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Research Article

## Silica Nanoparticles/Phenol Novalac Epoxy Resin Nanocomposites via Vacuum Shock Technique: Effect of Silica Nanoparticles on Curing Kinetic

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**Abstract:** In this study, curing kinetic of phenol novalac epoxy resin with and without presence of silica nanoparticles (SN) was evaluated. In this case, the dynamic curing process was studied by usage of differential scanning calorimetry (DSC) with and without addition of silica nanoparticles in 4 heating rates, 2, 5, 10 and 15°C/min. Despite of that, from DSC analysis, the reaction exotherm was processed in order to obtain the reaction kinetic data such as the degree of reaction and the rate of reaction at different times and temperatures. Besides, a suitable model was proposed to explain the reaction kinetic data obtained from experimental section. Moreover, unknown parameters of this model were determined by a nonlinear

regression analysis and then it was adapted by experimental data obtained from DSC analysis. Furthermore, the activation energy for sample containing ML-506/4 wt% NS was increased with respect to the neat resin which is due to the inhibitor effect of silica nanoparticles in the cure reaction. Moreover, transmission electron microscopy (TEM) was used in order to investigate the dispersion quality of silica nanoparticles within the mixture.

**Keywords:** phenol novolac epoxy resin, silica nanoparticles, curing kinetic, activation energy, nanocomposite

## INTRODUCTION

Reinforced polymeric nanocomposites have attracted considerable attention due to their selective applications. Among these reinforced polymeric matrices we can refer to the phenol novolac epoxy resin modified with unsaturated polyester (PNE/UPS)<sup>1</sup>, linear low-density-polyethylene (LLDPE)<sup>2</sup>, epoxy resin<sup>3-8</sup>, cresol novolac epoxy resin modified with unsaturated polyester (CNP/UPS)<sup>9</sup> and polyethylene terephthalate (PET)<sup>10</sup>. Phenol based resins which can be classified in thermoset group, have a wide range of applications in production of nanocomposites for different purposes. Despite of that, phenol based resins creation is due to aggregation compaction of phenols and aldehydes like formaldehyde and elimination of water sidelong group branch. Besides, phenol based resins can resist temperature range more than 300°C which is a great pros for them. By increase in temperature range, phenol based resins will convert from a thermoplastic and soluble substance to a thermoset, insoluble and immutable form due to crosslink connections formation<sup>4</sup>. In addition, phenol based resins resistance depends on crosslink connection that was formed by formaldehyde in resultant polymer. Also phenol novolacs with higher molecular weight and low concentration of terminal branches groups and passive phenols can lead to better crosslink connections. In addition, novolac resins have no methylol groups, therefore they cannot create a composite structure due to increase in heating rate. In this case, mixture of novolac resins and compositions such as hexamethylenetetramine (HMTA) that can make methylene connection can lead to creation of a thermoset structures<sup>11,12</sup>. In spite of that, non-porous structures products can obtained by usage of epoxy instead of HMTA in curing process of phenol novolac epoxy resin. In this case, curing reaction process was performed by addition of hydroxy phenol to epoxy without subtraction of volatile groups in a nucleophile process reaction. Besides, due to the high epoxy percentage in the suspension with the presence of phenol novolac curing system, these structures were became important in microelectronic applications.

Although, these materials do not have suitable fire retardant properties of phenol networks and they were constituted from flammable epoxy resin. Moreover, in order to achieve fire retardant and sufficient toughness, high amount of heavy molecular weight novolac should be cross-link to the low percentage of diepoxy. In this case, high percentage of novolac in presence of epoxy resin can lead to low phenol cross-link and thus a structure with good toughness and suitable module. Besides, the relation of high molecular weight and the cross-linking connection can lead to proper mechanical and fire retardant properties. Even though, commercial phenol novolacs cannot control the molecular weight. Besides, trivalent nature of phenol monomer can lead to inevitable gelation due to increase in the molecular weight. Despite of that, linear structure without branches could be achieved by usage of divalent O-cresol novolac or P-cresol novolac. Additionally, it is expected that low percentage of methyl groups next to O-cresol novolac has affected the chemical properties and other characteristics of the cross-link. Also, phenol novolac forms from combination of a tree functional phenol with formaldehyde<sup>13</sup>.

Furthermore, the production method and curing condition of composite samples have great role in their quality and structural shape<sup>10</sup>. In this case, nanoparticles properties can be improved by appropriate mixing and it is important to achieve a homogenous mixture in order to gain the best results. Besides, this aim can be obtained when silica nanoparticles were well dispersed in polymer matrix and formed cross-link connections<sup>4,13</sup>. In spite of that, curing conditions have to cognize in order to attain these special properties. In addition, kinetic surveys by usage of DSC apparatus and simultaneous analyzes with modelless and yazokin model showed that the activation energy of the curing reaction of liquid epoxy with low molecular weight occur at 30 kJ/mole in curing process and it remains constant during the process. However, activation energy range is between 39-94 kJ/mole for solid epoxy compound (high molecular weight) and it will increases as the process proceed. Although, this increase is too severe in upper 60 percent conversions and thermal analysis showed that the energy that releases during curing process of solid epoxy compound mixture is lower than the released energy during the liquid resin compound mixture in curing step<sup>13-16</sup>.

In spite of that, there are few models include phenomenological models and mechanistic models that were widely used for simulation of curing kinetic of epoxy resins in literatures. In this case, mechanistic models were attended rarely in industrial applications that is due to their difficult dissolvent and improper forecasting, so phenomenological models afford better results than mechanistic models. In addition, there are several disagreement in numbers of reaction involved in curing process, activation energy values, order of reaction and other kinetic parameters in phenomenological models that is need further investigation<sup>17-19</sup>. In a work that was conducted by Hayati *et.al.*<sup>14</sup>, they have studied the curing kinetic of epoxy resins by usage of DSC method at heating rates of 2.5, 5, 10°C/min. In this case, they have used Hexply 1454 prepreg epoxy resin that was included diglycidyl ether base on bisphenol A, dicyandiamide and reinforced by glass fiber.

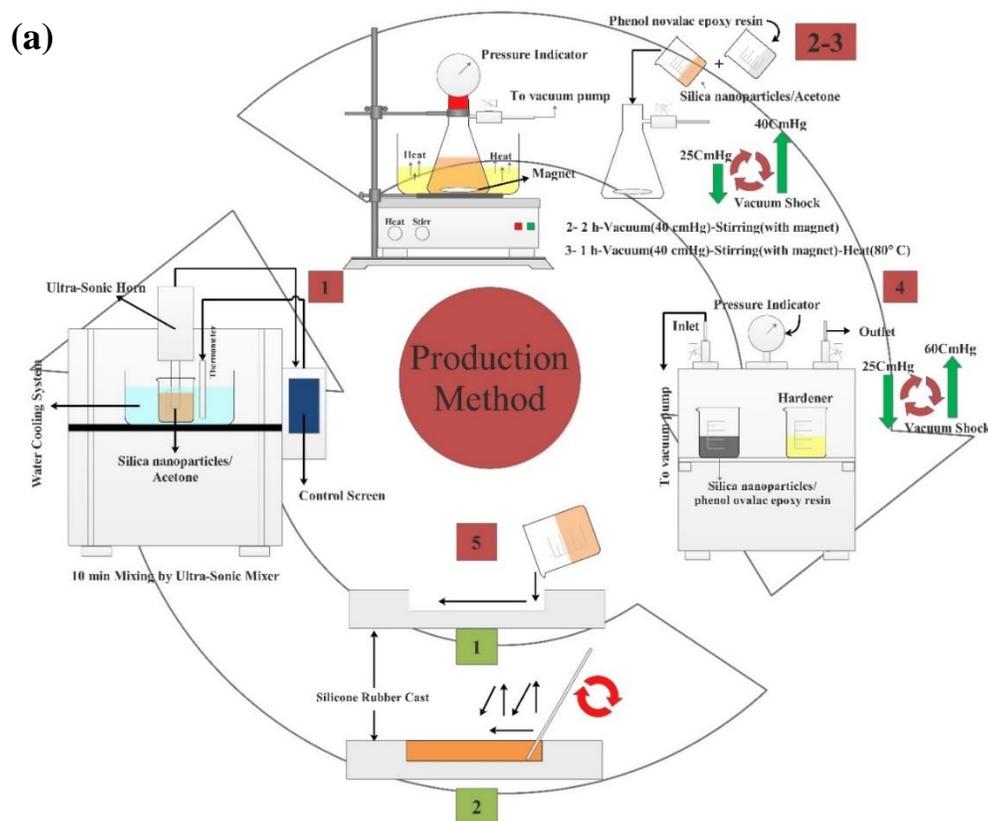
Curing kinetic parameters were acquired by three methods of Kissinger and Ozawa, Bourcharadt-Danielz and Sun and results were compared with each other. Based on their results, minimum activation energy was 76.8 kJ/mol for Kissinger method while maximum activation energy was 87.9 kJ/mol for Bourcharadt-Danielz method. In addition, mean pre-exponential factor ranged from  $0.0947 \times 10^9 \text{ s}^{-1}$  to  $2.60 \times 10^9 \times 10^9 \text{ s}^{-1}$  and order of reaction changed a bite when heating rate was changed that could be consider neglect. In spite of that, a model should be able to predict the relationship between reaction rate ( $\alpha$ ) and temperature, regardless of polymerization reaction nature. In this matter,  $\alpha$  could be calculated as a function of time empirically by usage of DCS data and suitable equations<sup>16</sup>. Furthermore, thermal decompositions plays an important role in determination of curing kinetic. Besides, thermoset resins exchange heat during curing process and networking, therefore curing process progress could recognize by thermal measurement. DSC apparatus which is an elected instrument in curing kinetic surveys can record the thermal energy that exchanged during curing process<sup>15,20-23</sup>.

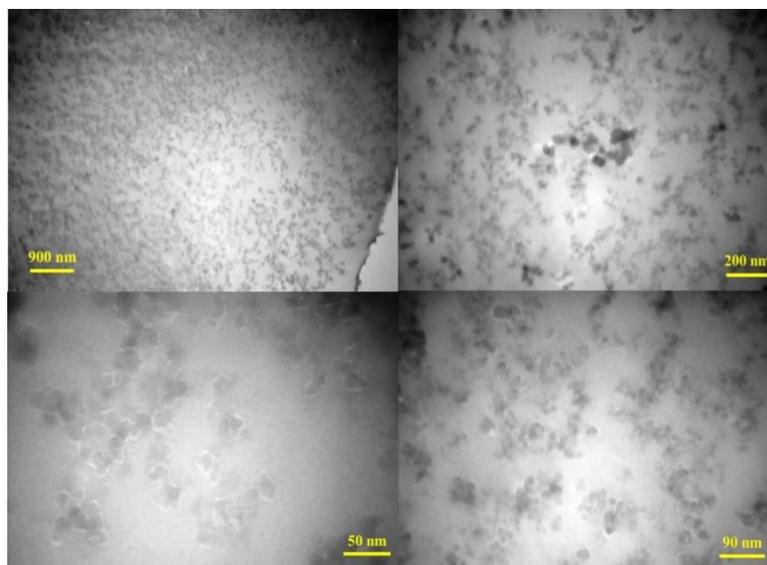
In addition, bubble based voids formation an activation can act as a stress concentration areas which can lead to sever destruction due to their activation. This stress concentration areas can either decrease the overall physical properties of composite samples or destroy and change the structure and shape of the composite samples respectively. In this case, removal of bubbles from the suspension before the curing step is very necessary and for this purpose vacuum shock technique can be used. By usage of this method the overall amount of bubbles can be reduced more than 98% and homogenous composite structure reinforced with desirable fillers can be obtained [6]. Besides, addition of silica nanoparticles to epoxy based resins can either improve their mechanical or thermal properties [2, 3] and studying the curing kinetic of epoxy based resins with presence of silica nanoparticles can be a great benefit for scientific research in matter of composites enhancement. In this study, by usage of vacuum shock technique [6], composite samples containing silica

nanoparticles were manufactured and by usage of DSC analysis, required thermal data for simulation of curing kinetic were obtained. Besides, by usage of phenomenological models, effect of silica nanoparticles on the curing kinetic of phenol novalac epoxy resin was obtained. The approach of this study is to present the most accurate simulation technique which has been adapted by experimental data.

## EXPERIMENTAL SECTION

For production of composite samples containing 4 wt% silica nanoparticles (supplied by INP corporation-Iran), vacuum shock technique was used [6]. In this case, in the first step, silica nanoparticles were dispersed in acetone for 10 min under 200 W power with 50°C temperature limit. In the second step, silica nanoparticles/acetone suspension and phenol novalac epoxy resin (supplied by Mokarar CO/model HA-11) were poured in vacuum erlenmeyer flask and above suspension was stirred with simultaneous vacuum shock by magnitude between 25-40 cmHg for 2 h. In the third step, 80°C heat was added to the previous section conditions and this step lasted for 1 h. In the fourth step, curing agent and resulting suspension were placed in vacuum chamber with vacuum shock between range of 25-40 cmHg for 30 min. In the fifth step, curing agent was added to the resulting suspension and poured in the silicone rubber cast. Furthermore, after completion of first curing step at room temperature, the composite samples were placed in heat oven under 100°C for 1 h. A view of these steps and dispersion of silica nanoparticles in the context of phenol novalac epoxy resin by TEM images can be seen in **Figure 1**.





**Figure 1:** (a) A view of production method with usage of vacuum shock technique (b) TEM images of silica nanoparticles/phenol novolac epoxy resin in different scales

Besides, the size of silica nanoparticles were determined by solving them in an ethylene glycol solvent. The size of nanoparticles was determined to be 61.5 nm.

In spite of that, some instruments such as OMU-3 ultramicrotome (manufacture by Reichert- Austria), TEM (manufacture by Carl Zeiss-Germany), DSC (manufactured by Mettler- Switzerland) were used in order to obtain required data. In this case, DSC tests were taken at heating rates of 2.5, 10 and 15°C/min. Besides, DSC tests were taken for both samples containing pure phenol novolac epoxy resin and sample containing 4 wt% silica nanoparticles/phenol novolac epoxy resin and obtained results were analyzed and modeled by three different theoretical methods.

## SIMULATION SECTION

In this study by usage of three different kind of theoretical methods based on phenomenological models, curing kinetic of phenol novolac epoxy resin with and without presence of silica nanoparticles was examined. In this case, a curing process kinetic model could be described as follow:

$$\alpha = \frac{\Delta H_t}{\Delta H_{total}} \quad \dots(1)$$

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad \dots(2)$$

Which  $\frac{d\alpha}{dt}$ ,  $k(T)$  and  $f(\alpha)$  are curing rate, reaction rate constant which depended on temperature and function of  $\alpha$ , respectively. In addition, the constant rate of  $k(T)$  can be expressed by Arrhenius equation:

$$k(T) = Ae^{-\left(\frac{E_a}{RT}\right)} \quad \dots (3)$$

Arrhenius' equation gives the dependence of the constant rate  $k$  of a chemical reaction on the absolute temperature  $T$  (in kelvin), where  $A$  is the pre-exponential factor (or simply the prefactor),  $E_a$  is the activation energy and  $R$  is the universal gas constant. Substitution of Eq. 3 in Eq. 2 yields are as follow:

$$\frac{d\alpha}{dt} = Ae^{-\left(\frac{E_a}{RT}\right)}f(\alpha) \quad \dots(4)$$

In a dynamic curing process with constant heating rate, temperature increases by increase in curing time. In this case, the relationship between  $\frac{d\alpha}{dt}$  and  $\frac{dT}{dt}$  can be show as below:

$$\frac{d\alpha}{dt} = \left(\frac{dT}{dt}\right) \frac{d\alpha}{dT} \quad \dots(5)$$

Where  $\left(\frac{dT}{dt}\right)$  is heating rate. In addition, substitution of Eq. 5 in Eq. 4 and rearrangement can be expressed as follow:

$$\frac{dT}{dt} = A\left(\frac{d\alpha}{dT}\right)^{-1}f(\alpha) e^{-\left(\frac{E_a}{RT}\right)} \quad \dots(6)$$

To determine  $A$  and  $E_a$  both side of Eq. 6 were logged and is as follow:

$$\ln\left(\frac{dT}{dt}\right) = \ln(A) - \ln\left(\frac{d\alpha}{dT}\right) + \ln f(\alpha) + \left(-\frac{E_a}{R}\right)\frac{1}{T} \quad \dots (7)$$

In this case,  $f(\alpha)$  may has different forms depending on curing mechanism, for autocatalytic model when initial rate taking account into zero,  $f(\alpha)$  could be put in the simple form as below:

$$f(\alpha) = \alpha^m(1 - \alpha)^n \quad \dots(8)$$

Besides, substitution of Eq. 8 in Eq. 7 can be expressed as follow:

$$\ln\left(\frac{dT}{dt}\right) = \ln(A) - \ln\left(\frac{d\alpha}{dT}\right) + \ln[\alpha^m(1 - \alpha)^n] + \left(-\frac{E_a}{R}\right)\frac{1}{T} \quad \dots(9)$$

Therefore, pre-exponential factor and activation energy can be determined by Kissinger and Ozawa kinetic methods. In spite of that, Malek method has explained Sestak-Berggren (SB) method and order of reaction RO ( $n$ ) in order to determine kinetic model. Also, it was considered only one reaction in Sestak-Berggren method and  $m$  &  $n$  depend to each other. In spite of that, in most reactions that were studied in Sestak-Berggren method by thermal analysis techniques, the kinetic equation is as follow:

$$\frac{d\alpha}{dT} = A e^{-x}f(\alpha) \quad \dots (10)$$

Where  $x$  is  $E/RT$ . In addition, the ratio of kinetic parameter  $p$  in SB ( $m,n$ ) is as follow:

$$p = m/n \quad \dots(11)$$

By usage of the following equation we can get to:

$$\alpha_m = \frac{m}{m+n} \quad \dots (12)$$

Moreover, the kinetic parameter ratio  $p$  can be written as follow:

$$p = \alpha_m / (1 - \alpha_m) \quad \dots (13)$$

Eq. 10 can be rearranged as follow:

$$\ln \left[ \left( \frac{d\alpha}{dt} \right) e^x \right] = \ln A + n \ln[\alpha^p(1 - \alpha)] \quad \dots (14)$$

In chart of  $\ln \left[ \left( \frac{d\alpha}{dt} \right) e^x \right]$  versus  $\ln[\alpha^p(1 - \alpha)]$ , when  $\alpha \in (0, 0.8)$  the slope of diagram,  $n$ , is kinetic parameter. The second kinetic power is  $m = pxn$ . According to the following equation:

$$n = \frac{1}{1 + \ln(1 - \alpha_M)} \quad \text{for } n > 1 \quad \dots (15)$$

The activation energy and kinetic model, pre-exponential factor ( $A$ ) for SB model can be obtained. Besides, an analytical model based on Bourcharadt-Danielz method can lead to autocatalytic model for dynamic curing process:

$$\frac{d\alpha}{dT} = A e^{-(E_a/RT)} \alpha^m (1 - \alpha)^n \quad \dots (16)$$

Furthermore, a linear expression for curing rate can be achieved by taking logarithm of both side of Eq. 16:

$$\ln \left( \frac{d\alpha}{dt} \right) = \ln A + m \ln \alpha + n \ln(1 - \alpha) + \left( -\frac{E_a}{RT} \right) \frac{1}{T} \quad \dots (17)$$

Eq. 17 can be solved by multiple linear regression where depended variable is  $\ln \left( \frac{d\alpha}{dt} \right)$  and independent variables include  $\ln \alpha$ ,  $\ln(1 - \alpha)$  and  $1/T$ . When orders of reaction ( $m$ ,  $n$ ) are determined,  $A$  and activation energy can be determined using low standard deviation by Barrett method. In this case, Eq. 16 can be rearranged to:

$$\frac{\left( \frac{d\alpha}{dt} \right)}{\alpha^m (1 - \alpha)^n} = A e^{-\left( \frac{E_a}{RT} \right)} \quad \dots (18)$$

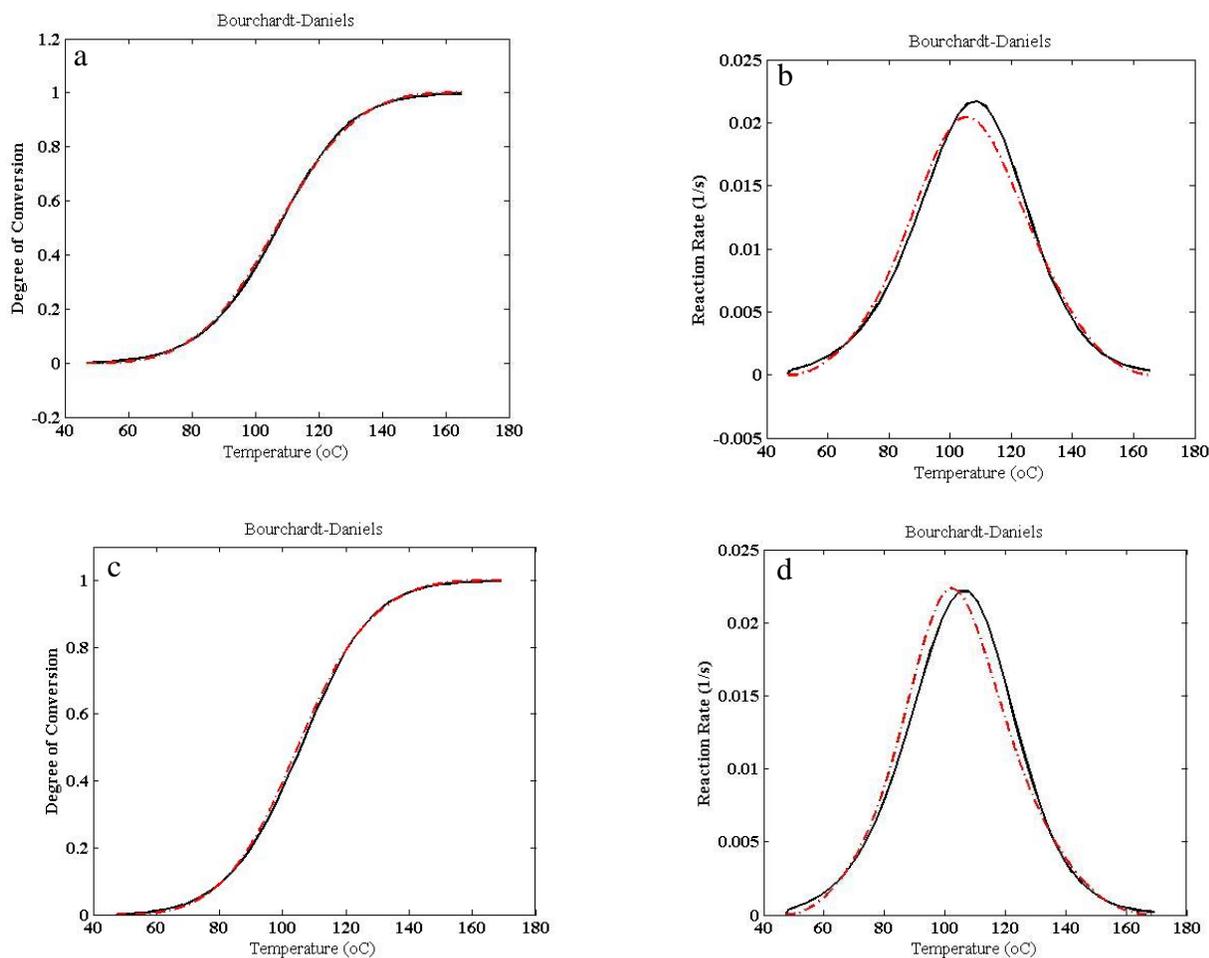
If a liner relationship between  $\log \left( \frac{\left( \frac{d\alpha}{dt} \right)}{\alpha^m (1 - \alpha)^n} \right)$  and  $1/T$  be exist,  $A$  and activation energy can be achieved from the slope and intercept of Eq. 18, where the standard deviation will significantly reduce. Therefore, the values of  $A$  and activation energy will be closer to real values. Besides, if all of kinetic parameters were known, curing order could be calculated by solving the following ordinary differential equation:

$$\frac{d\alpha}{dT} = \left( \frac{dT}{dt} \right)^{-1} A e^{-\left( \frac{E_a}{RT} \right)} \alpha^m (1 - \alpha)^n \quad \dots (19)$$

Curing degree ( $\alpha$ ) is dependent variable and absolute temperature is independent variable, Eq. 19 has no analytical solution, in this case, MATLAB could be used for numerical solution.

## RESULTS AND DISCUSSION

**Bourcharadt-Daniels method:** The variation of heat flow that was normalized by the sample weight and time at different temperatures is presented in **Figure 2**. Besides, it shows that the time taken to reach the peak heat flow decreased when the curing temperature increased. Also, the higher peak heat flow value is attained by the higher curing temperature.



**Figure 2:** Comparison between experimental data and Bourcharadt-Daniels modeling results at heating rate of  $10^{\circ}\text{C}$  for (a,b) pure phenol novolac epoxy resin and (c,d) silica nanoparticles/phenol novolac epoxy resin. left figure: degree of conversion versus temperature diagram, right figure: reaction rate versus temperature diagram.

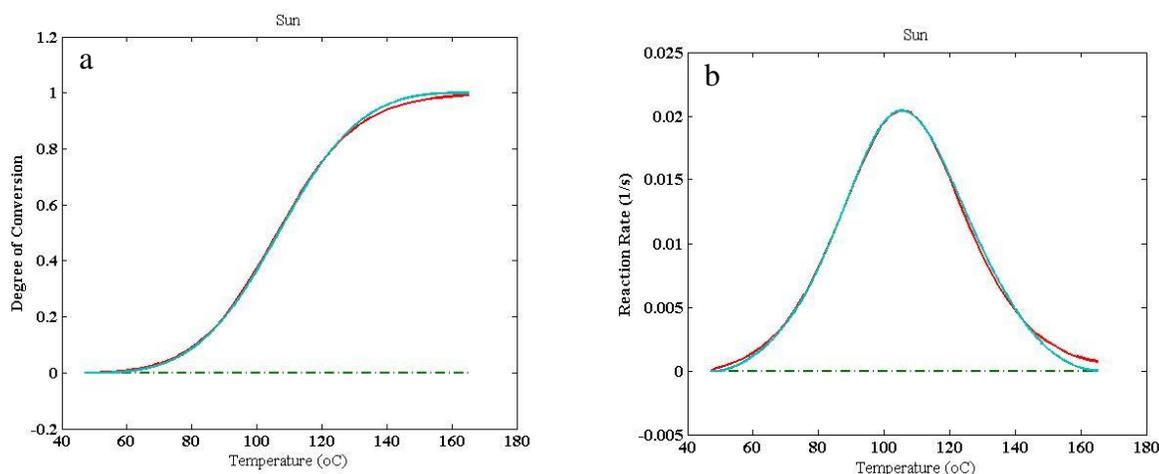
In addition, conversion versus temperature diagram at heating rate of  $10^{\circ}\text{C}/\text{min}$  can be seen in **Figure 2(a,c)**. In this case, good agreement between experimental data and modeled results were observed. In spite of that, reaction rate is derivation of this curve, reaction rate versus temperature diagram can be seen in **Figure 2(b,d)**. As can be seen in this Figure, maximum disagreement for Bourcharadt-Daniels model was observed at peaks

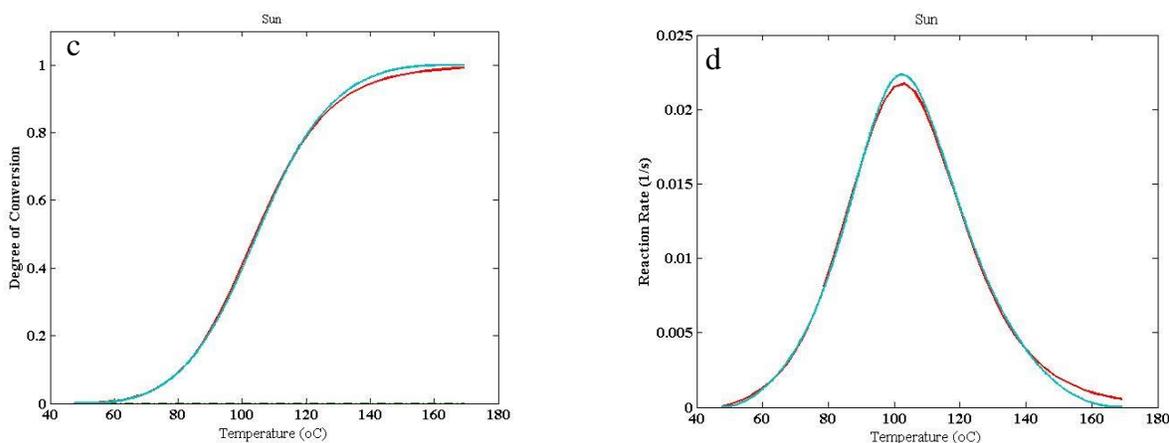
where derivative is zero. The results indicate that Bourcharadt-Daniels model was not the appropriate model for prediction curing kinetic of silica nanoparticles/phenol novolac epoxy resin and pure phenol novolac epoxy resin. Another reason that can be pointed out is that in this method the entire data cannot be used as a data source. Furthermore, kinetic parameters for Bourcharadt-Daniels method were shown in **Table 1**.

**Table 1:** Kinetic parameters for pure phenol novolac epoxy resin and silica nanoparticles/phenol novolac epoxy resin composite that was obtained from Bourcharadt-Daniels method.

	Heating rate(°C/min)	A	m	n	E <sub>a</sub> (kJ/mol)
Pure phenol novolac epoxy resin	2	3.95*10 <sup>6</sup>	0.140	1.350	60.99
	5	6.80*10 <sup>6</sup>	0.132	1.351	63.95
	10	5.82*10 <sup>7</sup>	0.125	1.411	70.96
	15	8.38*10 <sup>6</sup>	1.139	1.316	65.80
Silica nanoparticles/phenol novolac epoxy resin	2	4.06*10 <sup>5</sup>	0.171	1.290	55.18
	5	2.06*10 <sup>6</sup>	0.145	1.296	59.90
	10	1.31*10 <sup>8</sup>	0.131	1.455	73.02
	15	1.61*10 <sup>7</sup>	0.095	1.368	67.44

**Sun method:** Kissinger and Ozawa equation could be considered as Sun method base. Sun method using an average of four *A* for four different heating rate as  $\bar{A}$  in its calculations.  $\bar{A}$  can be calculated by using equations and in this case, Sun define  $A_r$ (correction factor) as  $A_r = A/\bar{A}$  to calculate *A* from  $\bar{A}$ . Besides, conversion versus temperature and reaction rate versus temperature at heating rate of 10°C/min for pure resin can be seen in Figure 3(a,b). Despite of that, good agreement between experimental data and modeling result by Sun method was observed in preliminary steps, but deviation from experimental data was observed at terminative steps. Moreover, it can be observes from reaction rate versus temperature that peak was predict accurately but deviation between experimental data and modeling results was observed after peak. It most notes that this Figure has showed the best fitting of Sun method in this work.





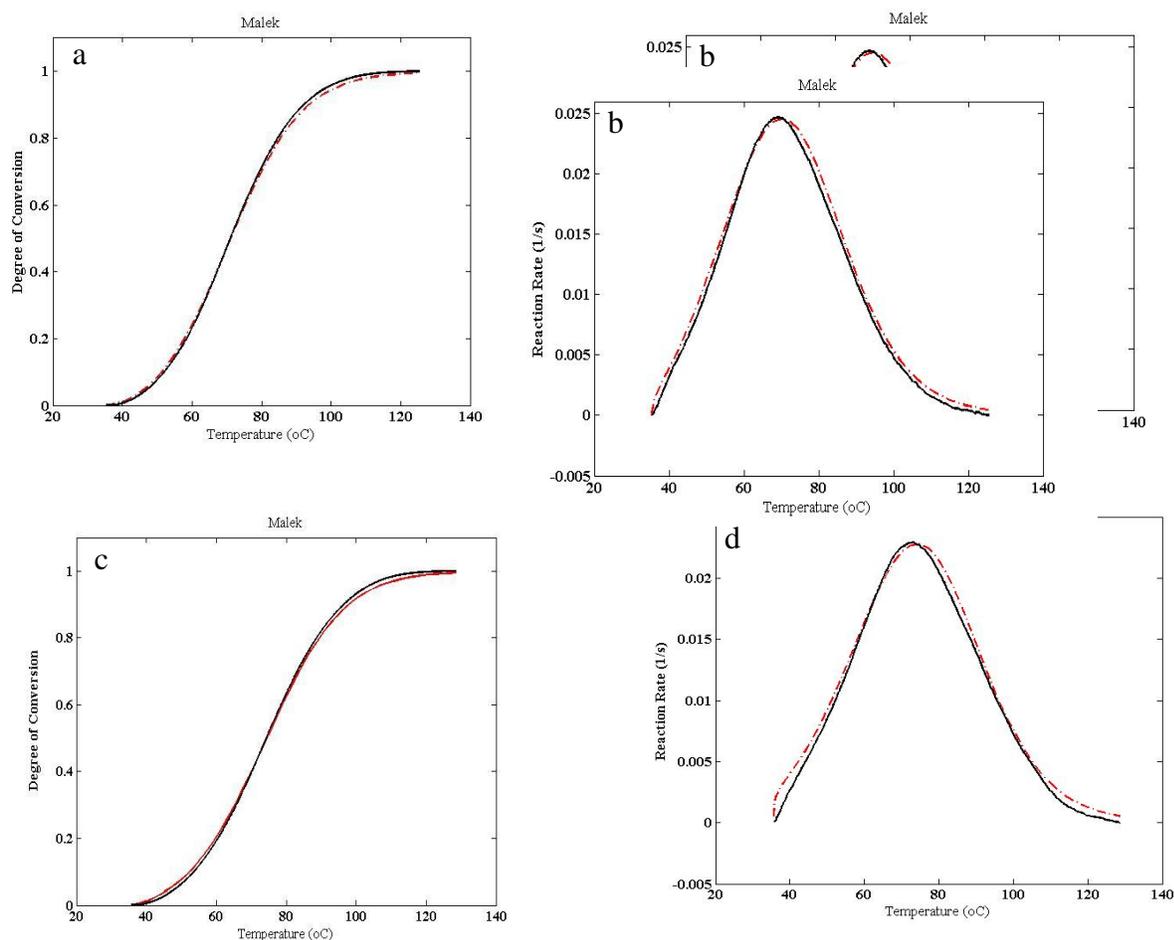
**Figure 3:** Comparison between experimental data and Sun modeling results at heating rate of 10°C for (a,b) pure phenol novolac epoxy resin and (c,d) silica nanoparticles/phenol novolac epoxy resin. left figure: degree of conversion versus temperature diagram, right figure: reaction rate versus temperature diagram.

In addition, reaction rate versus temperature and conversion versus temperature for silica nanoparticle/phenol novolac epoxy resin composite at heating rate of 10°C can be seen in Figure 3(c,d). As can be seen in this Figure, good agreements between experimental data and modeling result were not observed. In this case,  $\bar{A}$  is a source of this derivation, modeling data were calculated based on an  $\bar{A}$  value, while  $\bar{A}$  had a different value against  $A$ . the less difference between  $A$  and  $\bar{A}$  value the less derivation between actual data and modeling results will achieve. Besides, kinetic parameters for Sun method can be seen in **Tables 2**.

**Table 2** Kinetic parameters for pure phenol novolac epoxy resin and silica nanoparticles/phenol novolac epoxy resin composite that was obtained from Sun method.

	Heating rate (°c/min)	$A_r$	$A$	$m$	$n$
Pure phenol novolac epoxy resin	2	1	$3.94 \cdot 10^4$	0.317	1.356
	5	0.966	$3.25 \cdot 10^4$	0.320	1.375
	10	1.051	$3.82 \cdot 10^4$	0.375	1.394
	15	1	$3.73 \cdot 10^4$	0.388	1.421
Silica nanoparticles/phenol novolac epoxy resin	2	0.959	$1.64 \cdot 10^6$	0.231	1.577
	5	1	$1.84 \cdot 10^6$	0.268	1.834
	10	0.955	$1.76 \cdot 10^6$	0.347	1.631
	15	0.976	$1.51 \cdot 10^6$	0.311	1.665

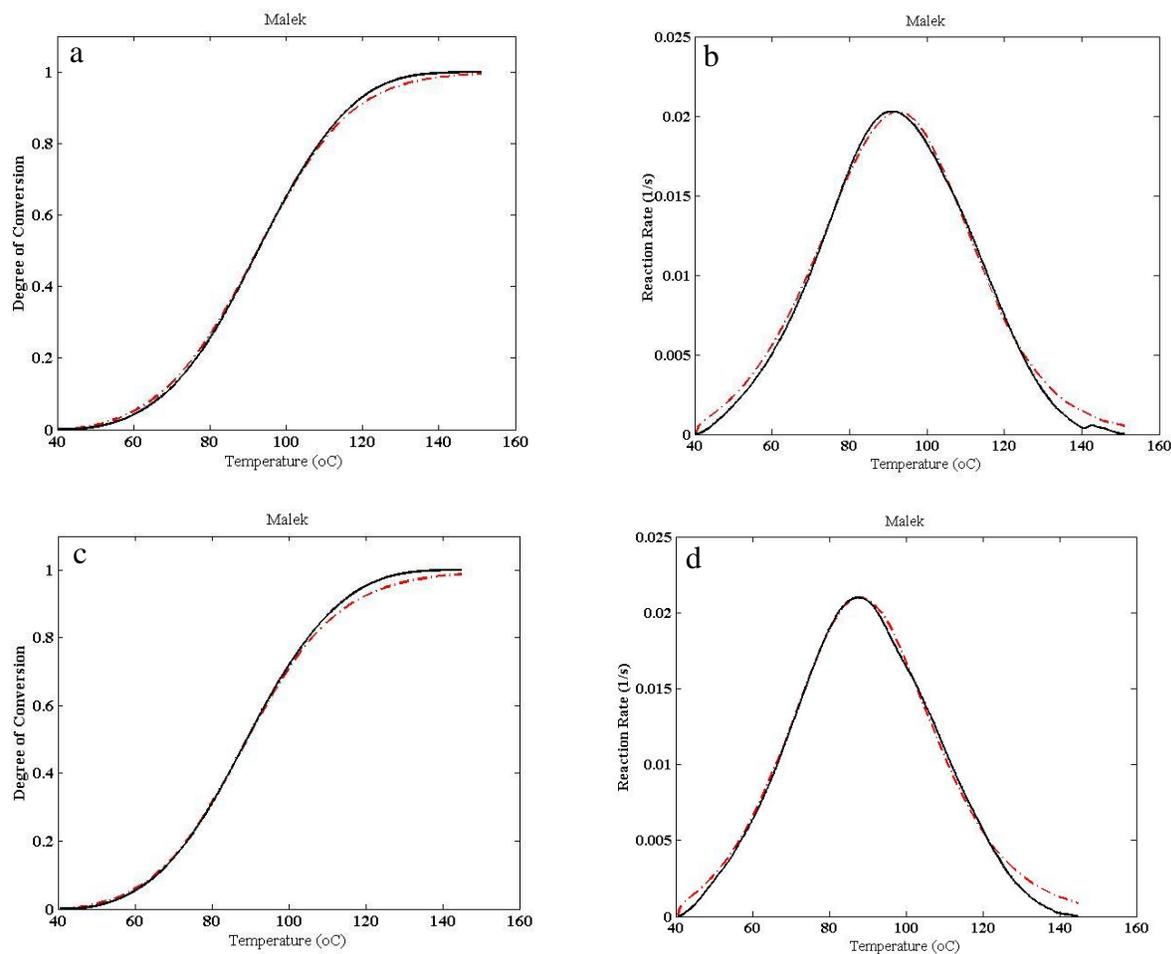
**Malek method:** As it was seen, Bourcharadt-Danielz and Sun methods were not appropriate for silica nanoparticle/phenol novolac epoxy resin, thus for achieving better results, Malek method was studied. In this case,  $E_a$  was calculated by slope of  $\ln d\alpha/dt$  versus  $1/T$  for the same curing rate. As it mentioned previously, in this method  $m$  and  $n$  are related to each other and was not calculated separately. Besides,  $n$  is the slope of  $\ln[(d\alpha/dt)e^x]$  versus  $\ln[\alpha^p(1-\alpha)]$  for  $\alpha \in (0.2, 0.8)$  and  $m = pn$  which  $p$  is defined to be  $(p = \alpha_M / (1 - \alpha_M))$ . In spite of that, Figure 4 shows conversion and its derivative (reaction rate) for pure phenol novolac epoxy resin and silica nanoparticles/phenol novolac epoxy resin composites versus temperature at heating rate of  $2^\circ\text{C}$ . Although, it is clear that experimental data and modeling results have a good conformity.



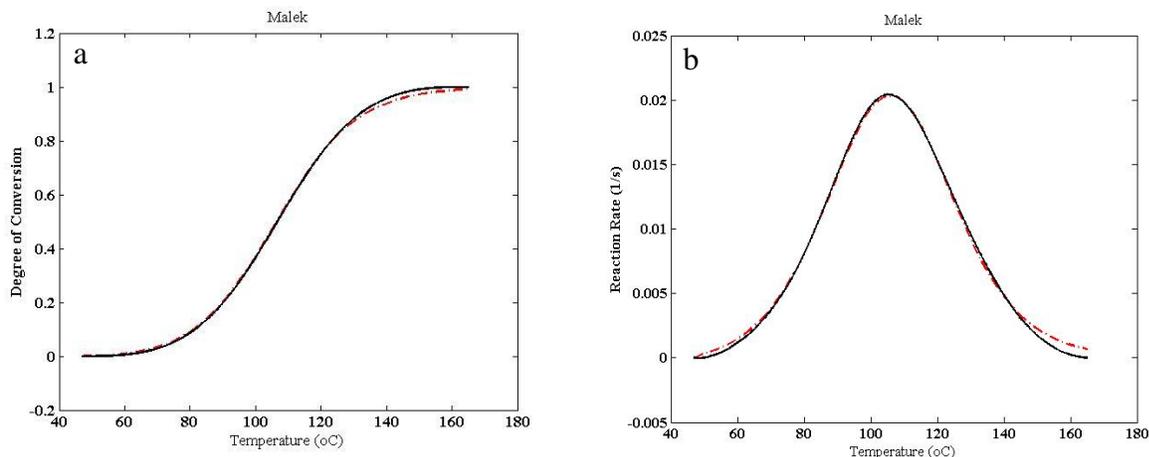
**Figure 4.** Comparison between experimental data and Malek modeling results at heating rate of  $2^\circ\text{C}$  (a,b) pure phenol novolac epoxy resin and (c,d) silica nanoparticles/phenol novolac epoxy resin. left figure: degree of conversion versus temperature diagram, right figure: reaction rate versus temperature diagram.

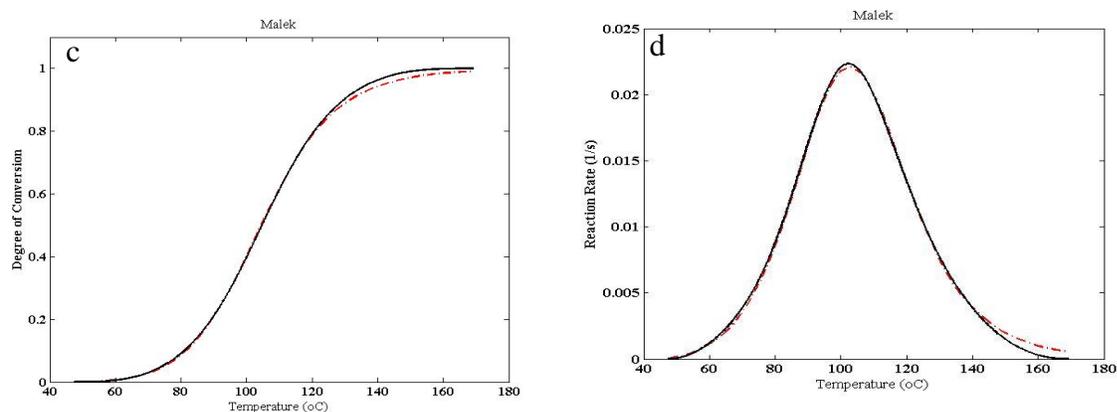
As can be seen in Figure 5, It can be observe that at heating rates up to  $2^\circ\text{C}$  experimental data and Malek modeling results have a good conformity, but a low deviation exist at terminative steps in Malek method.

Furthermore, in Figure 5-7, simulation results of curing kinetic for samples containing pure phenol novolac epoxy resin and silica nanoparticles/phenol novolac epoxy resin can in different heat loads can be seen.

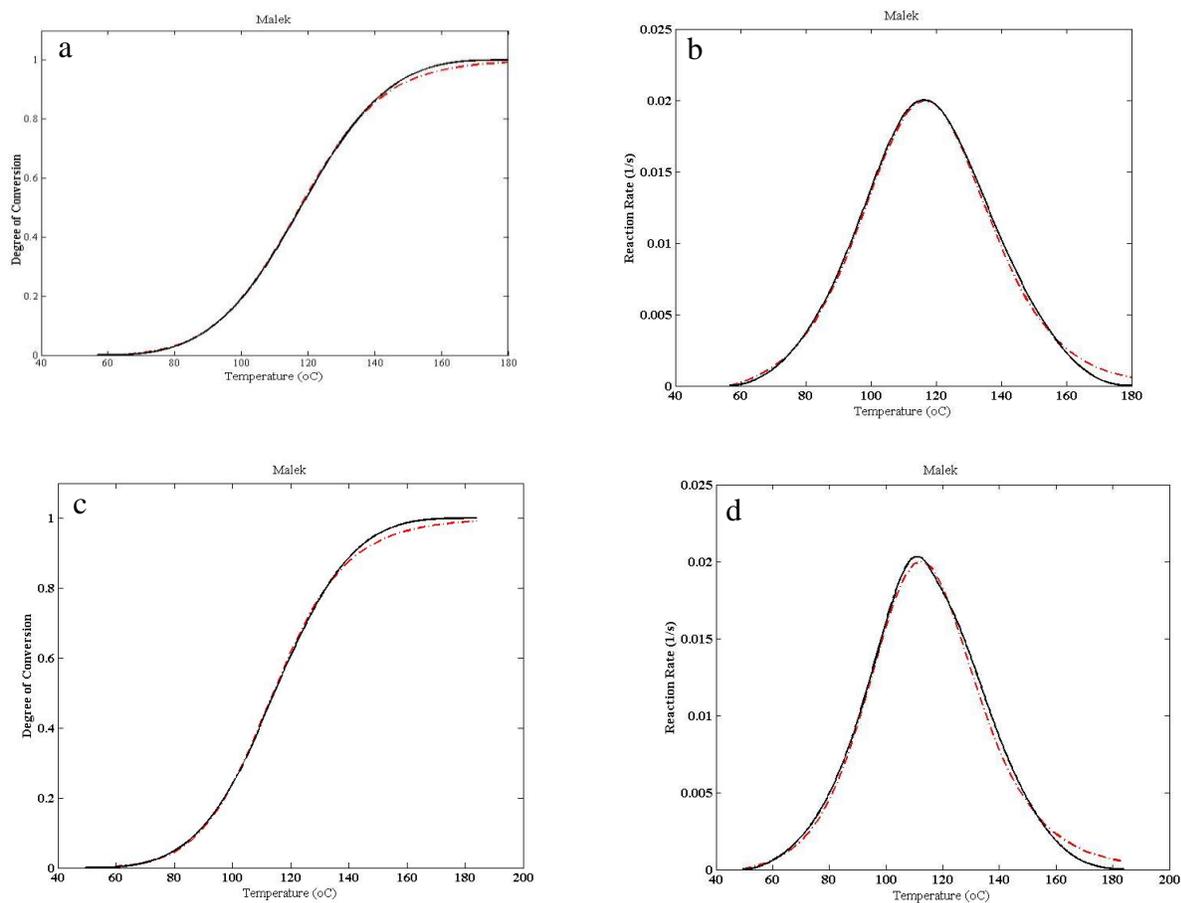


**Figure 5.** Comparison between experimental data and Malek modeling results at heating rate of 5°C for (a,b) pure phenol novolac epoxy resin and (c,d) silica nanoparticles/phenol novolac epoxy resin. left figure: degree of conversion versus temperature diagram, right figure: reaction rate versus temperature diagram.





**Figure 6.** Comparison between experimental data and Malek modeling results at heating rate of 10°C/min for (a,b) pure phenol novolac epoxy resin and (c,d) silica nanoparticles/phenol novolac epoxy resin. left figure: degree of conversion versus temperature diagram, right figure: reaction rate versus temperature diagram.



**Figure 7.** Comparison between experimental data and Malek modeling results at heating rate of 15°C/min for (a,b) pure phenol novolac epoxy resin and (c,d) silica nanoparticles/phenol novolac epoxy resin. left figure: degree of conversion versus temperature diagram, right figure: reaction rate versus temperature diagram.

Moreover, Table 3 shows kinetic parameters which was calculated by Malek method. Besides, addition of silica nanoparticles to the phenol novolac epoxy resin can lead to increase in  $A$  &  $n$  parameters and decrease in  $m$  parameter in all heating rates.

**Table 3:** Kinetic parameters for pure phenol novolac epoxy resin and silica nanoparticles/phenol novolac epoxy resin composite that was obtained from Malek method.

	Heating rate (°C/min)	A	m	n
Pure phenol novolac epoxy resin	2	$3.90 \times 10^4$	0.292	1.357
	5	$2.97 \times 10^4$	0.273	1.318
	10	$3.72 \times 10^4$	0.367	1.376
	15	$3.70 \times 10^4$	0.393	1.391
Silica nanoparticles/phenol novolac epoxy resin	2	$1.37 \times 10^4$	0.137	1.437
	5	$1.62 \times 10^4$	0.217	1.579
	10	$1.79 \times 10^4$	0.365	1.640
	15	$1.50 \times 10^4$	0.330	1.639

Based on achieved results, it is clear that Malek modeling results has best conformity with experimental data and obviously Malek method can predict behavior of phenol novolac epoxy resin more accurate than other methods.

## CONCLUSION

In this study, composite samples with and without silica nanoparticles with usage of vacuum shock technique were fabricated and by usage of DSC their thermal properties were extracted experimentally at heating rates of 2, 5, 10 and 15°C/min. Besides, obtained from experimental section was combined with simulation process in order to find the best method for prediction of phenol novolac epoxy resin behavior. Based on achieved results, by increase in heating rates, not only the area under the curves increases but also the temperatures in which peaks occur will increases. Furthermore, curing process was modeled with three different methods and activation energy of curing reaction at different heating rates was calculated for Bourcharadt-Danielz method. The values of activation energy in this method conation higher error than other methods. Also in Sun method there was deviation between experimental data and modeling results. Despite of that, Malek method which is based on Sestak-Berggren method, not only has best conformity with experimental data at all heating rates but also can predict peaks much more accurately in comparison with other methods. Besides, activation energy of curing process for ML-506/4 wt% silica nanoparticles in Malek and Ozawa method (58.45 kJ/mol) shows 11 kJ/mol increase in comparison with activation energy of pure phenol novolac epoxy resin (47.35 kJ/mol) that is due to inhibition effect of silica nanoparticles on curing reaction.

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