



## **Effect of Silica Nanoparticles on Activation Energy of Phenol Novolac Epoxy Resin/Unsaturated Polyester at Various Temperatures**

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### **ABSTRACT**

In the current study, the activation energy of modified phenol novolac epoxy (PNE) resin with unsaturated polyester (UPS) and silica nanoparticle (SN) at different filler loadings was investigated. In this case, effect of silica nanoparticles as a nano-size filler on the activation energy of PNE/UPS blend was evaluated. For this matter, tetraethylene pentamine (HA-11) which is an amine hardener was used as curing agent. SNs were dispersed in the mixture using ultrasonic equipment to prevent their agglomeration. The curing reaction of epoxy-based resins is exothermic. In this regard, the dynamic curing process was studied using differential scanning calorimetry (DSC) in four different heating rates, including 2, 5, 10 and 15 °C/min. Besides, various methods,

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including Ozawa, Flynn-Wall, Friedman and Butchart-Denilez were used to determine whether the activation energy of PNE/UPS blend or the best method for calculation of activation energy. Achieved results showed that the addition of SNs to the matrix can increase the activation energy and thus increase the curing time.

*Keywords: Nanocomposite; silica nanoparticle; activation energy; phenol novolac epoxy; unsaturated polyester.*

## 1. INTRODUCTION

Polymeric based matrices are among the most important and applicable materials in the field of composite industry. These effective materials have been widely used in variety of applications in various fields including surface coating, aerospace and marine industries and reinforcement of composites, etc., due to their perfect mechanical, thermal, chemical and adhesive properties. In this regard, some applicable polymeric-based materials, such as phenol novolac epoxy resin modified with unsaturated polyester (PNE/UPS) [1], linear low-density-polyethylene (LLDPE) [2], epoxy resin [3-8], cresol novolac epoxy resin modified with unsaturated polyester (CNP/UPS) [9] and polyethylene terephthalate (PET) [10] were widely used. However, these polymeric matrices are suffering from some serious disadvantages, which among them we can refer to poor resistance to crack propagation, brittleness and low wear resistance [11-15]. In order to overcome these kinds of problems, various additives were added to the polymeric system, among which silica nanoparticles showed significant improvement in the mechanical and electrical properties of modified nanocomposites [3,4,9].

Generally, phenolic resins from thermoset group have been widely used to develop nanocomposites. Phenolic resins are produced via polycondensation of phenols with aldehydes such as formaldehyde and thorough removal of the H<sub>2</sub>O side groups. Phenolic resins are ideal for high temperature applications up to 300 °C. As heat rises, phenolic resins are converting from a soluble thermoplastic material into a thermoset material, infusible due to the crosslinking and formation of 3-D networks. Strength of phenolic resins depends on the number of crosslinks formed by formaldehyde in the final polymeric system [16,17]. In fact, high molecular weight novolac chains promote crosslinking formation with low density unreacted phenols. Moreover, novolac resins cannot generate crosslinking with other materials due to

application of heat, which is due to the lack of methylol groups [18]. To produce crosslinking formation, novolac resins should be mixed with materials, such as hexamethylene tetramine, all of which can form methylene bridges and produce an infusible thermostable structure. Crosslink and cure of phenol novolac resin with epoxy resin instead of HMTA can lead to the creation of a non-porous structure. Curing reaction takes place during a nucleophilic process due to addition of hydroxyl phenol to the epoxy group without missing volatile groups [19, 20]. These kinds of materials contain high amount of epoxy and unreacted novolac resin that play an important role in some specific applications, such as microelectronic packaging. On the other hand, these materials do not present appropriate fire resistance property. To overcome this disadvantage, higher proportion of novolac resin should be networked with a low weight percentage of epoxy resin to achieve suitable fireproofing property and toughness along with higher modulus [21,22]. In fact, by controlling the molecular weight of the matrix via adding different proportion of novolac resin to the epoxy resin, a matrix with better mechanical performance can be achieved [23]. In addition, increase in the molecular weight of phenol monomer can improve the branching, due to the trivalent structure of phenol monomer. By usage of bivalent ortho- or para- cresol novolac, a linear structure with high molecular mass and without branching can be achieved. In addition, presence of methyl groups next to the hydroxyl groups in the cresol novolac structure can highly affect the chemical properties and structural stability of final composition. Phenol novolac is forming by combination of a three-functioned phenol with formaldehyde that can lead to production of a branched structure [24]. In order to achieve best results by addition of nanoparticles into the matrix system, a homogeneous distribution should be achieved. Homogeneous distribution of fillers, such as silica nanoparticle (SN), within the matrix can improve the interfacial bonding and thus establish crosslinking connections between fillers and matrix. Epoxy resins are among the most practical thermoset resins, due

to their special mechanical, chemical, thermal and physical features. Evaluation of the epoxy resin curing kinetic via Yazukin method showed that the activation energy of low molecular mass liquid epoxy resin during the curing process is about 48 kJ/mol and is constant during the whole process, while in high molecular mass cured epoxy compound, the activation energy is about 39 – 94 kJ/mol, which shows about 48% increase compared with low molecular mass epoxy resin. Obtained results from thermal studies showed that released heat during the curing process of solid epoxy compound is lower than the liquid epoxy compound. The outcome of various researches on the curing kinetic of epoxy resin showed that only limited models, including structural model and mechanistic model, were available. Besides, due to the difficulty of the issue and lack of anticipation, mechanistic models are less applicable in industry matters. Furthermore, in structural models, there are disagreements with respect to the number of reactions involved in the curing process, values of activation energy, reaction order and other kinetic parameters which demand further investigation [25,26].

In current research, nanocomposite based on PNE/UPS were reinforced with diverse weight

percentages of SN and their resulting properties were studied using non-isothermal differential scanning calorimetry (DSC) at four different heating rates (2,5,10 and 15°C). Thence, the activation energy of developed specimens was evaluated via Ozawa, Flynn-Wall, Friedman and Butchart-Denilez methods.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials and Methods

Phenol novolac epoxy (PNS) resin, unsaturated polyester (UPS) resin and epoxy hardener HA-11 supplied by the Mokarar engineering material corporation. Besides, silica nanoparticles were supplied by Merck & CO. For evaluation of silica nanoparticles size distribution, particle size analysis (PSA) (Horiba, Model LB550 based on dynamic light scattering (DLS)) was performed: obtained results can be seen in Fig. 1, which indicate that silica nanoparticles size lies between 34 and 100 nm.

For production of nanocomposites containing diverse weight percentage of silica nanoparticles, a multi-step manufacturing procedure was used. In this case, a proper proportion of PNE and UPS (50 wt%:50 wt%) were mixed and heated up to

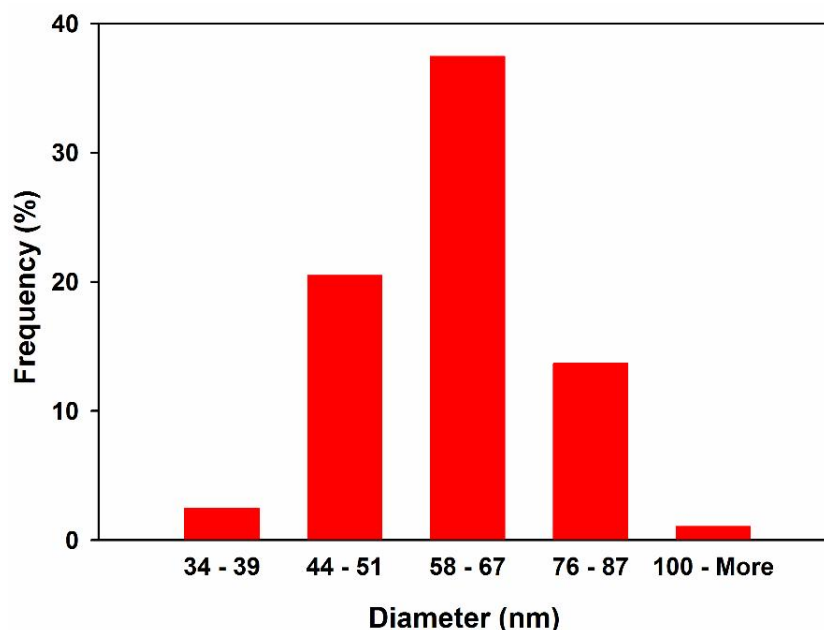
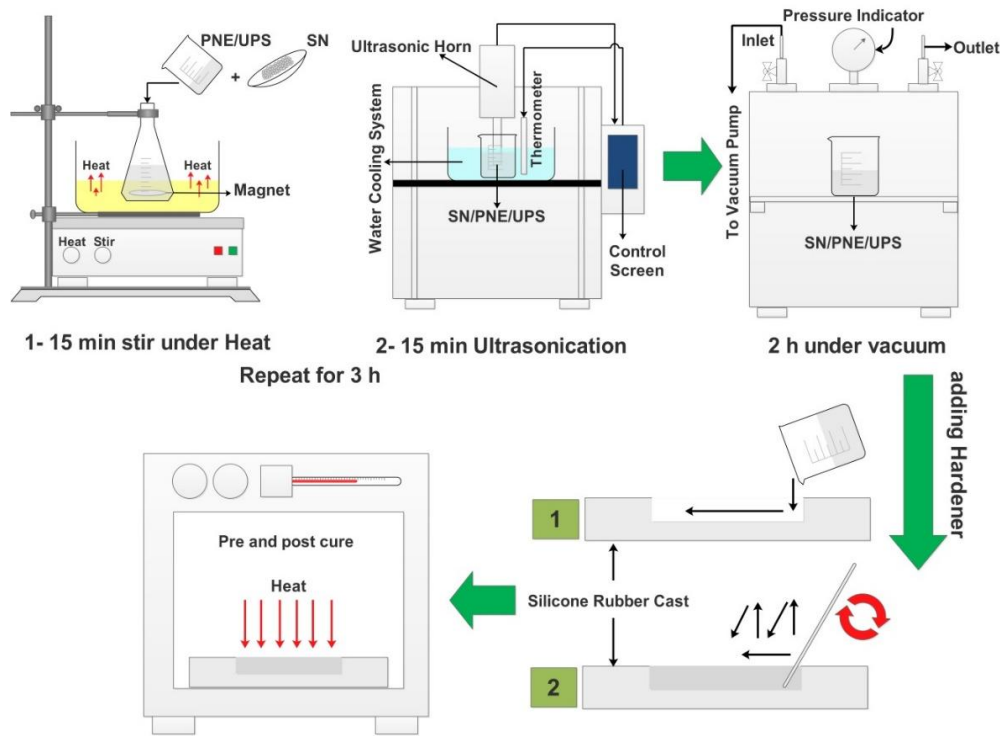


Fig. 1. PSA analysis of SN



**Fig. 2. Production procedure of specimens**

decrease the viscosity of matrix. Decrease in the viscosity can improve fillers distribution throughout the suspension. Thence, 4 wt% silica nanoparticle was added to the suspension and stirred for 15 min (500 rpm) followed by 15 min ultrasonication. This process was continued and repeated for 3 h to gain a homogeneous suspension. Thereafter, in order to remove bubbles from the suspension, the resulting suspension was kept in a vacuum oven for 2 h at room temperature (RT). Then, in order to cure the resulting composition, related hardener was added to the suspension with ratio 1:15, mixed for 10 min (200 rpm) and finally placed in heated oven for 6 h at 60°C, respectively. Primary cured composition was then post cured for 1 h at 100 °C. Production procedure of developed nanocomposites can be seen in Fig. 2.

Moreover, for evaluation of developed nanocomposites activation energy, non-isothermal differential scanning calorimetry (DSC) (Mettler, manufacture in Switzerland) technique was used, while each sample heated from 40 to 180 °C at different heating rates (2,5, 10 and 15°C) in nitrogen atmosphere. In this regard, pure indium and empty cell were used for calibration and as a reference, respectively. By

calculating the area under the exotherm peak, heat flow data as a function of time and temperature were acquired. Obtained data were further processed to get the functional conversion ( $\alpha$ ) and the rate of reaction. After this, the activation energy of developed nanocomposites with and without filler examined using Ozawa [27,28], Buchart-Danilez [29], Fridman [30] and Flynn-Wall [31] methods, according to related methodology.

### 3. RESULTS AND DISCUSSION

#### 3.1 Non-isothermal DSC Evaluation

In this study, for evaluation of activation energy of PNE/UPS matrix, four different methods were used, including Ozawa, Buchart-Denilez, Friedman and Flynn-Wall. For calculation of activation energy, it is assumed that the degree of matrix curing reaction is related to the heat of the reaction. In this regard, in order to study the effect of silica nanoparticles on the curing reaction of neat PNE/UPS, non-isothermal DSC technique at different thermal rates (2,5,10 and 15°C) was performed. In Figs. 3 (a) and (b), outcome of non-isothermal DSC test for neat matrix and reinforced nanocomposite with 4 wt%

SN can be seen, respectively. As can be seen in this figure, the lower the heat flow, the lower the related temperature peak. Moreover, the matrix curing process takes place at lower temperatures, but more time is needed for completion of the curing process. Besides, in Figs. 3 (a) and (b), it can clearly be seen that, as the heating rate decreased, the matrix curing process completed at lower temperature ranges.

### 3.2 Activation Energy of Developed Specimens

For evaluation of developed specimens activation energy, various methods such as Ozawa, Butchart-Denilez, Friedman and Flynn-Wall was used. In Ozawa method, for calculation of activation energy, the ratio of  $E_a/R$  is obtained from the gradient of the heating rate logarithm according to the inverse absolute peak temperatures. As a result, the same activation energy was obtained for all of considered heating rates (2,5,10 and 15°C). In Figs. 4 (a) and (b), the logarithm graph of heating rates, according to the inverse absolute peak temperature for neat matrix and nanocomposite reinforced with 4 wt% SN can be seen, respectively. Achieved results showed activation energy about 47.35 and 58.45 kJ/mol for a neat matrix containing PNE/UPS and reinforced nanocomposite with 4wt% SN, respectively. Besides, as can be seen in Figs. 4 (a) and (b), the addition of SN to the PNE/UPS can increase the activation energy about 11.1 kJ/mol, while the inhibitory effect on the curing reaction of the matrix can be observed.

What is more, in Flynn-Wall method, the gradient of the heating rate logarithm according to the inverse absolute temperature of different percentages of reaction process was used for calculation of activation energy. In Figs. 4 (c) and (d), the activation energy related to the Flynn-Wall method for neat matrix and specimens holding 4 wt% SN can be seen, respectively. As can be seen in this figure, for nine different  $\alpha$ , 9 activation energies were obtained, while the average of activation energy for the neat matrix and specimens holding 4 wt% SN is 44.23 and 52.31 kJ/mol, respectively.

Additionally, evaluation of activation energy based on the Friedman method for neat matrix and nanocomposite reinforced with 4 wt% SN can be seen in Figs. 5 (a) and (b), respectively. In this method, the gradient of  $\ln(d\alpha/dt)$  according to the inverse absolute temperature of different percentages of reaction process was used to determine the activation energy of developed specimens. As can be seen in Figs. 5 (a) and (b), for nine different  $\alpha$  values, nine activation energies were obtained that their averages for the neat matrix and reinforced sample with 4 wt% SN are 49.24 and 55.99 kJ/mol, respectively. Obtained results showed that measured activation energies for all methods are nearly same, while they were clarified that the addition of SN to the polymeric system of PNE/UPS can inhibit the curing reaction and thus delay the curing reaction and increase the required heat for the full cure of matrix.

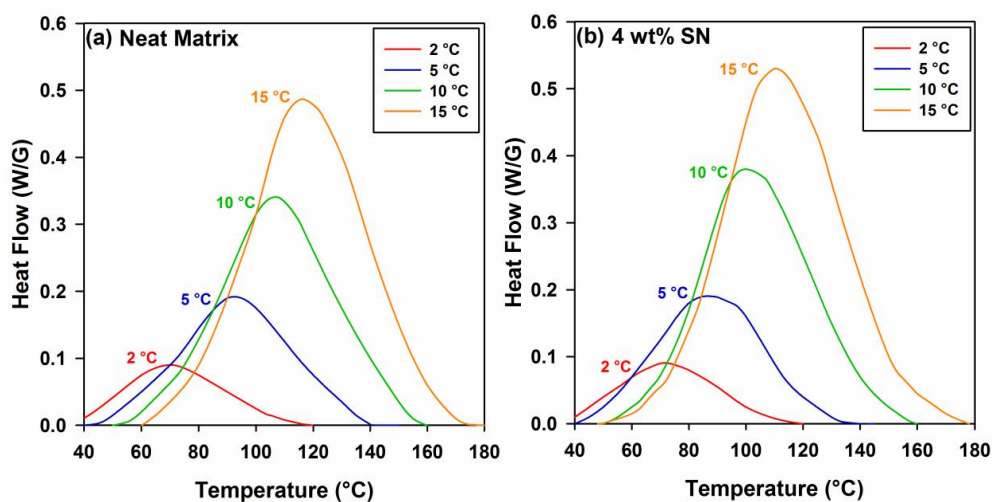


Fig. 3. Non-isothermal DSC curves at various heating rates (2, 5, 10 and 15 °C) for (a) neat matrix and (b) nanocomposite containing 4 wt% SN

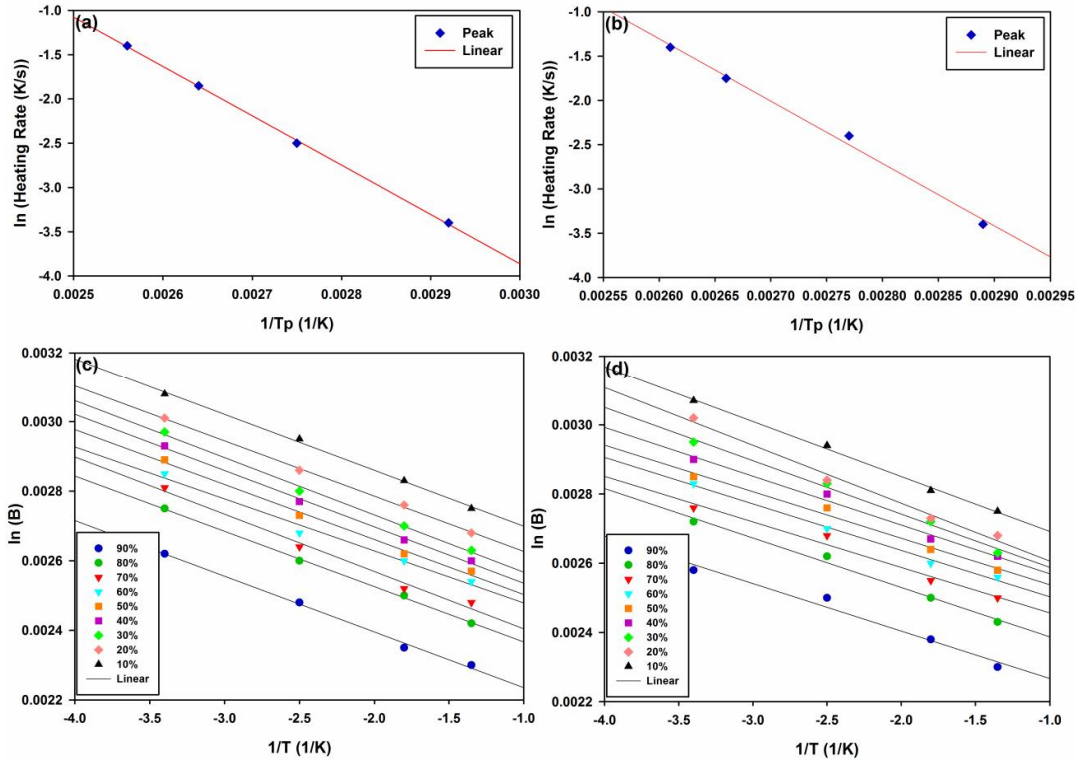


Fig. 4. Activation energy evaluation based on the Ozawa method for the (a) neat matrix and (b) specimens holding 4 wt% SN along with activation energy evaluation based on the Flynn-Wall method for the (c) neat matrix and (d) specimens holding 4 wt% SN

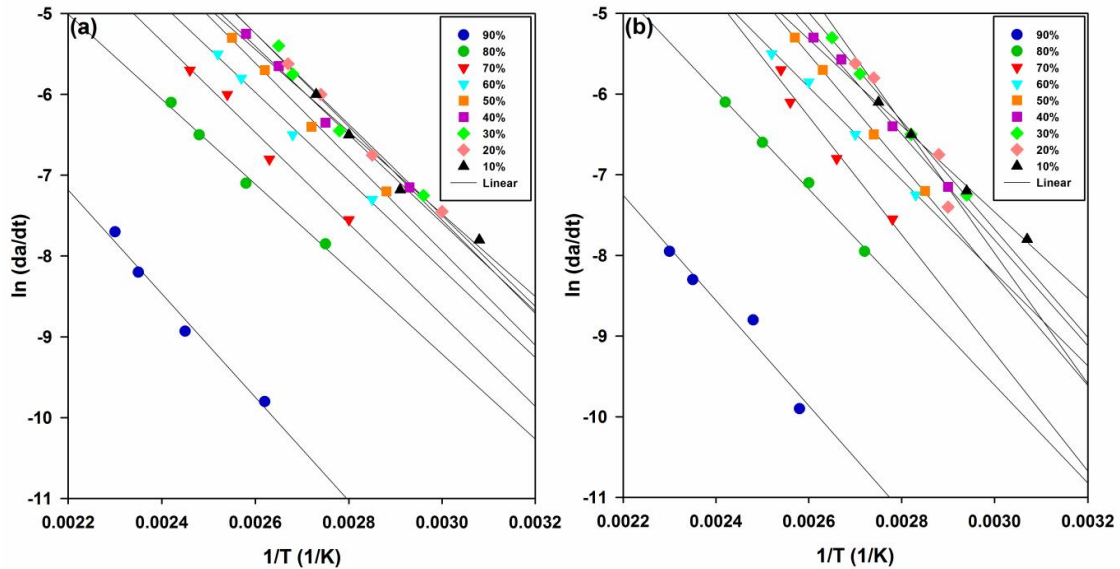


Fig. 5. Activation energy evaluation based on the Friedman method for (a) neat matrix and (b) reinforced nanocomposite with 4 wt% SN

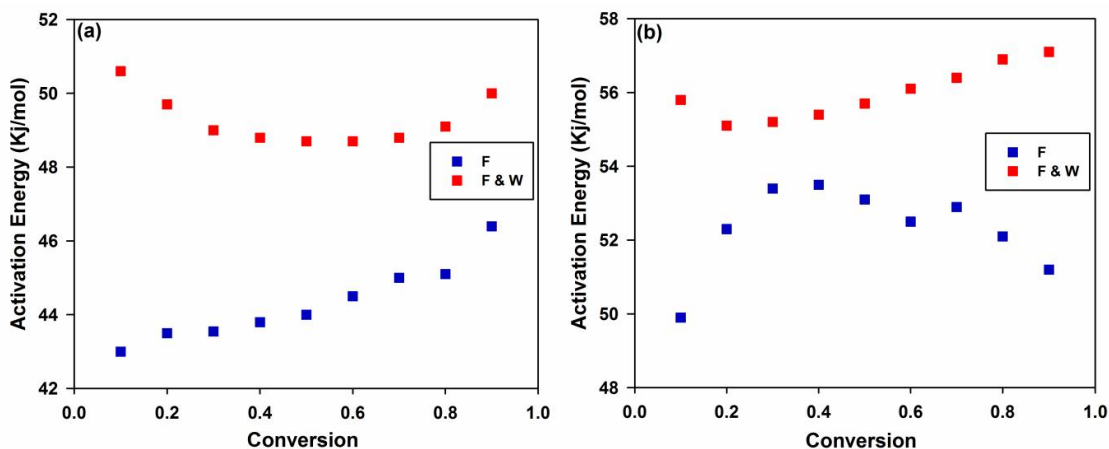
In addition, evaluation of activation energy based on the Butchart-Denilez method for the neat matrix and reinforced specimen with 4 wt% SN can be seen in Figs. 6 (a) and (b), respectively. By this method, the obtained results are achieved faster than by other methods. The kinetic parameters including A,  $E_a$ , m and n were simultaneously calculated using multiple linear regression. In this method, the linear area of log graph related to the curing rate, according to the inverse absolute temperature with negative slope was used as a main source for the calculation of kinetic parameters such as superficial  $E_a$ . Moreover, in Butchart-Denilez method, some systemic errors were happening during the measurement of A and  $E_a$ . By recalculation of A and  $E_a$  via Bart method, standard errors were significantly decreased. In Butchart-Denilez method, a separate  $E_a$  is calculated for every heating rates. In this case, the average activation energies for the neat matrix and reinforced specimen with 4 wt% SN are 65.42 and 63.89 kJ/mol, respectively. Obtained results showed about 1.53 kJ/mol decrease in the activation energy due to the addition of SN, which show that this method is not whether reliable or application for determination of PNE/UPS activation energy, with or without SN.

Obtained results from various methods, including Ozawa, Flynn-wall and Friedman showed that addition of SN to the PNE/UPS can delay the curing process of the final composition, while all of the method showed near values. On the other hand, achieved data from Butchart-Denilez method showed some decrease in the activation energy due to the addition of SN to the PNE/UPS

matrix, which shows that obtained data contained high amount of errors and they were therefore unreliable. This outcome could be due to several reasons, among we can refer to the filler loading, amount of whether added accelator or curing agent during the curing process and heating rate value. Increase in the filler loading can lead to their aggregation throughout the suspension and thus prevent homogenous transfer of heat throughout the cured nanocomposite which can highly affect the final outcome by avoiding the proper heat transfer in some regions of the nanocomposite. Moreover, increase in the heating rate and usage of accelator or curing agent can decrease the required time for full cure of the nanocomposite, thereby create some errors during measurements. Furthermore, related activation energy for specimens with and without SN obtained by various methods can be seen in Table 1.

**Table 1. Activation energy obtained from different method at diverse weight percentages of SN**

Method	Weight percentage of SN (wt%)	Activation energy (kJ/mol)
Ozawa	0	47.35
	4	58.45
Flynn-Wall	0	44.23
	4	52.31
Friedman	0	49.24
	4	55.99
Butchart-Denilez	0	65.42
	4	63.89



**Fig. 6. Activation energy evaluation based on the Butchart-Denilez method for (a) neat matrix and (b) reinforced matrix with 4 wt% SN**

#### 4. CONCLUSIONS

In this study, nanocomposites containing different filler loadings of SN within the content of PNE/UPS were fabricated and then studied using non-isothermal DSC analysis of diverse heating rates (2,5,10 and 15°C). Thereafter, the activation energy of PNE/UPS matrix with and without 4 wt% silica nanoparticles were evaluated via Ozawa, Flynn-Wall, Friedman and Butchart-Denilez methods. Obtained results from mentioning methods showed activation energies about 47.35, 44.23, 49.24 and 65.42 kJ/mol for neat matrix, while these values in a reinforced matrix with 4 wt% silica nanoparticles were 58.45, 52.31, 55.99 and 63.89, respectively. Moreover, obtained results from Ozawa, Flynn-Wall and Friedman showed that addition of silica nanoparticles to the PNE/UPS matrix can delay the curing process, while Butchart-Denilez method showed a reverse situation. In fact, while Ozawa, Flynn-wall and Friedman methods can be used for calculation of activation energy, the Butchart-Denilez cannot be used, because obtained results are full of errors and unreliability.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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