°C, was purchased from Scott Bader Co. (Dubai, U.A.E.). Silica nanoparticle with average diameter of 12 nm was provided by Nippon aero-sol Co. (Tokyo, Japan). Cobalt,

Dimethyl Amine (DMA) and Methyl Ethyl Ketone Peroxide (MEKP) were purchased from Merck Chemicals Company.

2.2 Devices and Equipment

DSC and TGA were measured by a Mettler Toledo (OH, USA) under nitrogen gas flow of 20 ml/min. Transmission electron microscopy (TEM) images were taken by CM 30 (Philips, Netherland). Ultrasonic Cleaner 7500S (Parsonic, Iran) was used for dispersion of silica nanoparticles in epoxy-silica nanocomposite.

2.3 Preparation of Materials and Nanocomposite

Epoxy Vinyl Ester Resin VE671 was cured by a curing agent, methyl ethyl ketone peroxide (MEKP 55%) and accelerated by three chemicals: cobalt (Co:6% solution), Dimethyl amine (DMA:10% solution) and cadox (L50A Catalyst). Samples of VE671 resin containing 4% of SN were mixed at 25°C and stirred for 20 min. The ultrasonic device was used for 20 min. Mixing and vibration by ultrasonic device were repeated three times to achieve a homogeneous and uniform mixture. Overall mixing and vibration time was about 2 hours. Then the mixture was well mixed with the stoichiometric amount of curing agent and accelerators at room temperature. In each case the mix ratio of the VE671 resin, hardener MEKP, accelerators Cobalt, Di-methyl amine (DMA) and cadox at 25°C were 100, 0.3, 1.0 and 1.25 wt.% for 25min gel time, respectively. The obtained samples were used for TEM, DSC and TGA tests.

2.4 DSC and TGA and TEM Tests

For starting the non-isothermal heating tests, 30 mg of the uniform viscous mixture was put in the DSC sample cell at room temperature. The sample was heated by

* arably@yahoo.com

† aghili@iaushiraz.ac.ir, alirezaaghili@yahoo.com

constant heating rate (5, 10 and 15 °C /min) from 25 to 160°C under nitrogen gas flow of 20 ml/min. Degradation and weight loss of the epoxy–silica nanocomposite was investigated by the TGA system under nitrogen gas flow of 20 ml/min and heating rate of 10 °C/min. Before beginning TGA and TEM tests, samples were cured at 100°C for 2 hours.

3. RESULTS AND DISCUSSION

3.1 Curing Kinetics and Modeling

Non-isothermal (DSC) technique was used at different heating rates to study the kinetics of cure reaction of VE671 resin with and without adding silica nanoparticles. The results are shown in Fig. 1. It can be observed that at each heating rate, the heat flow curve exhibited a peak at higher temperatures and a shoulder at lower temperatures. It can be assumed [10] that the curing is composed of two reactions, the first at lower temperatures and the second at higher temperatures which showed the shoulder and the peak, respectively. The exothermic peak temperature T_p for both systems containing VE671 and VE671+4% SN, shifted to lower temperatures with decreasing heating rates. The values of peak temperatures and heats of reaction are shown in Table 1. For the first reaction a turning point and for the second reaction the maximum point in DSC curves are reported as T_{p1} and T_{p2} , respectively [10]. A comparison of values for both systems shows a decrease in T_p for VE671+4% SN system. The exothermic heat of the samples containing SN is lower than that of the samples without SN and this result is in a good agreement with the previous reports [5, 11].

All kinetic models have a same basic equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where da/dt is the cure reaction rate, $k(T)$ is the rate constant and can be explained by the Arrhenius equation, α is the fractional conversion at a time t , $f(\alpha)$ is function of α and depends on the reaction mechanism. A kinetic model for a dynamic curing process with a constant heating rate can be explained as [2, 5, and 10]:

$$\frac{d\alpha}{dt} = Ae^{-Ea/RT} \alpha^m (1-\alpha)^n \quad (2)$$

where $k(T)$ and $f(\alpha)$ are replaced by Arrhenius equation and an equation based on an autocatalytic model, respectively. A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the absolute temperature. Autocatalytic model has independent reaction orders m and n and an initial da/dt of zero. The correlation between da/dt and da/dT can be explained by following equation:

$$\frac{d\alpha}{dt} = \left(\frac{dT}{dt} \right) \frac{d\alpha}{dT} \quad (3)$$

where dT/dt is constant heating rate. Substituting Eq. (2) and (3) gives:

$$\frac{d\alpha}{dT} = A \left(\frac{dT}{dt} \right)^{-1} \alpha^m (1-\alpha)^n \exp\left(\frac{-Ea}{RT} \right) \quad (4)$$

For determining the activation energy E_a , Kissinger and Ozawa kinetic methods were used. Following form is general linear eq. between the heating rate and peak temperature T_p as Ozawa [12] method:

$$\ln\left(\frac{dT}{dt} \right) = c + \left(\frac{-Ea}{R} \right) \left(\frac{1}{T} \right) \quad (5)$$

Equation (6) indicates Kissinger eq. [13].

$$-\ln\left(\frac{q}{T_p^2} \right) = \frac{Ea}{RT_p} - \ln\left(\frac{AR}{Ea} \right) \quad (6)$$

where q is the heating rate. A plot of $\ln(q/T_p^2)$ versus $1/T_p$ was made as a Kissinger plot and also $\ln(q)$ versus $1/T_p$ was made as an Ozawa plot for both peaks of individual DSC curve.

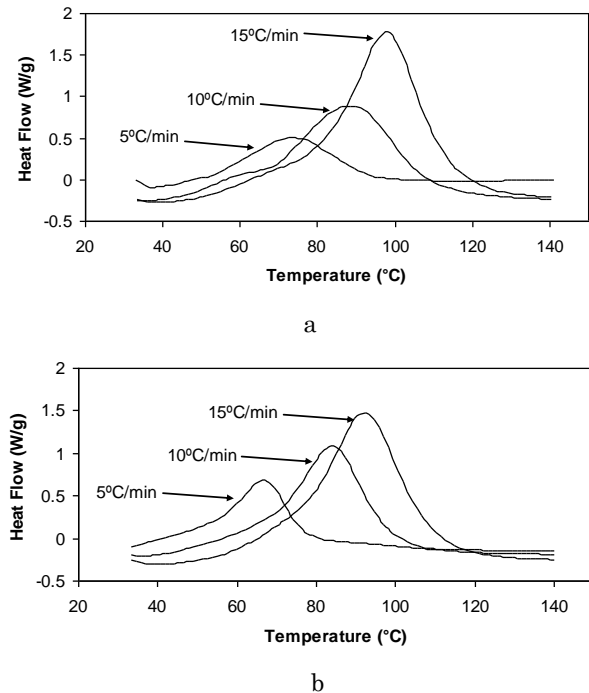


Fig. 1 – DSC curves of VE671 resin (a) and VE671+ 4% SN (b) at different heating rates

Table 1 – Dynamic DSC data for the curing of resin at different heating rates

Sample	VE671			VE671 + 4% SN		
q (°C /min)	5	10	15	5	10	15
T_p 1 (K)	321.75	334.15	342.55	319.75	331.75	340.15
T_p 2 (K)	346.95	361.75	371.35	340.15	356.95	366.5
Exo. Heat (J/g)	183	187	198	163.27	169.73	175.53

As mentioned earlier, each peak indicates a reaction. Values of activation energies for two reactions are shown in Table 2.

Table 2 – E_a values from Kissinger and Ozawa methods

Sample	VE671		VE671 + 4% SN	
	Reac.1	Reac.2	Reac.1	Reac.2
Kissinger	48.15	40.25	44.12	35.69
Ozawa	53.65	46.86	49.87	42.7

By comparing the E_a for both systems of epoxy resin (VE671 and VE671 + 4% SN), it can be suggested that silica nanoparticles as a catalyst, improved the cure reaction and decreased E_a values. Based on the logarithmic form of Eq. (4), the isoconversional plots were obtained from plotting the logarithm of heating rate versus reciprocal of the absolute temperature (T) and apparent E_a

Table 3 – E_a Values Calculated from Isoconversional Plots at different degrees of cure

Degree of Cure	5%	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%
E_a (kJ/mol) VE671	53.63	51.08	50.88	49.63	48.63	48.01	47.56	47.22	47.02	46.85	46.82
E_a (kJ/mol) VE671 + 4% NS	49.87	47.56	47.35	45.81	44.92	44.18	43.65	43.23	42.94	42.73	42.70

Table 4 – Dynamic Kinetic Parameters Determined using a Multiple Nonlinear Least-Squares Regression

sample	Heating rate (°C/min)	Reaction 1			Reaction 2		
		A_1	m_1	n_1	A_2	m_2	n_2
VE671	5	3.6467E+05	0.395	2.502	8.5833E+04	1.63	1.045
	10	2.4387E+05	0.2785	2.998	1.2817E+05	1.711	1.247
	15	2.2319E+05	0.3001	2.171	2.0209E+05	2.308	1.339
VE671+4% SN	5	6.2387E+05	0.4035	2.973	1.6385E+05	2.469	1.045
	10	3.8458E+05	0.3914	2.591	1.5647E+05	2.413	1.376
	15	4.4823E+05	0.4469	2.504	1.4941E+05	2.567	1.393

Having obtained the kinetic parameters for these two reactions, we could calculate the values for degree of cure (α) and cure rate (da/dt) for each reaction by solving the a system of differential equations:

$$\frac{d\alpha_1}{dT} = \left(\frac{dT}{dt}\right)^{-1} A_1 e^{-(E_{a1}/RT)} (\alpha_1 + \alpha_2)^{m_1} (1 - \alpha_1 - \alpha_2)^{n_1} \quad (7)$$

$$\frac{d\alpha_2}{dT} = \left(\frac{dT}{dt}\right)^{-1} A_2 e^{-(E_{a2}/RT)} (\alpha_1 + \alpha_2)^{m_2} (1 - \alpha_1 - \alpha_2)^{n_2} \quad (8)$$

where subscripts 1 and 2 are related to the first and second reactions, respectively. The system of ordinary differential equations has been solved using Matlab software. A program based on the Runge–Kutta (4, 5) algorithm was used to find the numerical solution for eqs. (7) and (8). As a typical example, the calculated values of degree of cure (α) versus temperature, along with the experimental results for VE671+4% SN at heating rate of 10°C/min, are shown in Figure 2. As shown in this figure, we have two calculations and two curves are plotted, because the overall curing consists of two reactions. The calculated degree of cure (α) agreed well with the experimental data for all heating rates. The cure rate da/dt versus temperature was obtained by using eq. (3). The predicted results, along with the experimental data, are shown in Figure 3.

for each α was calculated from its slope [10] and values are listed in Table 3. For each system, the apparent activation energies for all range of conversions are between the two activation energies of reaction 1 and 2 calculated from Ozawa method. At lower conversions the apparent E_a is very close to the E_a for reaction 1 and at higher conversions, it is very close to that of reaction 2. The values also indicate a decrease in E_a for all range of conversions (α) when 4% nanosilica was used.

Having the activation energies (E_a) for both reactions, a multiple nonlinear least-squares regression method based on the Levenberg–Marquardt algorithm [10] was used to find the best values for pre-exponential factor (A) and reaction orders (m and n) for both reactions 1 and 2. These dynamic kinetic parameters are listed in Table 4 for all heating rates.

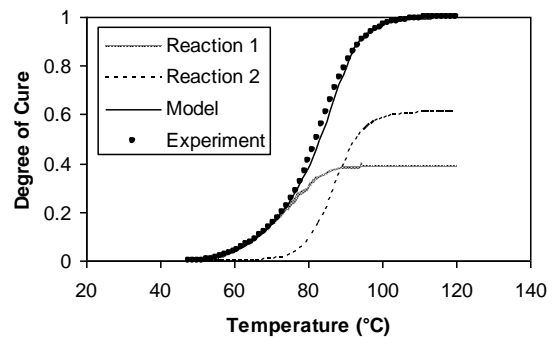


Fig. 2 – Comparison of model and experimental data for degree of cure as a function of temperature for VE671+4% nanosilica at heating rate of 10°C/min.

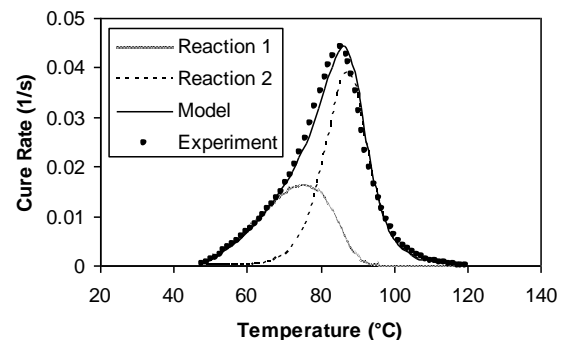


Fig. 3 – Comparison of model and experimental data for Cure rate as a function of temperature for VE671+4% nanosilica at heating rate of 10°C/min.

3.2 Dispersion of Nanoparticles in Nanocomposite

Figure 4 shows TEM image of cured epoxy resin filled with 4% of silica nanoparticles. The nanoparticles were dispersed well in the matrix and there was no aggregation.

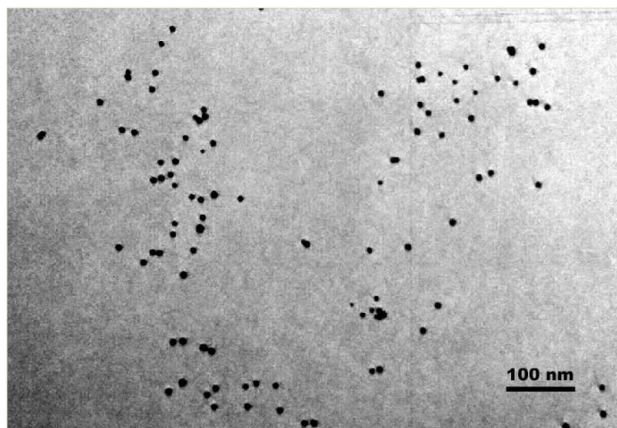


Fig. 4 – TEM image of cured epoxy – silica nanocomposite with 4 wt% of silica nanoparticles

3.3 Thermal Stability

Figure 5 shows the TGA curves for cured neat VE671 resin and the VE671+4%SN nanocomposite. It can be observed that the thermal degradation of nanocomposite takes place at higher temperatures than the neat resin. The thermal degradation data are also shown in Table 5. The char yields at 600°C increased from 6.8% to 12.4% with the addition of 4% of silica nanoparticles to the epoxy resin. The increasing of char yields agrees with the mechanism of flame retardancy. Therefore silica nanoparticles improved the polymer flame retardancy and thermal resistance [14].

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Table 5 – Thermal degradation data of the cured samples

System	IDT(°C) ^a	T(°C) ^b	T _{max} (°C) ^c	Chr.Y(%) ^d
VE671	387	400	416	6.8
VE671/SN	390	406	424	12.4

a) Initial Degradation Temperature
 b) Temperature for 30% of weight loss
 c) Temperature of maximum weight loss
 d) Char Yield at 600°C

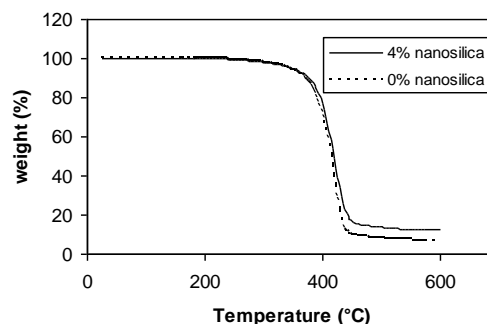


Fig. 5 – TGA curves of cured VE671 resin and its nanocomposite.

4. CONCLUSION

Effect of silica nanoparticles on the cure kinetics of epoxy resin in the presence of 4% nanosilica was studied. To determine activation energy E_a of cure reaction of VE671, non-isothermal DSC method, Ozawa and Kissinger equations were used. The E_a value of cure reaction of VE671 in the presence of 4% silica nanoparticle decreased about 5 KJ/mol. It is concluded that silica nanoparticles acted as catalyst in the reaction of VE671/SN. DSC curves were modeled by Matlab program. The models were agreed well with the experimental data for all heating rates. The char yields increased with the addition of 4% of silica nanoparticles to the epoxy resin and improved the polymer flame retardancy and thermal resistance at high temperatures.