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The effect of silica nanoparticles, thermal stability, and modeling of the curing kinetics of epoxy/silica nanocomposite

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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 was used to investigate the dispersion of the SN in the mixture. Non-isothermal differential scanning calorimetry technique was used to study the cure kinetics of VE671 resin with and without adding SN. The activation energy (E_a) was determined using Kissinger and Ozawa equations. The E_a values of curing for VE671/4 wt% SN system showed a decrease with respect to the neat resin. It means that there is a catalytic effect of SN in the cure reaction. The dynamic curing process was modeled to predict the degree of cure and cure rate of resin using the Sun method. In this method, the results showed a good agreement between the model and the experimental data for different heating rates. Thermal degradation of nanocomposite using thermogravimetric analysis technique was studied. The char yields increased with the addition of 4 wt% 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; cure kinetics; thermal stability; modeling

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.[1–7] To provide organic–inorganic hybrid materials, we can mix the nanoscale particles with polymeric materials.[8] The hybrid materials are also known as nanocomposites.[5,8] Epoxy–silica nanocomposites can be used in adhesives, coatings, packaging materials for electronic devices, matrices of advanced composites with improved performance, and many other fields.[6,9,10] Liu et al. have reported that nanoscale colloidal silica particles act as a curing agent in the curing state of epoxy–silica nanocomposite formation. It was showed an interesting reactivity of silica nanoparticles (SN) toward epoxy resins without the need of adding other catalyst in cure reaction. They have achieved epoxy–silica nanocomposites containing high silica contents up to 70 wt%. This percent of silica particles showed a decrease of activation energy but the nanocomposite was brittle and weak.[10] The addition of SN decreases

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activation energy.[11] In this research, an epoxy–silica nanocomposite was synthesized and the cure kinetics of reaction for neat epoxy and nanocomposite was investigated using non-isothermal differential scanning calorimetry (DSC) technique and experimental data were modeled by autocatalytic cure kinetics. The kinetic parameters were obtained using Malek, Borchardt Daniels, and Sun methods. The sun method was based on the Kissinger and Ozawa methods. Thermal degradation of nanocomposite using thermogravimetric 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). SN with average diameter of 12 nm was provided by Nippon aerosol Co. (Tokyo, Japan). Cobalt, Dimethylaniline (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 – TGA/DSC1 (OH, USA) under nitrogen gas flow of 20 ml/min. Transmission electron microscopy (TEM) images were taken by CM 30 (Philips, Netherland). QSONICA sonicator-Q700 (CT, USA) was used for dispersion of SN in epoxy–silica nanocomposite.

2.3. Preparation of materials and nanocomposite

Epoxy Vinyl Ester Resin was cured by a curing agent, MEKP (55%) and accelerated by cobalt (Co: 6% solution) and DMA (10% solution). Samples of VE671 resin containing 4% of SN were mixed at 25 °C and stirred for 20 min. The sonicator device was used for 20 min. Mixing and vibration by sonicator device was repeated three times to achieve a homogeneous and uniform mixture. Overall mixing and vibration time was about 2 h. 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 resin VE671, hardener MEKP, accelerators Cobalt, and DMA at 25 °C were 100, 1.0, 0.3, and 1.0 wt% for 25 min gel time, respectively. The obtained samples were used for TEM, DSC, and TGA tests.

2.4. DSC, TGA, and TEM test

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 constant heating rate (5, 10, 15, and 20 °C /min) from 25 to 160 °C under nitrogen gas flow of 20 ml/min. Degradation and weight loss of the epoxy–silica nanocomposite were investigated by the TGA system under nitrogen gas flow of 20 ml/min and heating rate of 10 °C/min. For optimum properties, samples were cured at 100 °C for 3 h before beginning TGA and TEM test. A mount 20 mg of the cured sample was used for TGA test and the small disc of cured sample with a diameter of about 2 mm was provided for TEM test.

3. Results and discussion

3.1. Curing kinetics

Non-isothermal DSC technique was used at different heating rates to study the kinetics of cure reaction of VE671 resin with and without adding SN. The results are shown in Figure 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 that the curing is introducing two reactions,[11,12] 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 neat epoxy resin (VE671) and nanocomposite (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. Lem et al. [13] suggested that the first peak is due to the thermal decomposition of the initiator (peroxide) by a redox mechanism and the second exothermic peak indicates cross-linking reactions initiated by non-catalytic decomposition of initiator at higher temperature. Walling et al. [14] suggested that the first peak may be due to the higher efficiency of radical production resulting from reactions between MEKP and DMA. The second peak attributed to

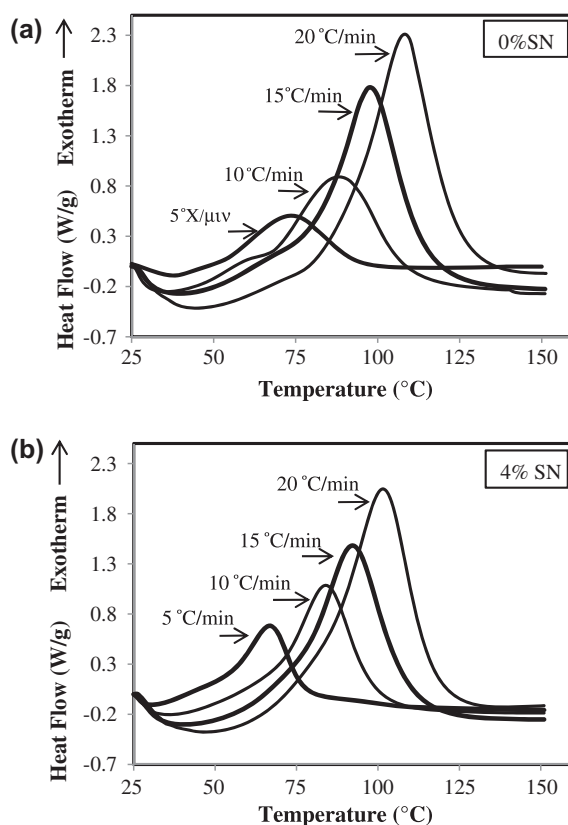


Figure 1. Dynamic DSC curves at different heating rates for (a) VE671 and (b) VE671 + 4% SN.

Table 1. Total dynamic heat of cure reaction and dependence of the peak properties at different heating rates.

Sample	Heating rate q ($^{\circ}\text{C}/\text{min}$)	VE671				VE671 + 4% NS			
		5	10	15	20	5	10	15	20
Heat of reaction (J/g)		183.00	187.79	197.90	201.49	163.27	169.73	175.53	181.00
Peak 1									
$Tp1$ (K)		321.75	334.15	342.55	346.49	319.75	331.75	340.15	344.35
(da/dT) (1/K)		0.00311	0.00299	0.002919	0.00289	0.00313	0.00301	0.00294	0.00291
$\ln(q/T^2p1)$		-9.938	-9.321	-8.964	-8.699	-9.9256	-9.306	-8.951	-8.688
Peak 2									
$Tp2$ (K)		346.95	361.75	371.35	380.90	340.15	356.95	366.50	375.00
(da/dT) (1/K)		0.00288	0.00276	0.00269	0.00263	0.00294	0.00281	0.00272	0.00267
$\ln(q/T^2p2)$		-10.088	-9.482	-9.131	-8.891	-10.049	-9.452	-9.091	-8.855

thermal curing of the residual components of the resin.[12] A comparison of values for both systems shows a decrease in T_p for nanocomposite of 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.[6,10] Therefore, we can save energy and time in nanocomposite.

In the dynamic curing process, the cure rate is function of degree of cure and function of temperature. The kinetic models have a same basic form [15]:

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

In Equation (1), $d\alpha/dt$ 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. Equation (2) shows Arrhenius equation:

$$k(T) = A e^{-(Ea/RT)} \quad (2)$$

where A is the pre-exponential factor, R is the gas constant, T is the absolute temperature, and Ea is the activation energy. Combining Equations (2) and (1):

$$\frac{d\alpha}{dt} = A e^{-(Ea/RT)} f(\alpha) \quad (3)$$

There is an equation that indicates relationship between $d\alpha/dt$ and $d\alpha/dT$. It can be described as follows:

$$\frac{d\alpha}{dt} = \left(\frac{dT}{dt} \right) \frac{d\alpha}{dT} \quad (4)$$

In Equation (4), dT/dt is the constant heating rate q . Combining Equation (4) into Equation (3) and taking the logarithm gives:

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

In Equation (5), the pre-exponential factor and activation energy obtained using the Kissinger and Ozawa methods.[16,17] $f(\alpha)$ may have different forms and it depends on the mechanism of curing. For the autocatalytic reaction, $f(\alpha)$ may have the following form with orders of cure reaction m and n [18,21]:

$$f(\alpha) = \alpha^m (1 - \alpha)^n \quad (6)$$

Putting $f(\alpha)$ from Equation (6) into Equation (5) gives:

$$\ln \left(\frac{dT}{dt} \right) = \ln A - \ln \left(\frac{d\alpha}{dT} \right) + \ln [\alpha^m (1 - \alpha)^n] + \left(-\frac{Ea}{R} \right) \left(\frac{1}{T} \right) \quad (7)$$

Following equation introduces the linear equation between heating rate dT/dt and the reciprocal of the peak temperature T_p :

$$\ln \left(\frac{dT}{dt} \right) = c + \left(-\frac{Ea}{R} \right) \left(\frac{1}{T_p} \right) \quad (8)$$

where $-Ea/R$ and c are the slope and intercept of the curve, respectively. The term of c can be expressed as follows:

$$c = \ln \bar{A} - \ln \left(\frac{d\alpha}{dT} \right)_p + \ln \alpha_p^m (1 - \alpha_p)^n \quad (9)$$

where \bar{A} is the average value of the pre-exponential factors for all of heating rates (5, 10, 15, and 20 °C/min), T_p is the absolute temperature for each exothermic peak, $(d\alpha/dT)_p$ is the derivative of degree of cure to temperature, and α_p is the degree of cure at the exothermic peak.[21] Equation (10) indicates Kissinger equation,[16] where q is the constant heating rate (dT/dt).

$$-\ln \left(\frac{q}{T_p^2} \right) = \frac{Ea}{RT_p} - \ln \left(\frac{AR}{Ea} \right) \quad (10)$$

To determine activation energy, Kissinger and Ozawa methods were used and are illustrated in Figures 2 and 3, respectively. There was a very good linear relationship between heating rate and the reversal of the exothermic peak temperature T_p for both methods. The values of activation energy were calculated from slopes of each peak (reaction) and are given in Table 2. By comparing the activation energy for neat epoxy resin (VE671) and nanocomposite (VE671 + 4% SN), it can be suggested that SN as a catalyst, improved the cure reaction and decreased Ea values. For example, in the Kissinger method, the activation energies for VE671 and VE671 + 4% SN in Reactions

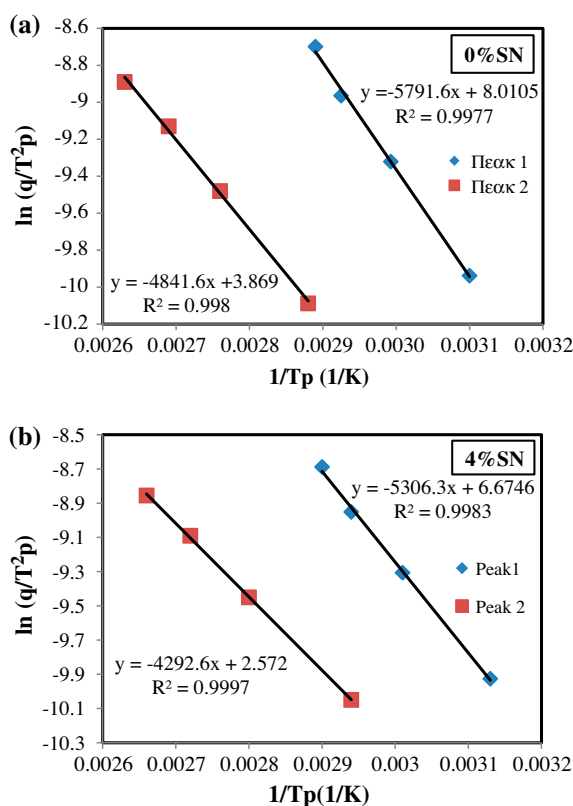


Figure 2. Kissinger plots for (a) VE671 and (b) VE671 + 4% SN. The activation energies were obtained by peak temperatures at heating rates of 5, 10, 15, and 20 °C/min.

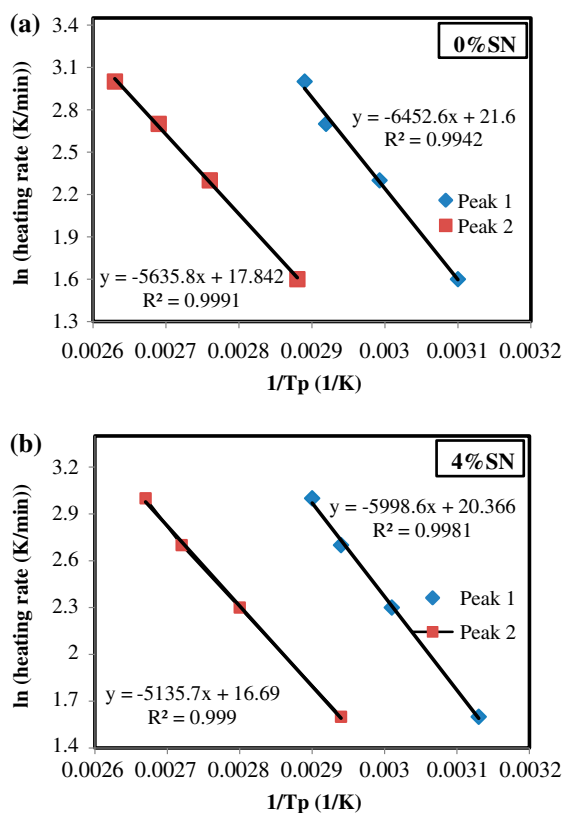


Figure 3. Ozawa plots for (a) VE671 and (b) VE671 + 4% SN. The activation energies were obtained by peak temperatures at heating rates of 5, 10, 15, and 20 °C/min.

Table 2. E_a values obtained by Kissinger and Ozawa method.

	VE671		VE671 + 4% SN	
	Peak1	Peak 2	Peak1	Peak 2
E_a (kJ/mol) ^a	48.15	40.25	44.12	35.69
E_a (kJ/mol) ^b	53.65	46.86	49.87	42.70

^aKissinger method.

^bOzawa method.

1 were 48.15 and 44.12 kJ/mol, respectively. In this case and Reaction 2, activation energies showed a decrease of about 4 kJ/mol. According to Table 2, activation energies were decreased in the Ozawa method for VE671 + 4% SN.

The isoconversional plots were obtained using Equation (5). The isoconversional plots indicated the details of the curing process. The isoconversional plots are plotted in Figure 4. In these plots, each curve has the same α . There was a good linear relationship for all the isoconversional curves. Activation energy calculated from slope at each degree of cure for VE671 and VE671 + 4% SN. The activation energy as a

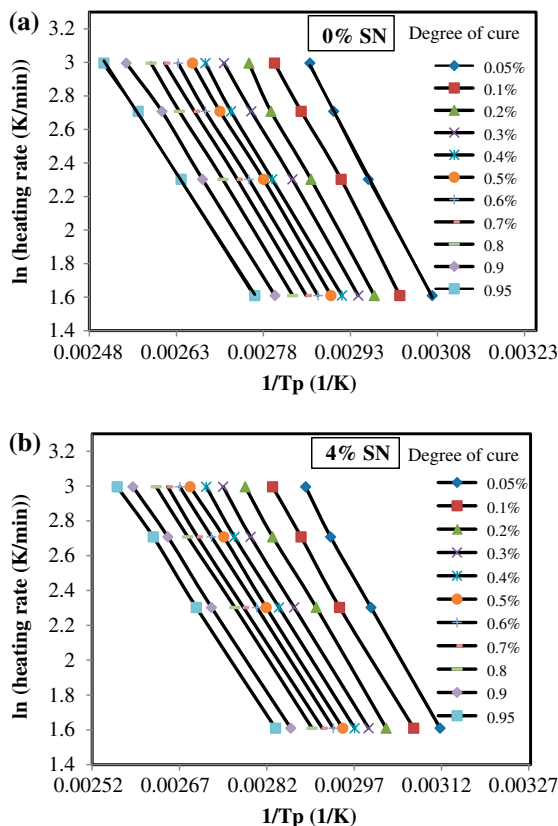


Figure 4. Isoconversional plots for the logarithmic heating rate vs. the reciprocal of the absolute temperature (T): (a) VE671 and (b) VE671 + 4% SN.

function of degree of cure is illustrated in Figure 5. As shown in Figure 5, activation energy decreased by adding 4% of SN. The values of E_a are listed in Table 3.

3.2. Modeling

In this section, the dynamic curing process was modeled to predict the degree of cure and cure rate of vinyl ester resin using the Malek,[19] Borchardt Daniels,[20] and Sun method.[21] Malek and Borchardt Daniels methods were predicted only reaction 2 at all of the heating rates and there was a good agreement between calculated and experimental data. The curing process of vinyl ester resin is complicated and these methods are not suitable to predict two reactions. For this reason, results are not shown and we applied the Sun method. In the Sun method, we need to obtain the pre-exponential factor A , activation energy E_a , and orders of cure reaction (m and n) for each reaction at the different heating rates. The terms of A and E_a determined by the specifications of the peaks and the orders of cure reaction (m and n) were obtained by the multiple regression operations.

The rearrangement of Equation (10) gives the average pre-exponential factor \bar{A} [21]:

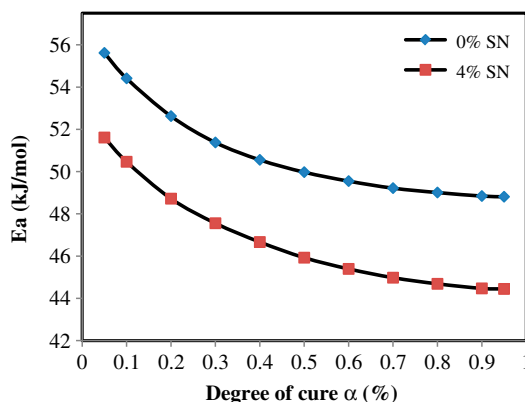


Figure 5. Plots of activation energy (E_a) as a function of degree of cure. E_a calculated by iso-conversional plots.

Table 3. E_a values obtained by isoconversional plots with different α values.

	α											
	5%	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%	
E_a (kJ/mol) ^a	55.63	54.42	52.62	51.38	50.55	49.97	49.56	49.22	49.02	48.85	48.82	
E_a (kJ/mol) ^b	51.61	50.46	48.72	47.55	46.66	45.93	45.39	44.97	44.69	44.47	44.45	

^aVE671.

^bVE671 + 4% SN.

$$\bar{A} = \frac{e^c \left(\frac{d\alpha}{dT} \right)_p}{\alpha_p^m (1 - \alpha_p)^n} \quad (11)$$

The pre-exponential factor A changes with the heating rate q . We can use a new parameter Ar ($Ar = A/\bar{A}$) to determine a form of the pre-exponential factor A at different heating rate. Ar is the correction factor and changes with the heating rate q . Apply the Ar improved the fitting results. If we put $\bar{A} = A/Ar$ into Equation (11), yields:

$$A = Ar \frac{e^c \left(\frac{d\alpha}{dT} \right)_p}{\alpha_p^m (1 - \alpha_p)^n} \quad (12)$$

Combining Equation (6) and (12) into Equation (3) gives the final form of the $d\alpha/dt$:

$$\left(\frac{d\alpha}{dt} \right) = Ar e^c \left(\frac{d\alpha}{dT} \right)_p e^{-(E_a/RT)} \frac{\alpha_p^m (1 - \alpha_p)^n}{\alpha_p^m (1 - \alpha_p)^n} \quad (13)$$

Multiple non-linear least-squares regression method (based on the Levenberg–Marquardt algorithm) was used to obtain the parameters of Ar , m , and n (Equation 13). There are two cure reactions during the dynamic curing process. The details of each reaction for different heating rates can be determined from the curve fitting results. To obtain better fitting results, we selected the early step (Reaction 1 dominated the curing process) of $d\alpha/dt$ as the source data to fit Reaction 1 (peak 1) first and then we used the difference between total $d\alpha/dt$ and fitting rate from Reaction 1 as the source data to

Table 4. Dynamic kinetic parameters determined by a multiple non-linear least-squares regression.

	Heating rate (°C/min)	Reaction 1				Reaction 2			
		Ar_1	A_1 (1/s)	m_1	n_1	Ar_2	A_2 (1/s)	m_2	n_2
VE671	5	0.02143	3.6467E+05	0.395	2.502	0.01149	8.5833E+04	1.63	1.045
	10	0.01575	2.4387E+05	0.2785	2.998	0.01502	1.2817E+05	1.711	1.247
	15	0.01600	2.2319E+05	0.3001	2.171	0.01362	2.0209E+05	2.308	1.339
	20	0.01783	1.5979E+05	0.3156	2.999	0.01427	1.6230E+05	1.826	1.359
VE671 + 4% NS	5	0.02536	6.2387E+05	0.4035	2.973	0.008656	1.6385E+05	2.469	1.045
	10	0.01675	3.8458E+05	0.3914	2.591	0.01242	1.5647E+05	2.413	1.376
	15	0.01615	4.4823E+05	0.4469	2.504	0.01191	1.4941E+05	2.567	1.393
	20	0.01718	4.2142E+05	0.4709	2.827	0.01279	1.7145E+05	2.742	1.44

fit Reaction 2 (peak 2). The range of da/dt was selected from about 0% degree of cure α to 15% degree of cure α . The values of the parameters of Ar , m , and n were determined using multiple non-linear regressions method. The values of Ar , m , and n for both reactions (1 and 2) at different heating rates are shown in Table 4. Reaction 1 and 2 for both system of VE671 and VE671 + 4% SN showed the behavior of the autocatalytic reaction.

The pre-exponential factor A at each heating rate was obtained using Equation (12) and listed in Table 4. The kinetic parameters for each reaction were obtained and we could determine the values for degree of cure α and cure rate da/dt for each reaction by solving the differential equations. According to Equation (3), total degree of cure α can be written as follows:

$$\alpha = \alpha_1 + \alpha_2 \quad (14)$$

Putting Equations (4), (6), and (14) into Equation (3) and after rearranging, we have Equation (15) for reaction 1 and Equation (16) for reaction 2:

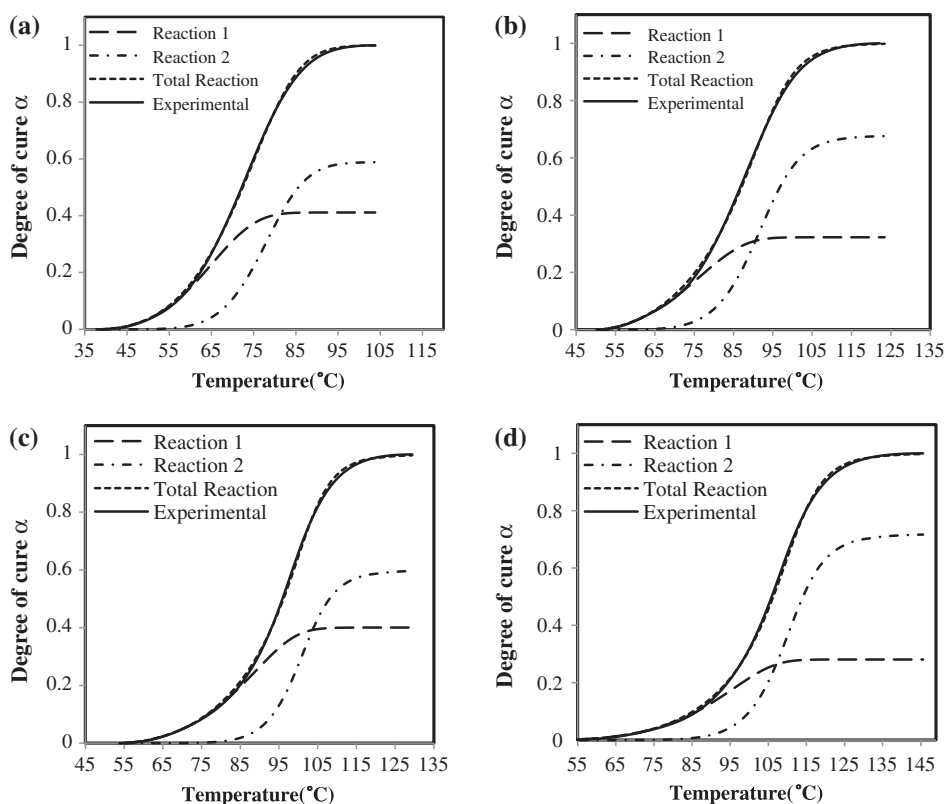


Figure 6. Comparison of model and experimental data for degree of cure as a function of temperature for VE671 by the method based on the Kissinger and Ozawa approach. (a) Heating rate of 5 °C/min, (b) heating rate of 10 °C/min, (c) heating rate of 15 °C/min, (d) heating rate of 20 °C/min.

$$\frac{d\alpha_1}{dT} = \left(\frac{dT}{dt}\right)^{-1} A_1 e^{-(E_{a1}/RT)} (\alpha_1 + \alpha_2)^{m1} (1 - \alpha_1 - \alpha_2)^{n1} \quad (15)$$

$$\frac{d\alpha_2}{dT} = \left(\frac{dT}{dt}\right)^{-1} A_2 e^{-(E_{a2}/RT)} (\alpha_1 + \alpha_2)^{m2} (1 - \alpha_1 - \alpha_2)^{n2} \quad (16)$$

Equations (15) and (16) are non-linear differential equations. The independent variable is the absolute temperature T and the dependent variables are the degree of cure α_1 and α_2 for reaction 1 and 2, respectively. There is no analytical solution to Equations (16) and (17). The Matlab software (ode45, Runge–Kutta 4, 5 algorithm) was used to determine the numerical solution. The values of the degree of cure α , α_1 , and α_2 were calculated at each heating rate. The plots of the degree of cure vs. the temperature for VE671 are shown in Figure 6. The procedure was repeated for nanocomposite (VE671 + 4% SN) and the plots of the degree of cure vs. the temperature are shown in Figure 7. At all the heating rates for VE671 and VE671 + 4% SN, the calculated total degree of cure α agreed well with the experimental data. The dependence of $d\alpha_1/dT$, $d\alpha_2/dT$, and $d\alpha/dT$ on temperature was determined by

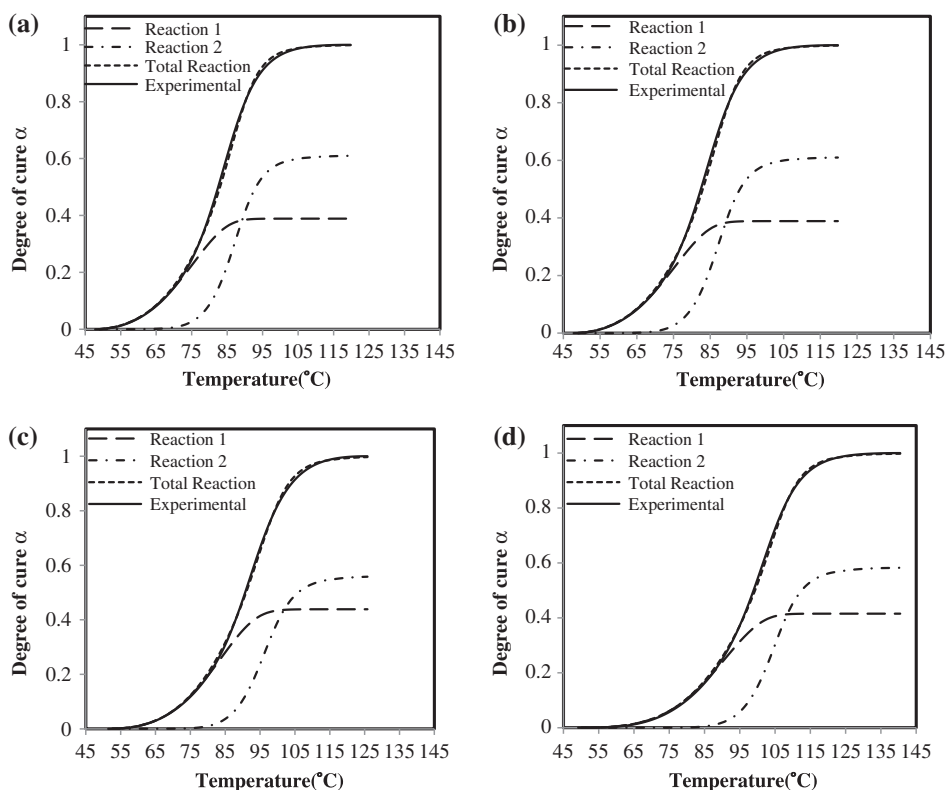


Figure 7. Comparison of model and experimental data for degree of cure as a function of temperature for VE671 + 4% SN by the method based on the Kissinger and Ozawa approach. (a) Heating rate of 5 °C/min, (b) heating rate of 10 °C/min, (c) heating rate of 15 °C/min, (d) heating rate of 20 °C/min.

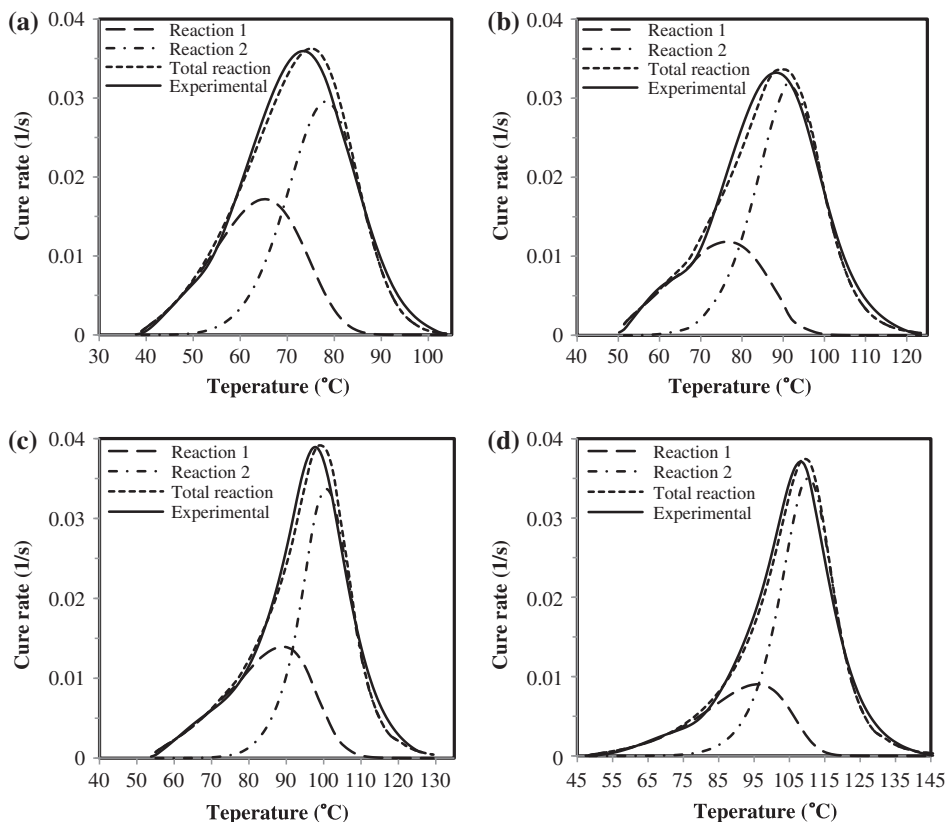


Figure 8. Comparison of model and experimental data for Cure rate as a function of temperature for VE671 by the method based on the Kissinger and Ozawa approach. (a) Heating rate of 5 °C/min, (b) heating rate of 10 °C/min, (c) heating rate of 15 °C/min, (d) heating rate of 20 °C/min.

differentiating the degree of cure α_1 , α_2 , and α with respect to temperature T . By Equation (4), the cure rates da/dt for α_1 , α_2 , and total α vs. temperature T were calculated. The results were plotted in Figures 8 and 9 for VE671 and VE671 + 4% SN, respectively. As shown in Figures 8 and 9, the calculated total cure rate predicted two peaks in the curing process and there was a good agreement between the model and the experimental data at different heating rates. Therefore, the Sun method is suitable to predict of the curing process of vinyl ester resin.

3.3. Dispersion of nanoparticles in nanocomposite

Transmission electron microscopy was used to study dispersion of the nanosilica particles in the nanocomposite structure. Figure 10 shows a TEM image of cured Epoxy Vinyl Ester Resin filled with 4% of SN. The nanoparticles were dispersed well in the matrix and there was no aggregation.

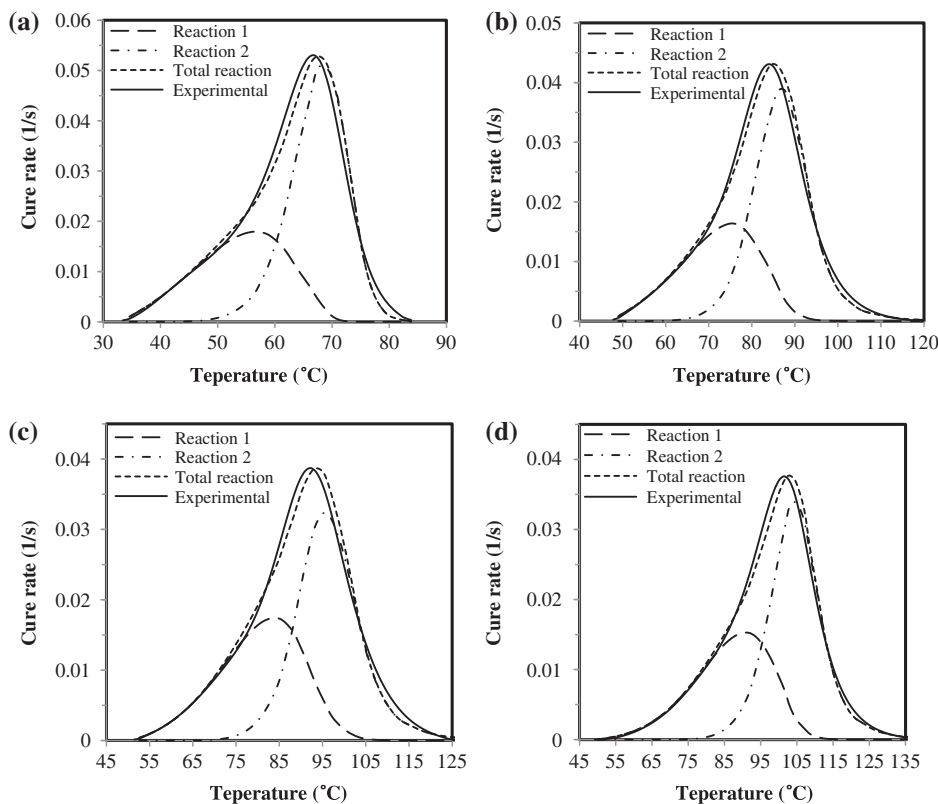


Figure 9. Comparison of model and experimental data for Cure rate as a function of temperature for VE671 + 4% SN by the method based on the Kissinger and Ozawa approach. (a) Heating rate of 5 °C/min, (b) heating rate of 10 °C/min, (c) heating rate of 15 °C/min, (d) heating rate of 20 °C/min.

3.4. Thermal stability

The thermal stability of the cured epoxy–silica nanocomposite was studied with TGA test. Figure 11 indicates TGA curves of the cured VE671 and VE671/SN systems under nitrogen atmosphere. The weight loss rates of the nanocomposite were reduced and thermal stability was improved in the epoxy–silica nanocomposite. The initial decomposition temperature (IDT), the temperature of maximum rate of weight loss (T_{max}), and the percent of char yield (Ch. Y.) are shown in Table 5 for compare. IDT for both cured samples (VE671 and VE671/SN) was almost near and about 387 and 390 °C, respectively. According to the other researches,[22–26] the thermal stability of the epoxy–silica mixture increased with increasing silica content. When the temperature is rising, the SN move toward the surface of the nanocomposite, because silica has low surface potential energy. The silica on the surface of the polymer acts as thermal insulating materials and protects the inner layer of the polymers. This thermal insulation effect can act at high temperatures.[22] As shown in Table 5, the char yields at 600 °C increased from 6.8 to 12.4% with the addition of 4% of SN to the epoxy resin. The increasing in char yields agrees with the mechanism of flame retardant.[26] Therefore, the addition of silica nanoparticles to the polymer improved the polymer flame retardancy and thermal resistance.

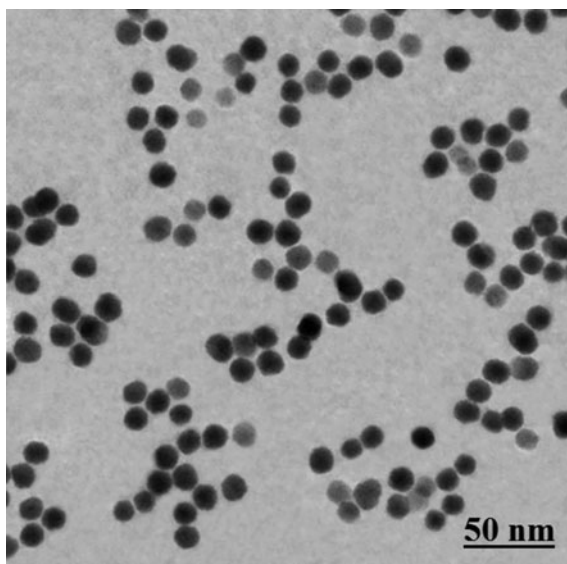


Figure 10. TEM image of cured Epoxy Vinyl Ester Resin with 4 wt% of SN.

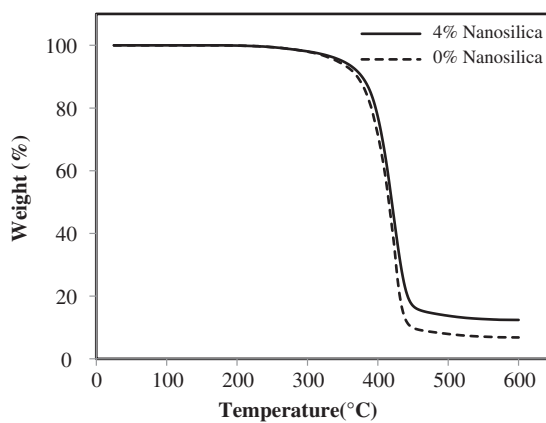


Figure 11. TGA curves of cured VE671 resin and its nanocomposite.

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

^aInitial decomposition temperature.

^bTemperature for 30% of weight loss.

^cTemperature of maximum weight loss.

^dChar yield at 600 °C.

4. Conclusions

Effect of SN 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% SN decreased about 5 kJ/mol. It is concluded that SN 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 SN to the epoxy resin and improved the polymer flame retardancy and thermal resistance at high temperatures.

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