

Thermokinetics behavior of epoxy adhesive reinforced with low viscous aliphatic reactive diluent and nano-fillers

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(Received 13 May 2017 • accepted 9 August 2017)

Abstract–The current study reports the effect of low viscous aliphatic reactive diluent (RD), MWCNT and VGCF on the curing kinetics of amine cured epoxy adhesive system employing non-isothermal differential scanning calorimetric (DSC) technique. Non-isothermal DSC thermograms of epoxy adhesive were studied at various heating rates: 5, 10 and 15 °C/min. The decrease in the exothermic peak height with the introduction of MWCNTs and VGCFs was taken as proof of the acceleration effect of nano-fillers on the epoxy-amine curing reaction. Also, increased T_{onset} , T_p and ΔH_{cure} values were observed for epoxy/RD adhesive system at all heating rates. The value of activation energy (E_a) was determined using Kissinger and Flynn-Wall-Ozawa methods. Experimental results showed that the addition of 10 wt% RD increased the E_a from 60 to 63 kJ/mol on account of the reduced viscosity, allowing better contact of resin with the curing agent. Furthermore, MWCNTs have an accelerating effect on the cure kinetics that does not change the autocatalytic cure reaction mechanism of epoxy resin. It was also found that the addition of MWCNT and VGCF decreases the overall degree of conversion, as evident with lower ΔH_{cure} and E_a of the cured adhesive when compared with epoxy/RD system. The dependency of E_a on degree of conversion ranging from $\alpha=0.1$ to 0.9 was also investigated. The two normalized functions $\gamma(\alpha)$ and $z(\alpha)$ were also considered in order to study the complex curing mechanism. The kinetic parameters m , n and $\ln A$ were obtained by using two parameter autocatalytic Sestak-Berggren model. The curves revealed good agreement between experimentally determined and theoretically obtained MWCNT/VGCF reinforced epoxy adhesive systems.

Keywords: Non-isothermal, Activation Energy, Kissinger, Flynn-Wall-Ozawa, Sestak-Berggren Model

INTRODUCTION

Adhesive technology has undergone rapid growth over the past few decades, and adhesives are now widely used in electronics, aerospace, automobile and other engineering applications. They provide many advantages, for instance, low weight, less expensive, low stress concentration, high specific strength and more durability than conventional mechanical fasteners [1,2]. Adhesively bonded joints are increasingly being integrated into consumer electronics as an alternative to conventional mechanical fasteners. For the development of multi-functional adhesives for both structural and conductive bonding, common thermoset adhesive materials based on epoxy resin are widely used in numerous formulations and forms due to their distinguished ability to accept a wide range of conductive fillers [3].

The curing of epoxy composite plays an important role in determining the quality of the final products as the linear epoxy resins are cured into three dimensional cross-linked networks using curing agent [4]. Recent studies have shown that the incorporation of

nano and micron-sized reinforcements have an essential influence on both homogeneous dispersion and strong interfacial interaction [5,6]. Consequently, studying the effect of reinforcement on the epoxy cure reaction is significant for the design, analysis and optimization of processing parameters of the products [7-9]. Therefore, a large number of investigations have been performed to get a better understanding of the cure behavior of epoxy resin [10,11]. Epoxy resin has been widely used in structural applications owing to its superior thermal and mechanical properties, high temperature stability and low curing shrinkage [12,13]. However, it has certain disadvantages in terms of brittleness, which limits its uses in structural engineering applications [14].

In recent years, reactive diluents (RD) based on monoglycidyl ether of C12-C14 fatty alcohols have been reported as successful toughening agents to overcome the inherent brittleness of epoxy networks. To achieve the optimum properties of the final product, study of curing kinetics has become prerequisite, since they are responsible for the morphological and structural changes during processing. In this regard, modelling of cure kinetics is important because it represents the effect of introduction of nano-fillers within epoxy matrix on the curing time and processing conditions.

A study involving the effect of carbon nanotubes (CNT) as the reinforcement has proved their potential for several lightweight auto-

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motive, aerospace and structural applications. Therefore, strong efforts have been undertaken to study the effect of CNT incorporation on the cure reaction of epoxy systems. Choi et al. [15] reported on the influence of chemical modification of multi-walled carbon nanotubes (MWCNTs) on the curing reaction of epoxy using differential scanning calorimetric analysis. MWCNT surfaces were chemically modified by introducing azomethine ylide groups containing anchored phenol structures. According to their research results, surface modification of MWCNTs had an effect on the curing temperature and kinetic parameters of the MWCNT/epoxy nanocomposites. The authors observed shifting in the peak temperature towards higher temperature regions. Higher activation energy (E_a) values were also observed for the MWCNT/epoxy nanocomposites indicating both the increasing effect of viscosity and acceleration effect of MWCNTs on the epoxy-amine curing reaction.

Jahan et al. [16] assured that understanding the fundamental aspects of the epoxy-amine curing reaction is crucial for developing new polymer materials. They studied the effect of the carboxyl acid functionalized MWCNTs on the curing behaviour of epoxy resin. The results indicated that the addition of small amounts of MWCNTs to epoxy significantly reduced the total heat of reaction and had better ability to hinder the movement of polymer chain segments. Experimental findings also corroborated that MWCNT facilitated the cure reaction of epoxy resin leading to a decrease in the E_a , in particular, at initial stages of curing. However at the later curing stage, MWCNTs imposed a retarding effect on the curing process. The observed variations in the curing behavior with respect to temperature have also been reported by several authors [3,9,17,18].

Carbon nanofibers (CNFs) also have a unique surface state combined with surface modification and cross-linking, which facilitates epoxy cure reaction to tailor/engineer the nanofibers in several technological applications [19]. Therefore, many research efforts have also been dedicated to explore the influence of incorporation of CNFs on the curing process. Xie et al. [19] reported on the cure kinetics of epoxy nanocomposites affected by CNFs. The results indicated that the cure reaction was promoted in its early stage, which may be due to the acceleration effect associated with the incorporation of CNFs. Furthermore, Wu et al. [20] reported an increase in total heat of the exothermic reaction being brought together to reduce the maximum peak temperature during curing process of epoxy/CNF system. The findings indicate that the reduction in peak temperature is closely related to the specific surface area of CNFs. The higher the surface area, the greater will be the

temperatures drop of exothermic epoxy cure reaction.

In the current investigation, the cure kinetics of epoxy resin has been evaluated using differential scanning calorimetric in non-isothermal mode. Non-isothermal DSC thermograms can be described by different kinetic models such as the Kissinger [12,21], Flynn-Wall-Ozawa (FWO) [12], Kissinger-Akhira-Sunose (KAS) [12,22-24] and Sestak-Berggren autocatalytic model [25-27]. Natarajan et al. [10] reported the cure kinetics of bio-based Diglycidyl Ether of Bisphenol-A (DGEBA) network using non-isothermal DSC technique. Kinetic parameters were calculated employing Kissinger and FWO method. The authors also used the autocatalytic Sestak-Berggren reaction model to investigate the reaction order. Similarly, Esmizadeh et al. [28] also investigated the epoxy/nanoclays-CNT hybrid nanocomposites using non-isothermal DSC techniques. Kissinger, FWO and Friedman methods were used to calculate the kinetic parameters and reported that FWO and KAS models give the best fit to experimental data.

The aim of this research was to study the combined effect of RD, MWCNT and VGCF on the cure kinetics of epoxy resin. MWCNT and VGCF dispersed in epoxy resin were prepared and the RD was used to facilitate the dispersion of fillers within the epoxy matrix. The activation energy (E_a) was determined by using two different methods: Kissinger and the FWO method. This methodology provides a basis for understanding the structural and morphological changes involved in the formation of epoxy nanoadhesives.

MATERIALS AND METHODS

1. Materials

Materials used were Araldite GY250, unmodified medium viscous epoxy resin based on Bisphenol-A; Aradur HY951, low viscous amine based curing agent, purchased from M/s Huntsman Advanced Materials Pvt. Ltd. Epotec RD108, reactive diluent based on mono-glycidyl ether of C12-C14 fatty alcohol was purchased from M/s Aditya Birla Chemicals Ltd. MWCNTs with the outer diameter of 10 nm, average length of 1.5 μm and an average purity >90% was supplied by M/s Nano-cyl Pvt. Ltd. VGCF (grade, Pyrograf-III) with an average density of 2 g/cm³ and outer diameter of 125-150 nm was purchased from M/s Sigma Aldrich Pvt. Ltd. India. The characteristic properties of Araldite GY250 and Epotec RD108 are displayed in Table 1.

2. Fabrication of Epoxy Nanoadhesive System

VGCF mats were first cut into nominal size of 20 mm length. These chopped forms of fibers along with as-received MWCNTs

Table 1. Characteristics of Araldite GY 250 and Epotec RD-108

Properties	Araldite GY 250	EPOTEC RD 108
Appearance	Clear and no contamination	Clear liquid
Epoxy value	5.30-5.55 eq/kg	3.34-3.64 eq/kg
Epoxy equivalent weight	180-189 g/eq	295-313 g/eq
Viscosity	10,000-12,000 mPa-s	5-10 mPa-s
Density	1.17 g/cm ³	0.9 g/cm ³
Epichlorohydrin content	-	10 ppm (max.)
Water content	-	0.1% (max.)

Table 2. Different epoxy adhesive formulations

Sample type	Mass of resin (gm)	Mass of hardener (gm)	Mass of RD (gm)	Mass of MWCNT (gm)	Mass of VGCF (gm)
Epoxy	20	2	-	-	-
Epoxy/10% RD	18	1.8	2	-	-
Epoxy/10%RD/1% MWCNT/1% VGCF	17.6	1.76	2	0.2	0.2

were immersed in a 70% ethanol solution to remove amorphous carbon present in the MWCNTs. After that, MWCNTs and VGCF were dried in a vacuum oven at 70 °C for 1 hr, and then cooled to room temperature for the adhesive preparation.

Epoxy nanoadhesives were prepared by dispersing specified weight percentage of MWCNTs and VGCF in acetone. The dispersed solution was then ultrasonicated (DT-151, 3.5 L capacity M/s Darsh Technologies Ltd.) for 30 min to get a homogeneous dispersion. Subsequently, epoxy and RD was added to the mixture followed by sonication for another 30 min. The reaction mixture was then kept in a vacuum oven for at least 2 hr at 80 °C to evaporate the solvent completely. Finally, it was cooled to room temperature, curing agent was added followed by gentle mixing for about 5 min. The optimum resin-to-hardener ratio was maintained at 100 : 10 ratio to achieve maximum degree of curing. Based on the mixing ratio of epoxy and curing agent, the following quantities were mixed during the fabrication of epoxy adhesive systems and indicated in Table 2.

3. Characterization

Non-isothermal curing kinetic analysis was carried out using differential scanning calorimetry (Q20 M/s TA instruments, USA). All the samples were heated from 30° to 200 °C at different heating rates (5, 10 and 15 °C/min) under N₂ atmosphere. Initially, the DSC instrument was calibrated with pure indium and then uncured sample of ca. 5-10 mg was subjected to dynamic curing over desired temperature range and various different heating rates to investigate curing behavior.

3-1. Curing Kinetic Behavior

The fundamental assumption in DSC analysis is that the area under the exothermic peak can be integrated to give heat of cure. When the resin system cross-links, the value of heat of cure decreases. These changes in heat of cure can be used to measure the degree of conversion (α) of the resin system. The degree of conversion (α) at any temperature T can be expressed as [12]:

$$\alpha(t) = \frac{H(t)}{\Delta H_T} \quad (1)$$

where ΔH_T is the total heat of cure and $H(t)$ is the partial heat of cure up to time t. The rate of conversion ($d\alpha/dt$) at any temperature (T) can be expressed as [27]:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = \frac{dH(t)}{\Delta H_T dT} \quad (2)$$

where β is the heating rate and $dH(t)/dT$ is the instantaneous heat flow. The rate of conversion ($d\alpha/dt$) of the cure reaction under constant heating rate can be correlated with the two functions expressed as [12,27]:

$$\frac{d\alpha}{dt} = K(T) \cdot f(\alpha) \quad (3)$$

where T is the absolute temperature, K(T) is the temperature dependent rate constant, $f(\alpha)$ is a dependent kinetic model function. The temperature dependent rate constant is generally expressed in the Arrhenius form as [10]:

$$K(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

Using Eq. (4), Eq. (3) can be transformed in the following form:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (5)$$

where A is the frequency factor (/min), R is the gas constant (8.314 J/mol·K) and E_a can be defined as the activation energy of the cure reaction. The value of activation energy can be calculated using various non-isothermal methods described below:

• Kissinger

According to the Kissinger analysis [29] based on Eq. (6), the E_a can be obtained from the slope of the plot between $\ln(\beta/T_p^2)$ and $(1/T_p)$.

$$E_a = -R \frac{d\left(\ln\left(\frac{\beta}{T_p^2}\right)\right)}{d\left(\frac{1}{T_p}\right)} \quad (6)$$

where T_p is the maximum peak temperature observed in the heat flow vs temperature curve.

• Flynn-Wall-Ozawa (FWO)

The FWO method is an iso-conversional method, where $\ln\beta$ can be plotted as a function of inverse of the peak temperature ($1/T_p$) at constant β and can be expressed as [30]:

$$E_a = -R \frac{d(\ln\beta)}{1.052 d\left(\frac{1}{T_p}\right)} \quad (7)$$

• Kissinger-Akhira-Sunose (KAS)

KAS method describes the activation energy at different conversion (α) values and can be defined as [31]:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \text{constant} - 1.0008 \times \left(\frac{E_a}{RT_\alpha}\right) \quad (8)$$

where T_α is the temperature at a fixed conversion (α). The value of activation energy can be calculated by plotting a graph between $\ln(\beta/T_\alpha^2)$ and $(1/T_\alpha)$.

For non-isothermal curing kinetics of epoxy resin, $f(\alpha)$ can be

assumed to be of the following form:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) (1-\alpha)^n \alpha^m \quad (9)$$

In Eq. (9), m and n stands for the two independent reaction orders.

Alternatively, the most reliable kinetic model proposed by Malek [32] suggested two functions $y(\alpha)$ and $z(\alpha)$, and their values can be derived using Eqs. (10) and (11) as:

$$y(\alpha) = \frac{d\alpha}{dt} \exp(x) \quad (10)$$

$$z(\alpha) = \pi(x) \frac{d\alpha T}{dt \beta} \quad (11)$$

where the function (x) is the reduced activation energy (E_a/RT) and $\pi(x)$ is the integral form of temperature which can be estimated using the 4th rational expression of Senum and Yang [33]:

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (12)$$

Taking characteristics of a kinetic model $y(\alpha)$ and $z(\alpha)$ functions were multiplied by a factor (a function, series or set of data) that makes the functions normalized within the interval [0,1]. $y(\alpha)$ and $z(\alpha)$ values can be calculated by substituting E_a , $d\alpha/dt$ and β . The kinetic parameter such as n , m and $\ln A$ can be calculated from

the graphs of normalized $y(\alpha)$ and $z(\alpha)$ as a function of degree of conversion. The two parameters α_M and α_p^∞ can be assigned to the maxima of the graphs $y(\alpha)$ and $z(\alpha)$, respectively. The mean value of α_M can be used to stimulate the kinetic parameters. Therefore the reaction order $P=m/n$ given by Malek can be replaced by:

$$P = m/n = \alpha_{Mm} / (1 - \alpha_{Mm}) \quad (13)$$

where α_{Mm} is the mean of α_M .

RESULTS AND DISCUSSION

1. DSC Analysis

The curing behavior of the epoxy adhesive samples at three different heating rates of 5, 10 and 15 °C/min are shown in the Fig. 1(a)-(c) and for comparison purpose the variation of heat flow vs temperature for all three epoxy adhesive system at a constant heating rate of 10 °C/min has also been represented in Fig. 1(d).

As shown in Fig. 1 there is only one exothermic peak for all the samples corresponding to the epoxy-amine curing reaction. Epoxy resins are high molecular weight polymers which normally contain at least two epoxide groups. During the epoxy-amine curing reaction, primary amine reacts with one of the epoxide group, leading to the generation of secondary amines. The secondary amine, which is now more sterically hindered than primary amine, can react with another epoxide group. Meanwhile, the hydroxyl groups generated

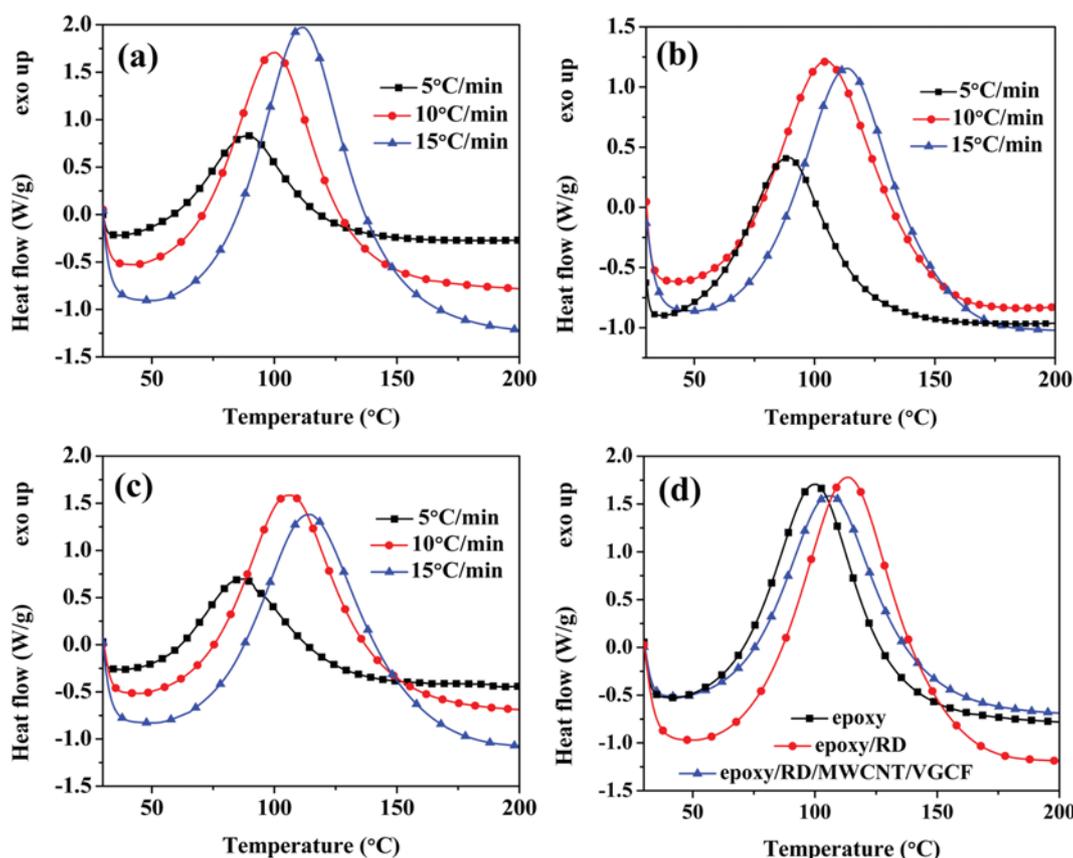


Fig. 1. Non-isothermal DSC thermograms for epoxy (a), epoxy/10% RD (b) and epoxy/10% RD/1% MWCNT/1% VGCF adhesive (c) at 5, 10 and 15 °C/min and comparison of all three epoxy adhesive systems at $\beta=10$ °C/min (d).

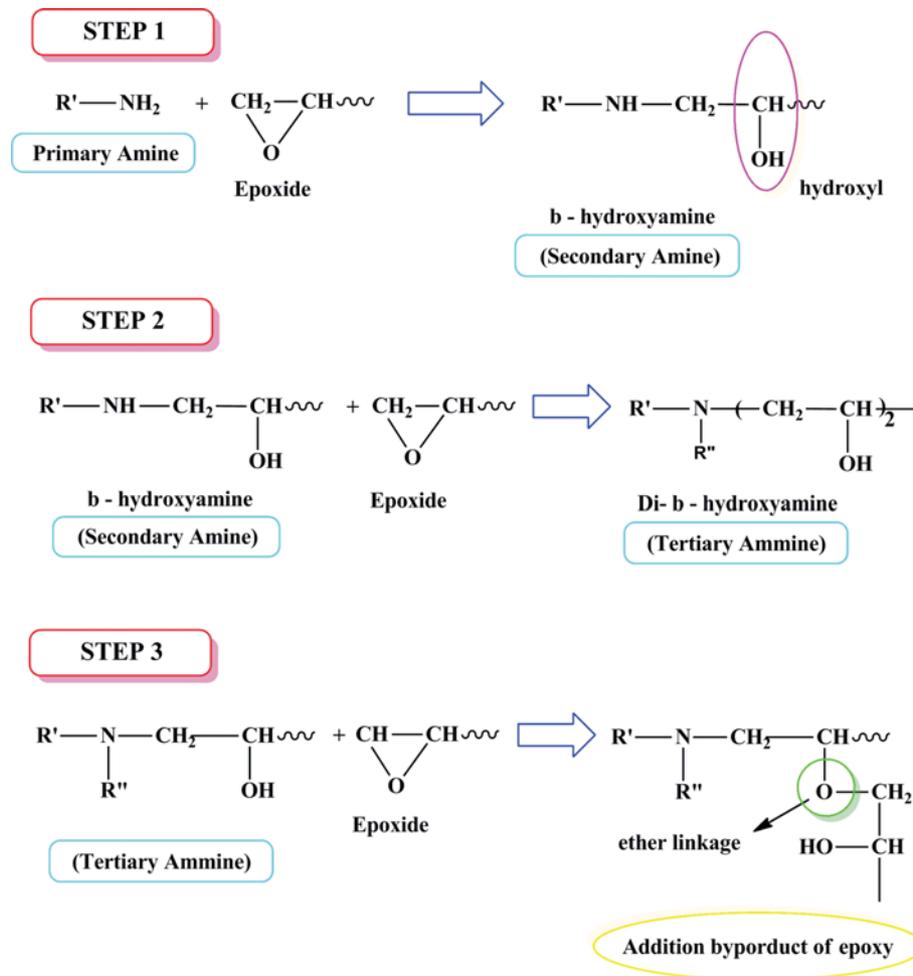


Fig. 2. Curing reaction mechanism involved between epoxy and amine curing agent.

by the reaction between the secondary amine and epoxide group will result in the formation of ether linkage. This reaction, generally termed as etherification, competes with the epoxy-amine curing reaction (Fig. 2, step 3). Etherification reaction might take place after depletion of amine hydrogens if epoxide groups are in excess. Fig. 2 illustrates the epoxy-amine curing mechanism.

Additionally, for the epoxy/10% RD/1% MWCNT/1%VGCF adhesive system the exothermic peak height decreases as compared with epoxy and epoxy/10% RD adhesive system. Maybe, this is sim-

ply because part of the mass is MWCNT/VGCF, so that the heat generated per unit mass of total sample will be less for these filled systems. The decreased peak height may also be attributed to the interaction between MWCNT and epoxy to a greater extent [16]. As a result, polymer chain mobility gets restricted due to physical hindrance caused by the MWCNTs. The effect of MWCNT and VGCF on the curing behavior of epoxy can be verified by determining specific parameters such as the onset temperature (T_{onset}), the peak temperature (T_p) and the total heat of reaction (ΔH_{cure}).

Table 3. Non-isothermal DSC data obtained at different heating rates, 5, 10 and 15 °C/min

Sample type	Heating rate β (°C/min)	T_{onset} (°C)	T_p (°C)	ΔH_{cure} (J/g)
Epoxy	5	56.6	89.63	515.7
	10	66.6	100.6	564
	15	76.9	112.0	542
Epoxy/10% RD	5	57.9	94.5	535.8
	10	66.9	106	597.4
	15	77.8	113.9	552.2
Epoxy/10%RD/1%MWCNT/1%VGCF	5	52.1	82.6	516
	10	70.6	106.8	579
	15	75.9	110	470

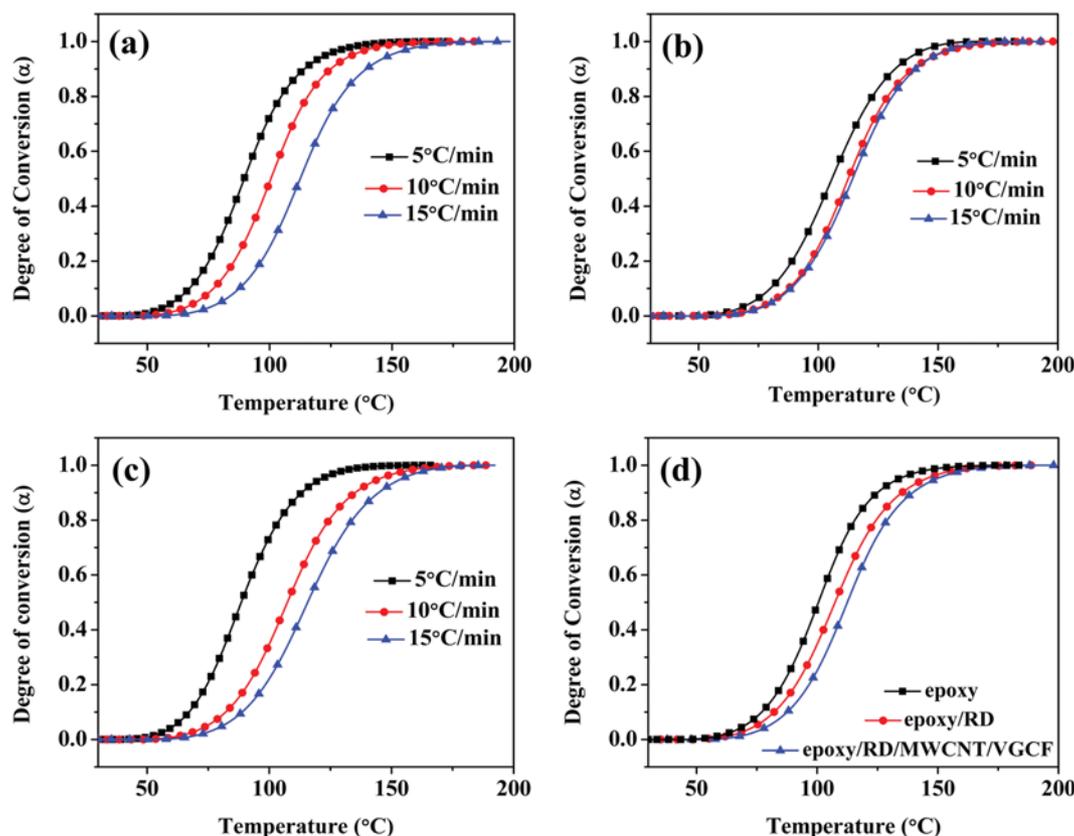


Fig. 3. Degree of conversion (α) as a function of temperature for epoxy (a), epoxy/10% RD (b) and epoxy/10% RD/1% MWCNT/1% VGCF (c) adhesives at 5, 10 and 15 $^{\circ}\text{C/min}$ and comparison of all three epoxy adhesive systems at $\beta=10^{\circ}\text{C/min}$ (d).

All the data calculated at different heating rates are summarized in Table 3.

From Table 3 it is clear that with increase in heating rate the exothermic peak shifts to higher temperature. Also, the T_{onset} , T_p and ΔH_{cure} of epoxy/10%RD adhesive system increased at all heating rates as compared to other adhesive systems. It is attributed to the fact that additional oxygen atom in the molecular structure of diluent might have contributed in retardation of the curing process [34]. Additionally, due to reduced viscosity there is a possibility for amine curing agent to make a better contact with epoxy resin. Consequently, the motion of the backbone chain was restricted in the highly cross-linked network of polymer molecules, which resulted in higher ΔH_{cure} value. Similar observation was reported by Vargas et al. [25].

Further, with the addition of MWCNT and VGCF to the modified epoxy resin, the T_{onset} and T_p of corresponding nanoadhesive considerably decreased at 5 and 15 $^{\circ}\text{C/min}$ except at the heating rate of 10 $^{\circ}\text{C/min}$. The heat of reaction (ΔH_{cure}) increased for both 5 and 10 $^{\circ}\text{C/min}$ heating rates. In the early stages of curing, MWCNT represented catalytic effect on the epoxy-amine curing reaction. This would be a direct result of the addition of VGCF, which improves the compatibility between the epoxy and MWCNT by higher degree of interaction leading to lesser free volume and hence increased viscosity [13].

2. Degree of Conversion (α) as a Function of Temperature

The curve of degree of conversion as a function of temperature

at different heating rates of epoxy, epoxy/10% RD and epoxy/10% RD/1% MWCNT/1% VGCF has been plotted and shown in Fig. 3.

In a non-isothermal cure the degree of cure increases as the temperature increases and it becomes significant in the case of all three epoxy adhesive system. It is also evident from Fig. 3(d) that the degree of conversion in the epoxy adhesive is higher compared to other two samples and it gradually increases and gets closer to each other at higher temperature. Also, the appearance of sigmoid or S-shaped curves in the conversion-temperature graph confirms that the reaction starts only after definite temperature is achieved. This type of behavior is usually observed in non-isothermal curing process and reported by other researchers also [23,35,36].

Comparing the curing behaviour of epoxy/10% RD and epoxy/10% RD/1% MWCNT/1% VGCF adhesive system, it is observed that the presence of both MWCNT and VGCF within the epoxy matrix resulted in lower degree of conversion. This behavior indicated that MWCNTs and VGCF have significant catalytic effect on the curing characteristics of epoxy. The catalytic effect may be attributed to the high specific surface area of both fillers and unique structural integrity in terms of steric hindrance, which is in accordance with the T_p value noted from heat flow curves.

The graph between degree of conversion (α) and rate of conversion ($d\alpha/dt$) for all three epoxy adhesive system at 10 $^{\circ}\text{C/min}$ is depicted in Fig. 4.

From the curve shown in Fig. 4, the maximum conversion rate appears at a conversion value of $\alpha=0.5$. This behavior indicates

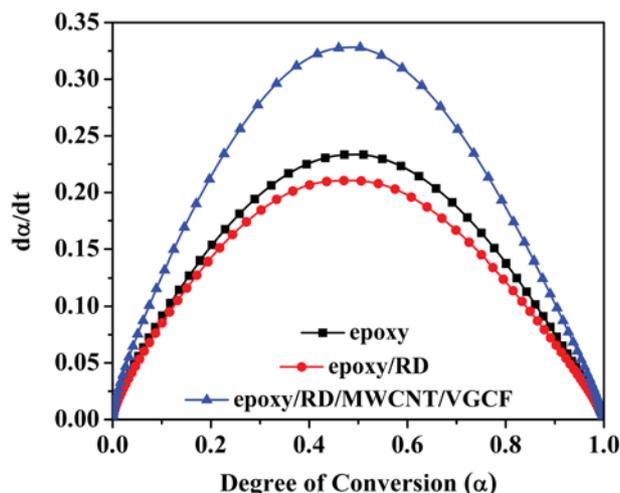


Fig. 4. Variation of degree of conversion (α) and rate of conversion ($d\alpha/dt$) for all three epoxy adhesive systems at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$.

that primary reaction mechanisms are not dependent on the heating rates. Moreover, the maximum conversion rate is in advance for the nanoadhesives filled with MWCNTs and VGCFs. The curing mechanism behind this observation can be related to the molecular motions and interactions of filler particles in a polymer network. The presence of hydroxyl groups on the surface of fillers has a catalytic effect on epoxy ring-opening reactions and evidently the source of the modified cure kinetics. However, the low conversion rate of epoxy/RD system is caused by the retarding effect of diluent on the cross-linking process. Fig. 4 also shows $(d\alpha/dt)=0$ at initial and final stages of curing. Similar results have been observed by

Natrajan et al. [10]. These observations indicate that a study on the cure behavior of epoxy-amine systems might help elucidate the complex interactions between filler and resin matrix, and control over curing reaction could lead to the development of smart materials and structures.

3. Determination of Activation Energy (E_a)

The activation energy (E_a) for the curing behavior of epoxy adhesive system was calculated by employing non-isothermal methods, Kissinger and Flynn-Wall-Ozawa, with the T_p value determined from the maxima of the heat flow curves.

In Fig. 5(a) the plot of $\ln(\beta/T_p^2)$ against $(1/T_p)$ gives a straight line. The E_a was calculated from the slope of the straight line and was found to be 45, 60 and 39 kJ/mol for epoxy, epoxy/10% RD and epoxy/10% RD/1% MWCNT/1% VGCF adhesive system, respectively. Table 4 shows the important parameters derived by Kissinger method.

The calculated E_a value increased when RD was added in the unmodified epoxy adhesive system. This was mainly attributed to the decreased viscosity due to the addition of diluent. The long aliphatic chain of diluents decreased the curing reaction rate by lowering the reacting unit concentration. Also, in the later stages of curing, the density of covalent bond that links two adjacent chains of epoxy increased and the diluents molecules protruded outside as separated domains in the epoxy matrix. These protruded diluent domains hindered the curing reaction, as a result of which E_a of the whole system increased [37,38]. On the other hand, in case of epoxy/10%RD/1%MWCNT/1%VGCF based adhesive system, the presence of MWCNT acted as a catalyst when added into the epoxy resin, which thereby lowered the E_a of the matrix polymer. This finding clearly contradicts the results obtained by Rosu [27] and Vertuccio et al. [39]. The authors indicated that the diluent

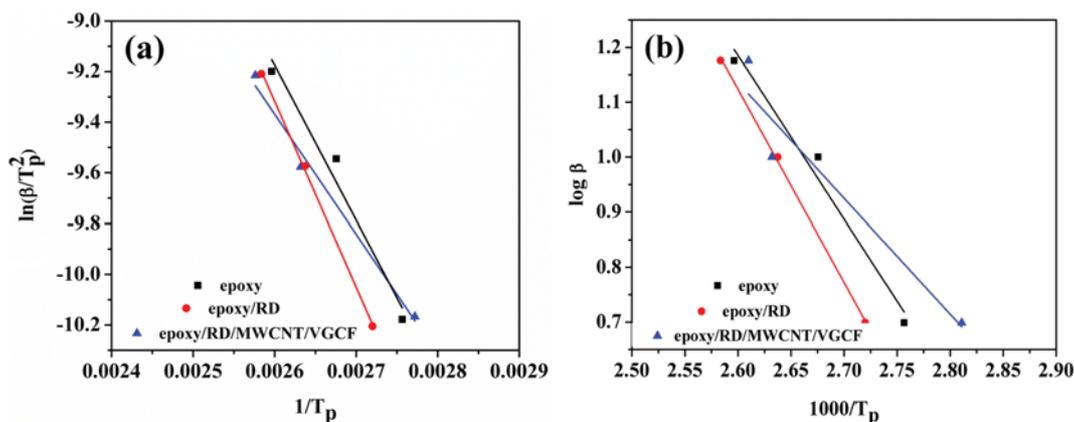


Fig. 5. Determination of activation energy using Kissinger (a) and Flynn-Wall-Ozawa (b) method.

Table 4. Values of activation energy obtained using Kissinger method

Sample type	T_p (in $^{\circ}\text{C}$)			$\left(-\frac{E_a}{RT}\right)$	E_a (kJ/mol)	R^2
	5	10	15			
Epoxy	89.63	100.6	112.0	5445	45	0.996
Epoxy/10% RD	94.5	106	113.9	7333	60	0.997
Epoxy/10%RD/1%MWCNT/1%VGCF	82.6	106.8	110	4738	39	0.998

decreases particularly the E_a of epoxy-amine curing reaction. The decrease in the E_a can be related to the more comprehensive cure to the decrease of viscosity obtained by using long aliphatic chains of epoxy as reactive diluent. The moderate viscosity increases the mobility of the segmental chains. This results in a small energy barrier on the long-range segmental relaxation corresponding to the motion of entire chains, resulting in decrease of E_a .

However, an increase in the E_a obtained in this work can be considered as a part of the effect of the cure schedule, resin-to-hardener combination and resin-to-hardener ratio on curing process. In the case of epoxy/RD, the resin-to-hardener ratio may affect both processing and curing behavior due to the effect of interphase properties on the epoxy-amine cure characteristics. The decrease in the resin-to-hardener ratio is a possible route to increase resin viscosity. Also, the introduction of aliphatic chains in the structure of the epoxy has not been compensated with an amount of hardener. Consequently, there are fewer activated molecules to begin the cure reaction. It would result in a shifting of the peak to higher

temperatures and becomes evident by the maximum temperature, T_p at different heating rates. It is therefore necessary to reach a higher temperature to activate the reaction, yielding higher activation energy. The results were interpreted in a manner similar to that described by Nunez-Regueira et al. [40]. The authors have reported an increase in E_a with an addition of higher wt% of RD into the epoxy/amine system.

The E_a for curing of epoxy adhesive system was also determined using the Flynn-Wall-Ozawa (FWO) method. In this method, the graph is plotted between $\log\beta$ as a function of $(1/T_p)$ at three different heating rates. The E_a was calculated from the slope of the straight line and was found to be 54, 63 and 43 kJ/mol. Table 5 summarizes the important findings obtained from FWO method.

From the results obtained, it can be concluded that the E_a shows marginal increased value in Flynn-Wall-Ozawa method. Since this method is derived from integral non-isothermal method and the integral method which yields lower deviation, this method provides a better fit of the data with the linear correlation coefficient

Table 5. Values of E_a obtained using Flynn-Wall-Ozawa method

Sample type	T_p (in °C)			$\left(-\frac{E_a}{RT}\right)$	E_a (kJ/mol)	R^2
	5	10	15			
Epoxy	89.63	100.6	112.0	-6868	54	0.997
Epoxy/10% RD	94.5	106	113.9	-8087	63	0.999
Epoxy/10%RD/1%MWCNT/1%VGCF	82.6	106.8	110	-5485	43	0.998

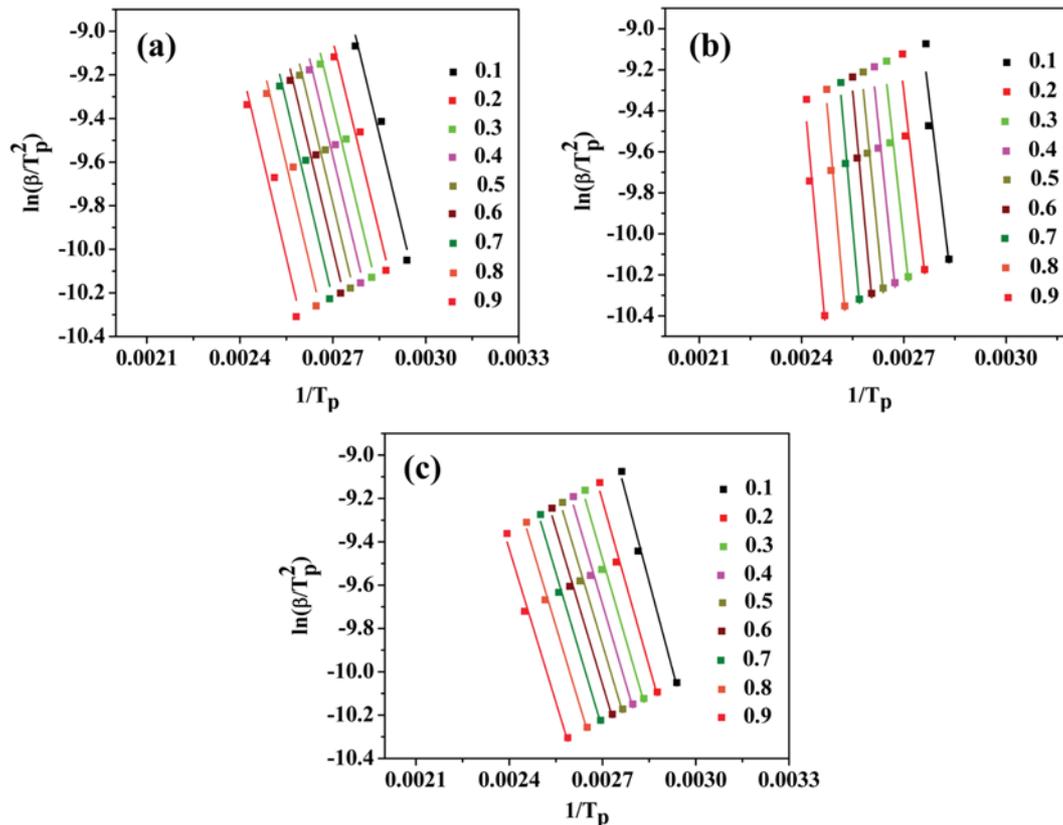


Fig. 6. Plot of E_a as a function of degree of conversion (α) for epoxy, epoxy/10% RD and epoxy/10% RD/1% MWCNT/1% VGCF adhesive systems.

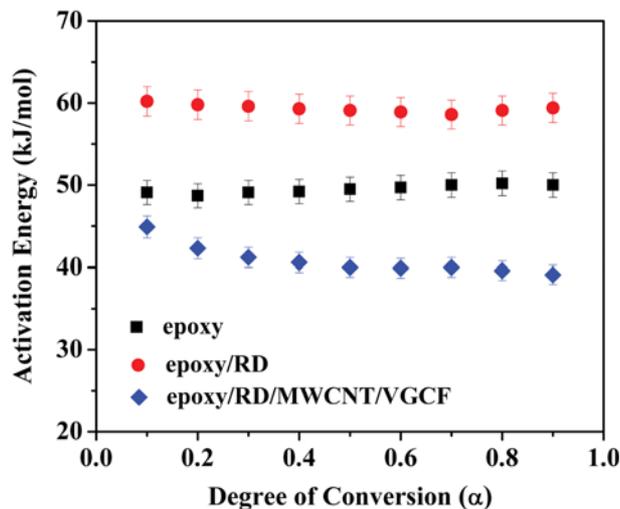


Fig. 7. Determination of activation energy (E_a) for epoxy adhesive systems at each degree of conversion (α).

(R^2) > 0.99 [25].

4. The Relationship between E_a and Degree of Conversion (α)

The variation of E_a at various relative degree of conversion (α) was obtained by applying Kissinger-Akhira-Sunose (KAS) method using Eq. (8). The E_a was calculated from the slope of an approximately linear relationship between $\ln(\beta T_c^2)$ and $(1/T_c)$ which has been presented in Fig. 6. The results obtained from Fig. 6 are used to plot Fig. 7; notice that the information about the E_a is much clearer in Fig. 7.

Fig. 7 shows the variation of E_a as a function of degree of conversion (α) for epoxy, epoxy/10% RD and epoxy/10% RD/1% MWCNT/1% VGCF adhesive system. In the graph, the value of E_a remained constant in the conversion range $0.2 < \alpha < 0.6$ beyond which there was a slight tendency to change.

For an epoxy/RD adhesive system, variation of the effective E_a in the early stages of curing process was attributed to decrease of viscosity and the effect of temperature on viscosity. It can be speculated that the interfacial adhesion and degree of dispersion dominated the viscosity of the system and were higher in case of epoxy/RD as compared to epoxy. Providing justification of the viscosity effects on the reaction mechanism stemmed solely from the outcome of literature report [41]. The higher E_a indicates the lower reactivity of the epoxy/RD system. For epoxy/10% RD adhesive system the E_a attained higher value in initial stages of conversion $\alpha = 0.1$, and thereafter it remained constant within the conversion range of $0.2 < \alpha < 0.6$. This suggests that the reaction mechanism in the case of epoxy/RD is most likely affected by chemical compositions and structures, since physically dominated processes like molecular diffusion of reactants and decrease in mobility of the reactive groups is not observed for the degree of conversion of epoxy groups. Such difference is understandable, as mentioned in the literature [42]. Beyond $\alpha = 0.4$ the E_a value decreased followed by a gradual increase up to $\alpha = 0.9$. It is believed that in initial stages of curing, the reaction between primary amine and epoxy is prominent and secondary amine does not take part in the curing process at this stage. As a result the E_a remains constant up to

$\alpha = 0.9$ because of single step primary amine reaction. After that the hydroxyl groups generated due to reaction between epoxy and primary amine support the ring opening reaction. Thus the E_a value decreases, whereas, etherification is expected to take place in the later stages of curing. As a result, there is an increase in the cross link density that restricts the polymer chain mobility and makes it relatively difficult for reactive species to react.

In case of epoxy/10% RD/1% MWCNT/1% VGCF adhesive system, the E_a was found to be much lower than epoxy and epoxy/10% RD adhesive system at each fraction of conversion. In initial stages of curing, E_a value increased due to increase in viscosity. It has also become evident that the acceleration effect of MWCNTs on the E_a of epoxy cure reaction is more noticeable in the initial stages of curing or in lower temperature regions. The acceleration effect of MWCNTs on the epoxy curing reaction was also reported by Puglia [18] and Xie et al. [43] in the cure kinetics study of CNT/epoxy nanocomposites. Test results indicated that addition of MWCNT reduced the E_a and claimed an acceleration effect. Moreover, the presence of hydroxyl groups on the surface of MWCNTs is the source of the modified epoxy ring opening reactions.

The addition of MWCNT and VGCF blocks the reactivity of amine group to attacks the epoxide groups in epoxy resin; as a result, E_a remains constant within the range ($\alpha = 0.4-0.7$). However, in later stages of curing the E_a showed a drastic drop, which can be explained due to catalyzing effect of hydroxyl groups present in VGCF, which forms H-bonding with the matrix. Comparable results have been obtained by Wu et al. [20]. The authors have reported that the presence of VGCF accelerates the curing process by decreasing the maximum peak temperature. This is similar in the results reported in Table 3 where a significant decrease in peak temperature has been noticed with an addition of VGCF filler. The authors have also reported that VGCF accelerates the curing process by increasing the specific surface area, but it has a negligible effect on ΔH_{cure} which was substantiated in our experimental findings. The acceleration effect of carbon fibers has also been reported by Xie et al. [19] while the decrease of the E_a with an addition of fiber content were taken as the proof of the acceleration in the early stage of the curing process.

5. Reaction Kinetics

The calculated E_a values obtained from Kissinger and Flynn-Wall-Ozawa were used to estimate the kinetic model given by Malek using Eqs. (10) and (11), respectively. The variation in $y(\alpha)$ and $z(\alpha)$ as a function of degree of conversion was studied and is shown in Figs. 8 and 9. $y(\alpha)$ and $z(\alpha)$ functions are normalized within the interval [0, 1] for all epoxy adhesive systems. $y(\alpha)$ exhibits maximum at α_M and $z(\alpha)$ exhibits maxima at α_p^∞ and their values have been summarized in Table 6 at all heating rates.

The maxima of $y(\alpha)$ and $z(\alpha)$ fall within the range $0.15 < \alpha_M < 0.28$, $0.49 < \alpha_p^\infty < 0.52$ and $\alpha_p^\infty \neq 0.632$. The results are in good agreement with those in other studies, and $\alpha_p^\infty < 0.632$ indicated that the two parameter Sestak-Berggren autocatalytic model was found to be most adequate in describing the curing kinetics of epoxy resin. A few authors also reported that $y(\alpha)$ strongly affects the autocatalytic property of the reaction, $\alpha_M < 0$ indicates less autocatalytic tendency, while $\alpha_M > 0$ indicates more autocatalytic tendency of the

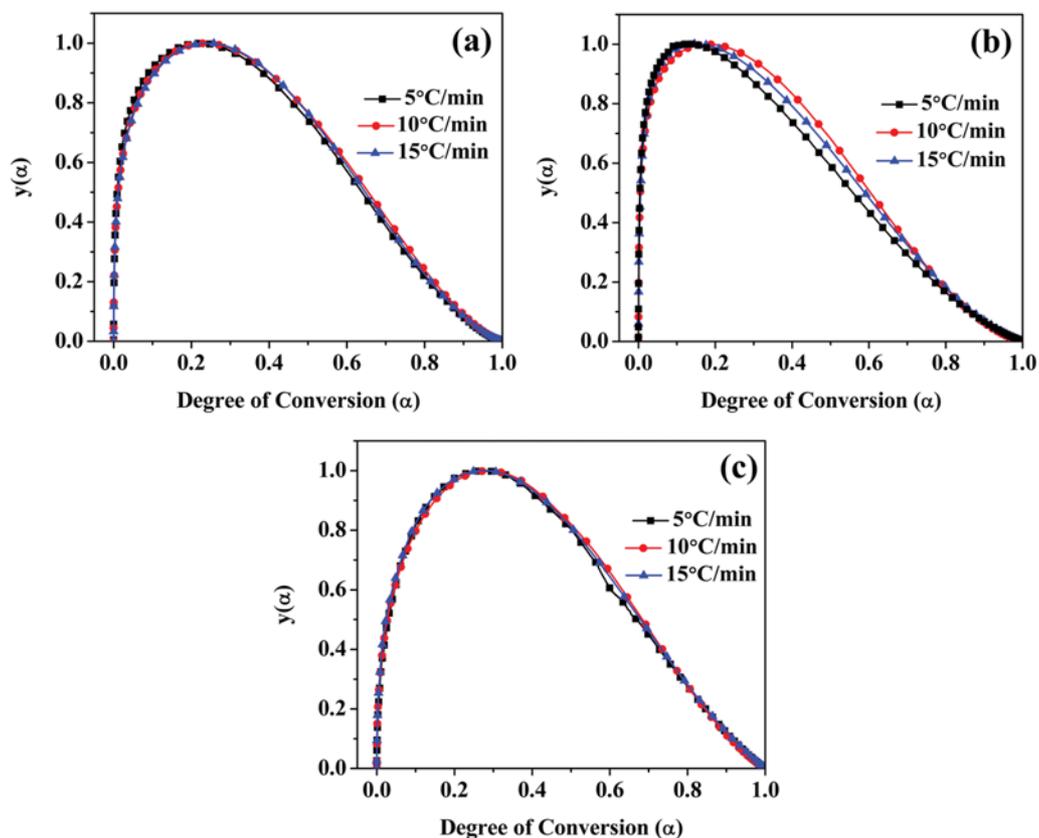


Fig. 8. Curve of normalization $y(\alpha)$ as a function of degree of conversion for epoxy adhesive system.

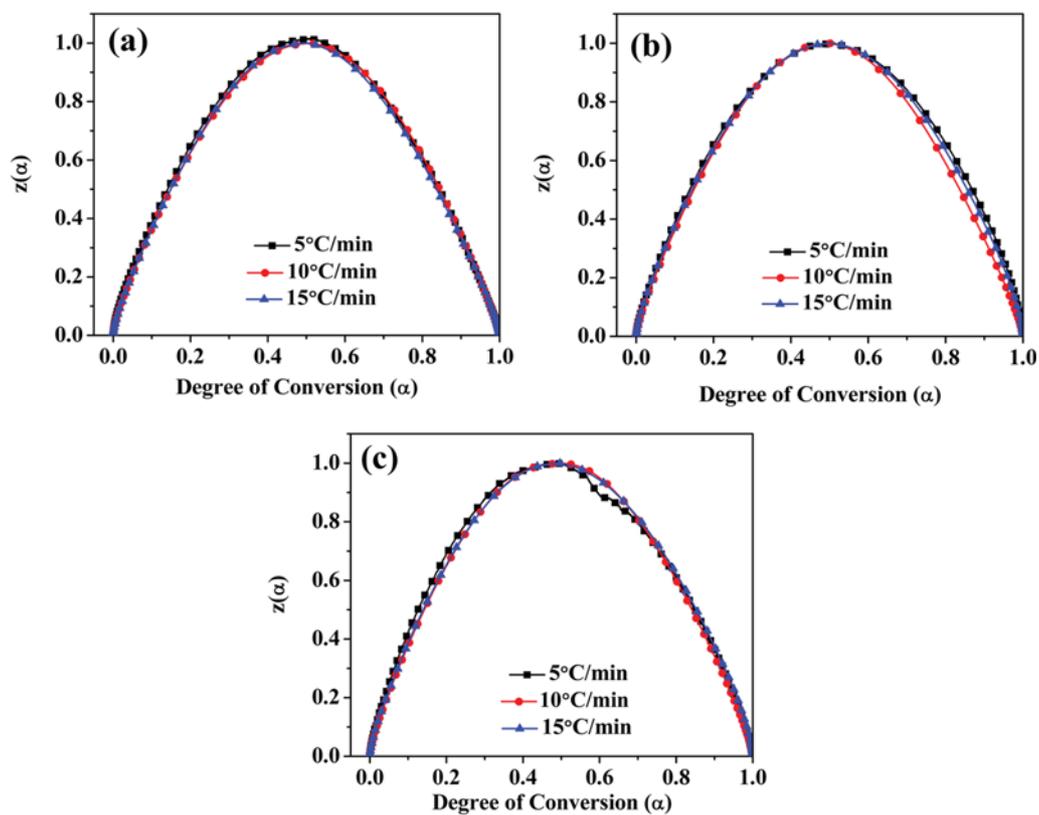


Fig. 9. Curve of normalization $z(\alpha)$ as a function of degree of conversion for epoxy adhesive system.

Table 6. Characteristics peak conversion α_M and α_p^∞

Sample	Heating rate (β) ($^{\circ}\text{C}/\text{min}$)	α_M	α_p^∞
Epoxy	5	0.22	0.51
	10	0.23	0.52
	15	0.24	0.50
	Mean	0.23	0.51
	S.D.	0.01	0.01
Epoxy/10% RD	5	0.16	0.50
	10	0.17	0.51
	15	0.15	0.52
	Mean	0.16	0.51
	S.D.	0.01	0.01
Epoxy/10%RD/1%MWCNT/1%VGCF	5	0.27	0.49
	10	0.28	0.49
	15	0.28	0.50
	Mean	0.28	0.49
	S.D.	0.005	0.005

*S.D.=standard deviation

Table 7. Estimation of the thermokinetic parameters for Sestak-Berggren model

Sample type	β ($^{\circ}\text{C}/\text{min}$)	p	m	n	lnA
Epoxy	5	0.28	0.24	0.85	13.30
	10	0.30	0.26	0.86	13.55
	15	0.32	0.28	0.86	13.50
	Mean	0.3	0.26	0.86	13.45
	S.D.	0.02	0.02	0.01	0.13
Epoxy/ 10% RD	5	0.19	0.16	0.86	15.77
	10	0.20	0.17	0.83	15.16
	15	0.18	0.17	0.92	16.73
	Mean	0.19	0.17	0.87	15.89
	S.D.	0.01	0.01	0.05	0.8
Epoxy/10%RD/1%MWCNT/1%VGCF	5	0.37	0.33	0.90	10.55
	10	0.39	0.36	0.93	10.78
	15	0.39	0.39	0.99	11.49
	Mean	0.38	0.36	0.94	10.94
	S.D.	0.01	0.03	0.05	0.5

*S.D.=standard deviation

reaction [25].

The two-parameter autocatalytic Sestak-Berggren model was determined to be the most adequate one to describe the cure kinetics of the studied system at various heating rates. From Eq. (9), the ratio of m to n i.e. ($P=m/n$) is transformed into $P=(\alpha_M/1-\alpha_M)$. Thus Eq. (9) can be transformed into following form: [25,35]

$$\ln\left[\left(\frac{d\alpha}{dt}\right)\exp\left(\frac{E_a}{RT}\right)\right] = \ln A + n \ln\left[\alpha^{\frac{\alpha_M}{1-\alpha_M}}(1-\alpha)\right] \quad (14)$$

The kinetic parameters n, m and lnA can be calculated from the slope and intercept of an approximately linear relationship between $\ln[(d\alpha/dt)\exp(E_a/RT)]$ and $\ln[\alpha^{(\alpha_M/1-\alpha_M)}(1-\alpha)]$. All the data shows good linearity. The kinetic parameters n, m and lnA were calculated at different heating rates and their average values have been

Table 8. Explicit rate equations for epoxy adhesive systems derived with Sestak-Berggren autocatalytic model

System type	Reaction rate equation
Epoxy	$\frac{d\alpha}{dt} = 7 \times 10^5 \left(\frac{-51000}{RT}\right) \alpha^{0.86} (1-\alpha)^{0.26}$
Epoxy/RD	$\frac{d\alpha}{dt} = 8 \times 10^6 \left(\frac{-60000}{RT}\right) \alpha^{0.87} (1-\alpha)^{0.17}$
Epoxy/RD/MWCNT/VGCF	$\frac{d\alpha}{dt} = 5.6 \times 10^4 \left(\frac{-39000}{RT}\right) \alpha^{0.94} (1-\alpha)^{0.36}$

summarized in Table 7. The average of n, m and lnA along with E_a was used to determine the explicit rate equation for epoxy ad-

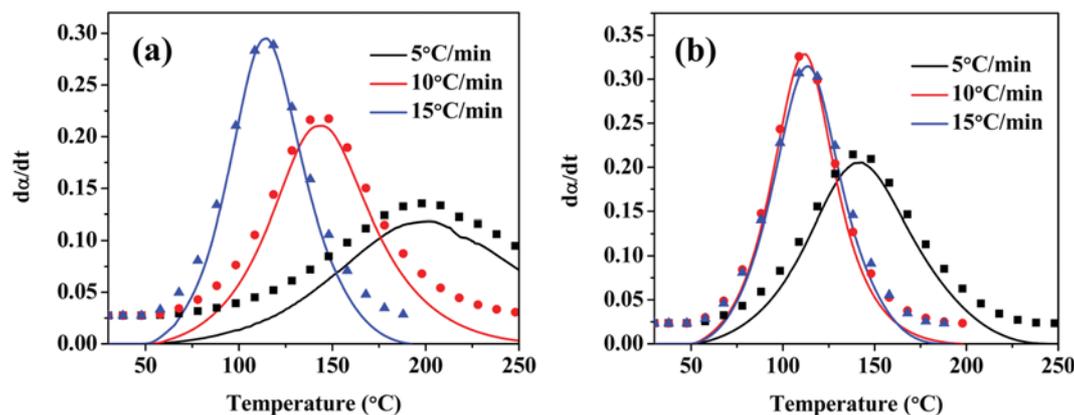


Fig. 10. Comparison of calculated (symbol) rate curves with experimental data (line) for epoxy/10%RD (a) and epoxy/10%RD/1%MWCNT/1%VGCF (b) adhesive system.

hesive systems with the help of Sestak-Berggren model and shown in the Table 8.

For validation of the reaction rate equations, calculated rate curves were compared with the experimental data and shown in Fig. 10.

The predicted rate curves were fitted to experimental curves by plotting $d\alpha/dt$ and temperature. The calculated rate curves are in good agreement with the experimental rate curves, with only a slight marginal observed. Thus Sestak-Berggren autocatalytic model should be considered to study the curing behaviour and reaction kinetics of studied epoxy adhesive systems.

CONCLUSIONS

The curing kinetic analysis of an epoxy adhesive system was carried out using non-isothermal DSC techniques. Test results showed that the epoxy-amine cure reaction strongly depends on the temperature and the reaction rate. The peak temperature in non-isothermal DSC thermograms of all the three epoxy adhesive systems shifted towards higher temperature from 30 to 200 °C. The change in the heat of reaction of epoxy nanoadhesives reinforced with MWCNTs and VGCFs decreased by 17.5% with a heating rate of 15 °C/min. This suggests that both types of nanoparticles act as a catalyst in the amine cured epoxy/RD system. The limited movement of small sections of the main polymer chains backbone and/or accumulation of reactants were the main reasons for the alteration of the epoxy-amine cure mechanism.

The curing kinetic parameters and the curing behaviour of all the three epoxy adhesive system were studied using Kissinger and Flynn-Wall-Ozawa methods. These methods were able to calculate the activation energy at different degrees of conversion, which became significant for better understanding of the curing behaviour of epoxy adhesive system. The addition of RD content in the epoxy matrix resulted in significant improvements in the E_a attributed to the reduced viscosity and increase in the number of reactive epoxy groups. The presence of aliphatic groups of diluent in epoxy resin system significantly reduced the reactivity of the cured epoxy system. During epoxy-amine cure process, higher E_a was obtained for the lower reactivity system. It revealed that the presence of

nano-fillers lowered the E_a significantly, thereby resulting in increasing the reactivity of the whole epoxy adhesive system. Malek model was used to calculate the kinetic parameters. The two parameter autocatalytic Sestak-Berggren model was used to analyze the curing behavior of the epoxy adhesive system. The calculated kinetic parameter data by Sestak-Berggren model was found to be in good agreement with the experimental data curves for epoxy adhesive system.

ACKNOWLEDGEMENTS

The authors would like to thank the Board of Research in Nuclear Sciences (BRNS), Department of Atomic Energy (DAE), Government of India for the financial support, sanctioned under the project no. 39/11/2015-BRNS.

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