

Thermal Stability and Kinetics Analysis of Epoxy Composites Modified with Reactive Polyol Diluent and Multiwalled Carbon Nanotubes

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ABSTRACT: The effect of polyether polyol and amino-functionalized multiwalled carbon nanotubes (NH₂-MWCNTs) on the thermal stability of three-phase (epoxy/polyol/NH₂-MWCNTs) epoxy composites was investigated. Thermal stability and degradation characteristics of polyol/MWCNTs modified epoxy composites was evaluated using thermogravimetric analysis. The kinetics of thermal degradation was assessed from data scanned at 5, 10, and 20°C/min. Activation energy for degradation of epoxy nanocomposites was calculated using different differential and integral methods, that is, Kissinger's, Flynn–Wall–Ozawa, Coats–Redfern, and Horowitz–Metzger methods. In addition, the integral procedure decomposition temperature was determined to evaluate the inherent thermal stability of the modified composite system. Rate of thermal degradation in MWCNT/Polyol samples was found to be reduced significantly while activation energy of degradation was increased compared to unmodified epoxy composite. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41558.

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INTRODUCTION

Epoxy resins are frequently used in structural and high performance composite applications because of their unique combination of properties unattainable by other thermoset resins. Epoxy resins exhibit superior adhesive properties, high mechanical properties, better resistance to fatigue and micro cracking, and less degradation from water ingress.¹ The highly reactive epoxide group present in epoxy molecules reacts with various substances to form a crosslinking structures resulting in excellent stiffness, strength and thermomechanical properties with low toughness. Three-dimensional crosslinked structures formed in cured epoxies dictate the mechanical, physical, and thermal properties of the epoxy composites.² However, the mechanical and thermal properties of a cured epoxy resin also depend largely on its constituent materials. Inherent brittleness can be overcome by using various plasticizing modifiers but at a cost of lowered strength, stiffness and glass transition temperature. Because of their excellent elasticity and significant impact strength, a number of polyol-based reactive diluents have been

considered to be a convenient option to increase the resistance to brittle fracture behavior of epoxy resins.^{3,4} In addition to the toughness effect on the epoxy system, lower viscosity, and extended pot life increase the resin wetting action and the amount of filler loading when used for the fabrication of fiber reinforced laminated composites.

In our earlier study, it was found that while an increase in toughness can be achieved by adding polyether polyol in the epoxy system, a reduction in flexural strength and stiffness occurs.⁵ Besides, the inclusion of the polyol in epoxy resin system resulted in a more flexible system with a corresponding decrease in the thermomechanical properties.⁶ The reduction in properties of toughened epoxy blends can be countered by incorporation of nanoparticles as reinforcing materials. Addition of uniformly dispersed 0.3 wt % loading of amino-functionalized multiwalled carbon nanotubes (NH₂-MWCNTs) in polyol toughened epoxy was found to have a synergistic effect on various mechanical and thermomechanical properties of epoxy composites.^{5,6} The improved crosslink interactions among

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NH₂-MWCNTs, epoxy-terminated polyol and epoxy resin were considered to be the reason for increase in thermomechanical properties.

Nanoparticles, at lower loading, usually increase the thermal stability of epoxy composites.⁷ Compared to untreated carbon nanotubes, modified MWCNTs have tendency to increase the thermal degradation properties of composites much better.⁸ Amino-functionalized MWCNTs dispersed in epoxy resin increase decomposition temperature indicating improvement of thermal stability.⁹ Amine-modified MWCNTs having a stronger affinity toward the polymer matrix compared to unmodified MWCNTs, restrict the motion of the macromolecules, resulting in stabilization of the nanocomposites.¹⁰ TGA analysis by Kuan et al.¹¹ indicated improvement in the thermal stability of Epoxy/MWCNTs nanocomposites. They have also calculated the integral procedure decomposition temperature (IPDT) proposed by Doyle and showed that the thermal stability of the Epoxy/MWCNTs nanocomposites exceeded that of control system.

The addition of polyol was found to influence the rigidity and decomposition characteristics of polymeric compounds.¹² Among the various kinds of polyols, polyether polyols are most dominant form of polyols used currently although, polyester polyols were used initially.¹³ The high molecular mass of polyether polyol attains the same or better thermal stability than polyester polyol.¹⁴ Till now, no studies have been conducted to investigate the thermal degradation characteristics of polyether polyol modified epoxy compounds. Sekkar et al.¹⁵ found that the kinetic parameters of polyol based compounds strongly depend on the evaluation method. As a result, several evaluation techniques should be applied for better understanding of the thermal kinetic properties of polyol modified epoxy composites.

This study investigates the thermal stability and degradation characteristics of a three-phase (NH₂-MWCNT/polyol/epoxy) system through thermogravimetric analysis (TGA). All results are compared with those of a control epoxy composite containing no MWCNTs and polyether polyol. Although incorporation of polyether polyol increases toughness of epoxy composites, reduction in strength and thermo mechanical properties occurs due to reduced crosslinking density.⁵ On the other hand, MWCNT modified epoxy system has higher strength but lower toughness compared to control system. However, it was observed that polyether polyol and NH₂-MWCNT have a synergistic effect on the mechanical and thermomechanical properties of epoxy composites^{5,6} and provide a good combination of various properties. As three-phase NH₂-MWCNT/polyol/epoxy system was established to be the superior system compared to epoxy systems containing only polyol or MWCNTs, these two systems were not analyzed in this study.

The kinetics of thermal degradation was evaluated and activation energy for degradation of modified sample is calculated using different differential and integral methods, that is, Kissinger's Method, Flynn-Wall-Ozawa method, Coats and Redfern method and Horowitz-Metzger method. Activation energy E_a is a key parameter because it represents the potential barrier for thermal degradation. In addition, the IPDT has been deter-

mined for estimating the inherent thermal stability of the modified composite system.

THEORETICAL CONSIDERATIONS

Integral Procedure Decomposition Temperature

Thermal stability is usually expressed in terms of initial degradation and decomposition temperatures. However, these temperatures are highly dependent on several powerful influential procedural details including the size and fineness of the samples, size, and shape of the container, type and flow rate of the gas used and the rate of heating.¹⁶ Consequently, these temperatures cannot be taken as definitive. Doyle¹⁶ proposed an IPDT which can be used for estimating the inherent thermal stability of polymeric materials. IPDT was developed to correlate the volatile parts of the polymeric compounds.¹⁷ IPDT is calculated using,

$$\text{IPDT } (^{\circ}\text{C}) = A * K * (T_f - T_i) + T_i \quad (1)$$

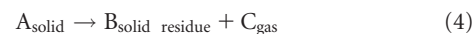
Here, T_i is the initial experimental temperature and T_f is the final experimental temperature. A^* and K^* are the ratios of area under experimental curve defined by the total TGA thermogram. A representation of S_1 , S_2 , and S_3 for calculating A^* and K^* was described by Chiang et al.¹⁷

$$A^* = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \quad (2)$$

$$K^* = \frac{S_1 + S_2}{S_1} \quad (3)$$

Thermal Kinetic Analysis

Generally, decomposition of solid polymer is associated with the following reactions:



In TGA, degree of decomposition or conversion is the ratio of loss of weight at time t to total loss of weight at complete decomposition temperature.

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (5)$$

Where m_0 , m_t , and m_f are the initial weight, residual weight at the temperature t and final weight of the sample, respectively, and α is the degree of decomposition. The rate of decomposition ($\frac{d\alpha}{dt}$) depends on weight of sample and temperature.

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (6)$$

Where, k is the rate constant and $f(\alpha)$ the conversion functional relationship. This equation is the basis of all thermal kinetic analyses.¹⁸ $f(\alpha)$ is a function of conversion that is proportional to the concentration of nondegraded material:

$$f(\alpha) = (1 - \alpha)^n \quad (7)$$

Here, n is the order of decomposition reaction. The temperature dependence of the rate constant, k may be described by the Arrhenius expression:

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (8)$$

Where, E is the activation energy, A is the preexponential factor, R is the gas constant, and T is the absolute temperature.

Combining eqs. (4–6), the overall rate of loss of active material is given by eq. (7):

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

If the temperature of the sample is changed by a controlled and constant heating rate, $\beta = \frac{dT}{dt}$, variation in the degree of decomposition can be analyzed as a function of temperature. Therefore, the rearrangement of eq. (7) gives

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) \cdot (1-\alpha)^n \quad (10)$$

Integration of eq. (8) from an initial temperature T_0 , corresponding to a degree of conversion, $\alpha = 0$, to the peak temperature T , where degree of conversion = α , is generally expressed as,

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT \quad (11)$$

Several techniques have been developed for solving the integration of eq. (9). The methods used for solving this equation can be classified into those based on data acquired for one or multiple heating rates. Both types of methods may be further classified as differential and integral methods.¹⁹ Among the methods used in this study, Kissinger method is differential method and, Flynn–Wall–Ozawa, Coats–Redfern, and Horowitz–Metzger methods are Integral methods.

Methods Based on Multiple Heating Rates. Kissinger method (differential method). Kissinger's method is based on the variation of the heating rate, β and is the most powerful differential method for thermal kinetic analysis which. Kissinger method assumes that reaction occurring in a Thermal Analysis corresponds to a peak.²⁰ The temperature at the peak of the first derivative weight loss curves is the maximum temperature (T_{\max}) which is obtained at different heating rates.²¹

When $\frac{E}{RT} \gg 1$, eq. (9) becomes,

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT \cong \left(\frac{ART_{\max}^2}{\beta E}\right) \exp\left(\frac{-E}{RT}\right) \quad (12)$$

Differentiating both sides and then taking natural logarithm, Kissinger developed the following equation,

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \left\{ \ln \frac{AR}{E} + \ln[n(1-\alpha_{\max})^{n-1}] \right\} - \frac{E}{RT_{\max}} \quad (13)$$

Taking into account the Kissinger's approximation which states that

$$f'(\alpha_{\max}) = n(1-\alpha_{\max})^{n-1} \cong \text{const.} \quad (14)$$

The activation energy E can be determined from the slope of straight line plot of $\ln(\beta/T_{\max}^2)$ against $1/T_{\max}$.

Flynn–Wall–Ozawa method (integral methods). Flynn–Wall–Ozawa method calculates activation energy at different weight conversion based on weight loss versus temperature data obtained at different heating rates.²² This method is based on Doyle's approximation.²³ The value of the right side of eq. (9)

is expressed and tabulated by Doyle's as the following function, p :

$$\int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT = \frac{E}{R} P\left(\frac{-E}{RT}\right) \quad (15)$$

The eq. (9) becomes,

$$g(\alpha) = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT = \frac{AE}{\beta R} P\left(\frac{-E}{RT}\right) \quad (16)$$

Using Doyle's approximation, if $20 < \frac{E}{RT} < 60$, the integral $P\left(\frac{-E}{RT}\right)$ can be expressed as:

$$\log P\left(\frac{-E}{RT}\right) \approx -2.315 - 0.4567\left(\frac{-E}{RT}\right) \quad (17)$$

Taking logarithm on both sides of eq. (10),

$$\begin{aligned} \log \beta &= \log \frac{AE}{g(\alpha)R} + \log P\left(\frac{-E}{RT}\right) \\ &= \log \frac{AE}{g(\alpha)R} - 2.315 - 0.4567\left(\frac{E}{RT}\right) \end{aligned} \quad (18)$$

This method assumes that A and E are independent of α and T . The activation energy can be calculated from the slope of straight line plot of $\log \beta$ versus $1/T$ for a constant α without any knowledge of reaction order.

Methods Based on Single Heating Rate. Coats and Redfern method. Coats and Redfern method²⁴ provides an alternative kinetic analysis in solid state processes that uses an asymptotic approximation for the solution of eq. (9) at different conversion values. Using integration by parts, the right side of eq. (9) can be expressed as:

$$g(\alpha) = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT = \frac{ART^2}{\beta E} \times \left(\frac{-2RT}{E}\right) \exp\left(\frac{-E}{RT}\right) \quad (19)$$

For $n = 1$, $g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = -\ln(1-\alpha)$. For a value of $\frac{E}{RT} > 20$, the value of $\frac{2RT}{E}$ becomes much less than 1. As a result, $(1-\frac{2RT}{E})$ becomes constant and approximately equal to 1. A natural logarithmic form of eq. (18) can be obtained as follows:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (20)$$

According to this method, the plot of $\ln\left[\frac{g(\alpha)}{T^2}\right]$ versus $\frac{1000}{T}$ gives a straight line with a slope equal to $-\frac{E}{R}$ and an intercept that gives the value of activation energy and pre-exponential factor respectively.

Horowitz–Metzger method. Horowitz–Metzger method simplifies the exponential integral and introduced a characteristic temperature T_s , and a parameter θ such that, $\theta = T - T_s$. If the reaction order is 1, T_s is defined as the temperature at which $(1-\alpha) = \frac{1}{e} = 0.368$ which corresponds to the inflection point in TGA curve and the expression becomes:

$$\ln(1-\alpha) = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT = -\exp\left(\frac{-E\theta}{RT_s^2}\right) \quad (21)$$

Finally, the expression is:

$$\ln [\ln (1-\alpha)^{-1}] = \frac{E\theta}{RT_s^2} \quad (22)$$

The activation energy can be determined from a linear fit to the plot of $\ln [\ln(1-\alpha)^{-1}]$ versus θ .

EXPERIMENTAL

Materials

An unmodified diglycidylether of bisphenol A (DGEBA) epoxy resin, cyclo-aliphatic amine hardener as curing agent and epoxy terminated polyether polyol (propoxylated glycerin triglycidyl ether) as plasticizing modifier, supplied by Applied Poleramics, were used in this study. Amino functionalized multiwalled carbon nanotubes (NH₂-MWCNT) having an average diameter of 10 nm, length of 1 μ m and carbon purity >95% were purchased from Nanocyl, Belgium.

Manufacturing Process

Dispersion of NH₂-MWCNTs into Epoxy Resin. NH₂-MWCNTs (0.3 wt %) was mixed with unmodified DGEBA epoxy resin. To ensure proper dispersion of NH₂-MWCNTs, sonication and three roll shear mixing technique were used. The mixture was sonicated at room temperature for 1 h at 35% amplitude and a 30 s on/30 s off cycle pulse mode. The sonicated mixture was then passed multiple times through a three roll shear mixing device with a varying gap setting between the rollers (20 μ m for first pass, 10 μ m for second pass and 5 μ m for third pass), to induce high shear force in the mixture. In all the three passes, the roller speed of the three rolls was maintained at a ratio of 1 : 3 : 9 with a maximum speed of 200 rpm.

Dispersion of Polyether Polyol into Epoxy Resin Blends. A high speed mechanical stirrer was used to thoroughly mix Polyether polyol with modified NH₂-MWCNTs/epoxy resin blends as per calculated weight ratio. The mixture was stirred at room temperature for 10 min at a speed of about 800 rpm.

The formulation of Epoxy/Polyol/CNT three phase system was 90 phr of resin, 10 phr of polyol and 0.3 wt % of MWCNTs. The amount of hardener was 30 phr for both control and modified samples. This modification was chosen because in our earlier studies modification of epoxy with 10 phr of polyol and 0.3 wt % of MWCNTs was found to have superior mechanical and thermomechanical properties compared to other formulations.^{5,6}

Preparation of Cured Epoxy Composites. The curing agent was added at a stoichiometric ratio of 10 : 3 (DGEBA: Hardener) to the control and modified systems and blended with a high speed mechanical stirrer for 10 min. at a speed of about 800 rpm. The resulting blend was placed in a degasification chamber at room temperature to remove entrapped air bubbles generated due to the intense mechanical mixing. After complete removal of bubbles, the mixture was poured into a Teflon coated metal mold and cured for 2 h at 60°C. The cured material was taken out of the mold and placed in an oven for post cure at 100°C for 5 h. Finally, samples were prepared for TGA by machining.

Material Characterization

Micrograph Analysis. The analysis of the surfaces of control and modified samples was done using a Zeiss EVO50 scanning electron microscope (SEM) at 20 kV accelerating voltage and optical microscope. Specimen surfaces for SEM observations

were coated with thin gold film to protect the fracture surfaces from beam damage and to prevent charge build up. The dispersion state of the MWCNTs in the epoxy resin was investigated by transmission electron microscopy (TEM) using a Zeiss EM10 Transmission Electron Microscope operated at 60 kV.

Thermogravimetric Analysis. Thermal degradation of control epoxy resin and Polyether polyol modified NH₂-MWCNTs/epoxy resin was measured by TGA Q 500 (Manufacturer: TA Instruments) apparatus from room temperature to 600°C under a flow of 60 mL/min nitrogen gas. Data were collected at three different heating rates of 5°C/min, 10°C/min and 20°C/min as recommended by ICTAC kinetics committee.²⁵ Samples (10–15 mg) were used in this analysis and three samples from each category were investigated to ensure repeatability. Average values were taken into consideration for calculation.

RESULTS AND DISCUSSION

Degradation Characteristics

TGA thermograms show the weight percentage of the experimental materials as a function of temperature. Initial degradation temperature, final decomposition temperature and residual mass can be measured directly from the weight loss curve. The onset of degradation corresponds to the inflection point of thermal degradation curve. Decomposition temperature is defined as the point of maximum weight loss, and the residual mass is the char yield after heating. When modifiers like nanoparticles and toughener are added, the weight loss pattern of polymer should be changed; hence the degradation temperature and char yield should also change. Figure 1 represents the typical thermal degradation behavior of control samples and MWCNT-polyol modified samples at different heating rates. Although TGA was done from 30 to 600°C, Figure 1 is shown from 250 to 500°C to clearly present the difference between the degradation behavior of control and modified samples. Beyond this range, the degradation of the samples was not significant. The relationships between the conversions and temperature at various heating rates are also exhibited in Figure 1. Table I shows the degradation temperature and char yield of control epoxy and MWCNT/Polyol modified Epoxy at different heating rates.

The rate of weight loss can be measured from the slope of weight versus temperature curves. It was observed that compared to the control epoxy samples, the TGA curves of MWCNT-Polyol modified samples shifted to a higher temperature while retaining almost the similar shape. As shown in Table I, it becomes evident that the initial degradation temperatures for modified samples were higher than control samples at different heating rates while the decomposition temperatures for both kinds of samples were almost similar. The initial degradation of modified samples might have been delayed due to higher crosslinking density of the modified sample.⁶ However, at higher temperature all the covalent bonds and corresponding crosslinking structure among the constituent materials might have been degraded which resulted in final decomposition temperature comparable to the control epoxy. Although the char yield of modified samples were slightly higher than the control samples, no conclusions can be drawn as the differences were not statistically significant.

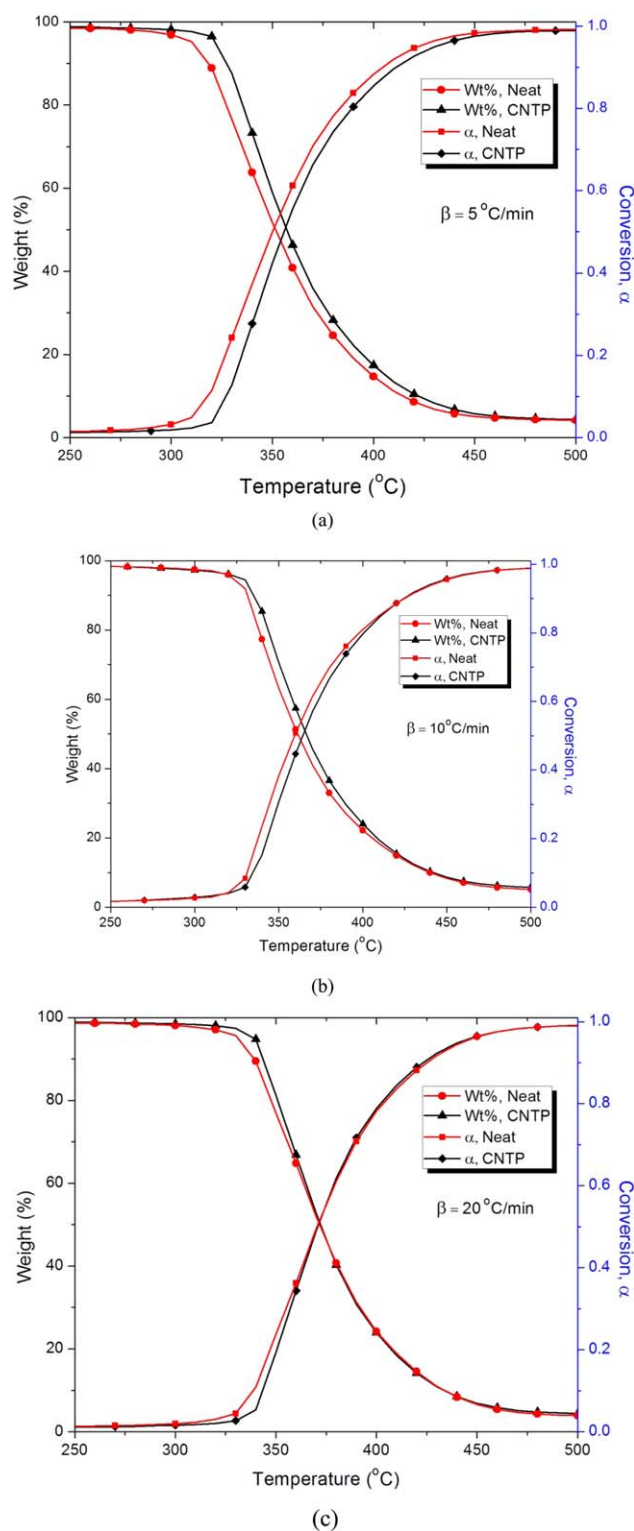


Figure 1. TGA thermograms showing weight (%) and conversion (α) against temperature for control and modified samples at (a) 5°C/min, (b) 10°C/min, and (c) 20°C/min heating rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It was also observed that a particular conversion corresponded to a higher temperature for MWCNT/Polyol modified epoxy indicating delayed degradation and increased thermal stability.

Figure 2 represents derivative weight change ($\%/^{\circ}\text{C}$) with temperature for control and modified epoxy samples at 5°C/min, 10 and 20°C/min heating rate. As shown in Figure 2, the derivative weight change ($\%/^{\circ}\text{C}$) versus temperature curves also exhibited similar trend. The peaks of derivative weight change occur at a higher temperature for modified samples. For samples tested at different heating rates, modified samples started to degrade, reached the peak and finished degrading at higher temperatures compared to control one.

Integral Procedure Decomposition Temperature

IPDT was calculated by integrating the areas in TGA thermograms. Basically, IPDT summarizes the whole shape of the normalized data curve to estimate the inherent thermal stability of the samples. Unlike initial degradation and final decomposition temperatures, IPDT does not depend on procedural details and gives a good estimate of the inherent thermal stability of polymeric materials.¹⁶ Table II shows the IPDT for control and MWCNT/Polyol modified epoxy. IPDT was found to increase due to the addition of MWCNT/Polyol in epoxy system for samples tested at different heating rates. This increase in IPDT implies improved thermal stability of the modified samples.

Activation Energy

Thermogravimetric data was analyzed using several methods to understand the kinetics of thermal degradation of the MWCNT-Polyol modified samples compared to control samples. To do so, activation energies for both control and modified epoxy were calculated from the plots obtained using Kissinger, Flynn–Wall–Ozawa, Coats–Redfern and Horowitz–Metzger methods.

Kissinger's Method. Figure 3 shows a straight line plot of $\ln(\beta/T_{\text{max}}^2)$ against $1/T_{\text{max}}$ for both kinds of samples using Kissinger's equation (11) and the activation energy E was calculated from the slope of these straight lines. The peak temperatures of derivative weight curves were taken as T_{max} . The slopes of the linear fitted curves were calculated to obtain the activation energy and the calculated activation energies are presented in Table III. The activation energy for control epoxy was found to be 191.90 KJ/mol, and for the modified samples it was 258.26 KJ/mol indicating around 35% increase of activation energy.

Flynn–Wall–Ozawa Method. To calculate the activation energy by Flynn–Wall–Ozawa method, straight line plots of $\log\beta$ versus $1/T$ was obtained from eq. (18). The onset of degradation temperature was taken as the value of T for calculating the activation energy. Figure 4 shows the straight line plots of $\log\beta$ versus $1/T$ for control and modified epoxy. Activation energy for degradation (E) was calculated from the slope of the lines since the slope gives the value of $-0.4567E/R$. Table IV shows the calculated activation energy for control and modified samples for different values of the conversion factor (α). The activation energy for modified epoxy is higher than control epoxy for different conversions. The peak of derivative weight loss usually occurs between 5 and 20% conversion. The activation energies obtained by Flynn–Wall–Ozawa method in this range of conversion were on average around 183 KJ/mol for control samples

Table I. Initial Degradation, Decomposition, Peak Derivative Temperature, and Char Yield of Control Epoxy and MWCNT/Polyol Modified Epoxy at Different Heating Rates

Heating rate	Sample	Initial degradation temperature (°C)	Decomposition temperature (°C)	Peak derivative temperature (°C)	Avg. char yield @ 600°C (%)
5°C/min	Control epoxy	314.26 ± 2.16	392.87 ± 2.20	325.26 ± 2.34	3.8
	MWCNT/polyol/epoxy	322.83 ± 3.12	392.93 ± 2.68	331.77 ± 2.43	3.9
10°C/min	Control epoxy	324.33 ± 2.56	401.14 ± 3.96	335.83 ± 1.58	4.5
	MWCNT/polyol/epoxy	331.96 ± 1.88	403.89 ± 2.96	340.40 ± 1.26	5.1
20°C/min	Control epoxy	334.09 ± 2.34	408.25 ± 2.98	345.94 ± 1.88	3.3
	MWCNT/polyol/epoxy	339.33 ± 1.92	407.96 ± 3.48	347.81 ± 1.98	3.8

and around 255 KJ/mol for modified samples. These values are very similar to those obtained by Kissinger method.

Figure 5 shows the values of activation energy obtained by Flynn–Wall–Ozawa method. For control epoxy, the value of activation energy remained almost constant up to around 35% of conversion. However, from around 50% conversion the activation energy for degradation started to increase rapidly. On the other hand, the activation energy of the MWCNT-polyol modified epoxy increased at a modest rate up to around 35% of conversion. Similar to control epoxy the increase of activation energy from around 50% of conversion is very rapid. However, the rate of increase is even faster than that of control epoxy. Consequently, the percentage increase of activation energy for the modified sample is greater for the higher amount of conversion. This phenomenon may have been caused by the formation of charred layers on the surface of epoxy matrix by MWCNTs. The peak derivative temperature obtained from TGA thermograms of pristine MWCNT is around 530°C²⁶ which is far higher than the peak derivative temperature of control epoxy. Consequently, MWCNTs degrade at a higher temperature and during degradation charred layers formed by MWCNTs on the surface of epoxy matrix act as heat barriers and increase degradation temperature of the entire epoxy system.²⁷ At higher conversion, more number of MWCNTs might have been added and leading to a higher barrier effect and increased activation energy for degradation.

Coats–Redfern Method. Equation (20) was used to plot $\ln\left[\frac{g(z)}{T}\right]$ versus $\frac{1000}{T}$ for calculation of activation energy by Coats–Redfern method. Figure 6 displays the linear fitted curve plot for Coats–Redfern method at different heating rates. This method takes into consideration a large degradation region and provides an average or characteristic value of activation energy for that region. In this study, 5 to 95% conversion region was selected for calculation. The calculated activation energy values are showed in Table V for control and MWCNT/Polyol modified samples. From the results shown in the table, it is clear that modified samples need higher activation energy for degradation at different heating rates.

Horowitz–Metzger Method. Equation (21) was used to calculate activation energy by Horowitz–Metzger method and $\ln[\ln(1-\alpha)^{-1}]$ versus $T - T_s$ was plotted. Figure 7 displays the linear fitted graph plots of control and modified samples at

5°C/min, 10°C/min and 20°C/min heating rates. Activation energy of control and modified samples obtained by this method are presented in Table VI. It is evident that the activation energy of degradation is higher for the MWCNT/Polyol modified samples and the values are similar to those obtained by Coats–Redfern method. A region of ±45°C around 63.2% conversions was considered for calculating activation energy by Horowitz–Metzger method. This region is almost similar to the region considered for Coats–Redfern method. Furthermore, the activation energy values calculated by these two methods are very close to each other.

All four methods used for kinetic analysis confirm increased activation energy due to the modification of epoxy matrix by MWCNT/polyol. However, the values obtained by methods based on experiments under various heating rates were dissimilar to those obtained from methods based on a single experiment. This variation in activation energy based on mathematical approach was observed by many researchers.^{28–30} The differences of calculated activation energy among various methods arise from the assumption of various parameters and approaches used for solving the eq. (11). Although Kissinger's and Flynn–Wall–Ozawa methods were based on multiple heating rates, activation energy was calculated based on a particular temperature. These methods are known as isoconversional methods. Kissinger method uses only the point of maximum degradation rate while Flynn–Wall–Ozawa method calculates activation energy at a particular conversion. As a result, sometimes these methods are considered to have limited applicability. On the other hand, Coats–Redfern and Horowitz–Metzger methods uses only a single heating rate. However, these methods investigate a broad region of conversion and calculate the average activation energy for that region. Due to the consideration of broader regions in these methods, the calculated activation energy tend to give dissimilar results compared to the methods using a particular point.²⁸

Some researchers proposed that methods based on multiple heating rates are considered to give more reliable results.³¹ They propose that evaluation of thermogravimetric data based on a single heating rate does not lead to reliable data.³⁰ On the contrary, Zsako³² suggested that Coats–Redfern method is the superior method as it demonstrates the best linearity of the data. Horowitz–Metzger method removes the problem of arbitrary selection of reference temperature by considering the

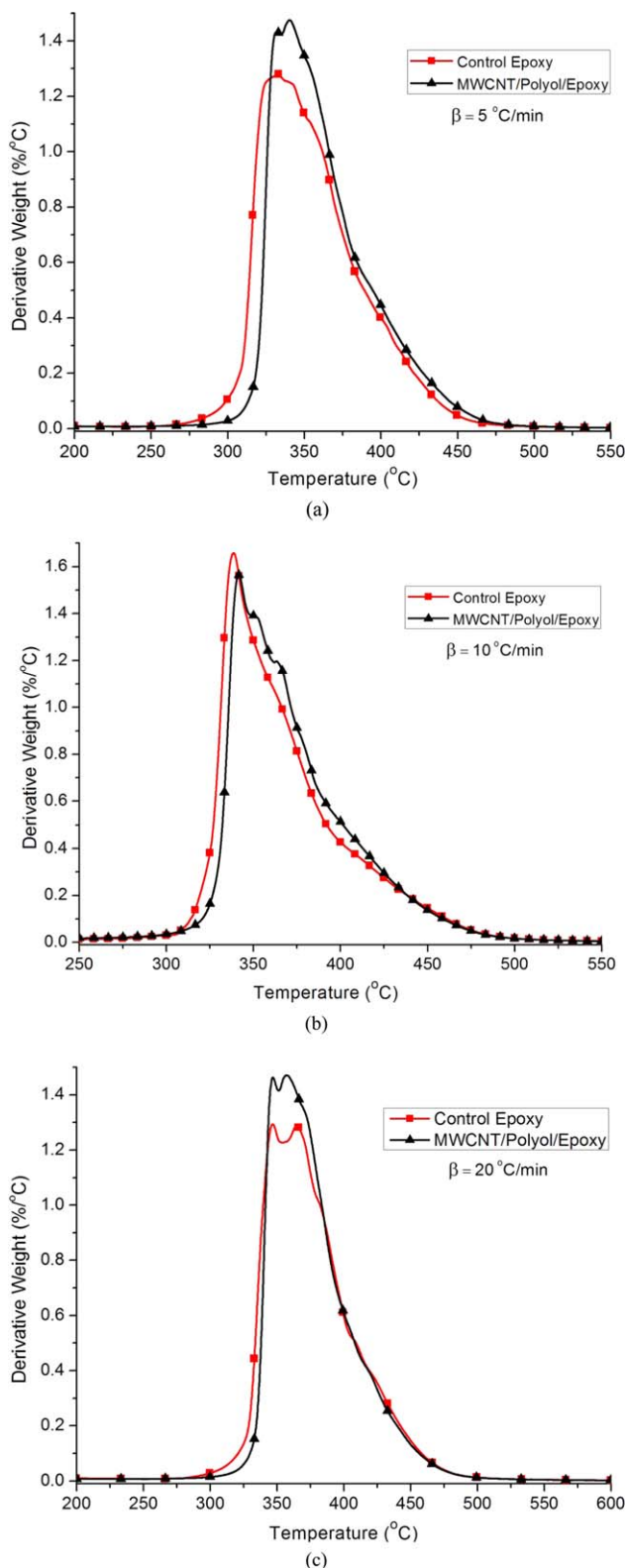


Figure 2. Derivative Weight (%/°C) versus Temperature curve for ncontrol and MWCNT/Polyol modified epoxy at (a) 5°C/min, (b) 10°C/min, and (c) 20°C/min heating rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Calculation of Average IPDT of Control and MWCNT/Polyol Modified Epoxy Composites at Different Heating Rates

Heating rate	IPDT (°C)	
	Control epoxy	MWCNT/polyol/epoxy
5	387.8	405.5
10	407.1	416.6
20	412.7	420.4

temperature corresponding to inflection point in TG curves. As a result, some researchers proposed that kinetic behavior and activation energy of a polymeric material can be properly describe by using several kinetic methods.^{25,30,33}

From this detail study, it was evident that the degradation temperature and the activation energy required for degradation of the cured epoxy system modified with MWCNT-polyol are higher than those of control epoxy. This may have happened due to the thermal resistance of MWCNTs and increased crosslinking density as a result of covalent bond formation between NH₂ and epoxide groups.³⁴ Addition of 1% or more nonfunctionalized nanotubes was found to reduce the heat release of polymeric compounds by forming a protective layer over sample surface.^{35,36} However, in this study, only slight amount of NH₂ functionalized MWCNTs were added. As a result, the physical presence of nanotubes did not significantly affect the thermal stability, rather the chemical reaction between functionalized nanotubes and epoxy resin became the dominating factor for improvement of thermal stability. Because of this reason, the amount of char yield obtained for control and MWCNTs modified samples may not have varied due to the addition of MWCNTs.

The crosslink density of epoxy composites decreased upon polyol loading and increased with MWCNT loading.⁶ Crosslinking decreased after addition of polyol, as polyol is a plasticizer.

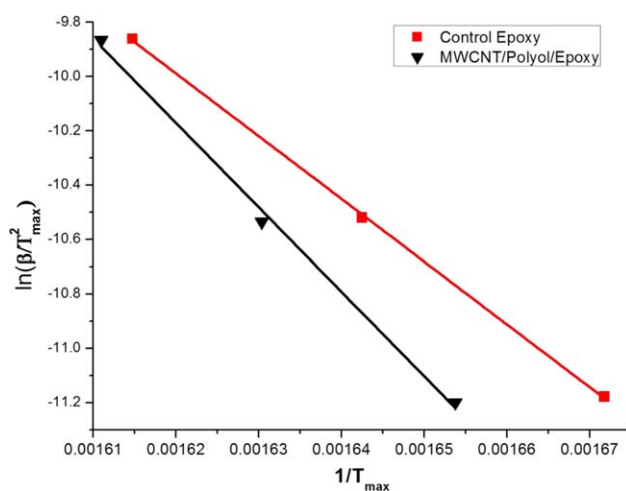
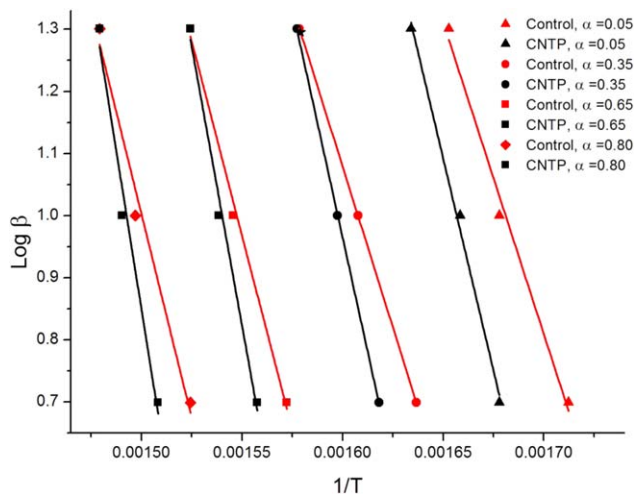
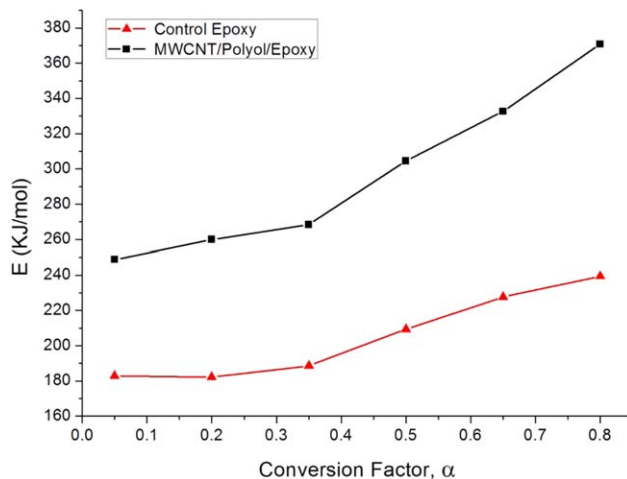


Figure 3. Plots of $\ln(\beta/T_{\max}^2)$ versus $1/T_{\max}$ for control and MWCNT-Polyol modified epoxy to calculate activation energy by Kissinger method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Calculated Activation Energy of Degradation for Control and MWCNT/Polyol Modified Epoxy Composites by Kissinger's Method

Sample	Heating rate β ($^{\circ}\text{C}/\text{min}$)	T_{max} (K)	Activation energy E (KJ/mol)	Correlation COEFFICIENT R^2	% Increase w.r.t. control
Control epoxy	5	598.2	191.90	0.9995	-
	10	608.8			
	20	618.9			
MWCNT/ polyol/epoxy	5	604.7	258.26	0.9938	34.6
	10	613.4			
	20	620.8			

**Figure 4.** Plots of $\log\beta/T$ versus $1/T$ for control and MWCNT/Polyol modified epoxy to calculate activation energy by Flynn–Wall–Ozawa method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Figure 5.** Activation Energy at different conversion (α) according to Flynn–Wall–Ozawa method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Table IV.** Calculated Activation Energy of Degradation for Control and MWCNT/Polyol Modified Epoxy Composites by Flynn–Wall–Ozawa Method at Different Conversion Factors

Conversion (α)	Sample	Activation energy E (KJ/mol)	Correlation coefficient, R^2	% Increase w.r.t. control
0.05	Control	182.8	0.9831	-
	CNTP	248.8	0.9917	36.1
0.20	Control	182.1	0.9989	-
	CNTP	259.9	0.9999	42.7
0.35	Control	188.5	0.9999	-
	CNTP	268.4	0.9999	42.3
0.50	Control	209.3	0.9994	-
	CNTP	314.2	0.9844	50.1
0.65	Control	227.6	0.9912	-
	CNTP	332.6	0.9844	46.1
0.80	Control	239.4	0.9698	-
	CNTP	370.8	0.9621	54.9

*CNTP refers to MWCNT/Polyol modified epoxy.

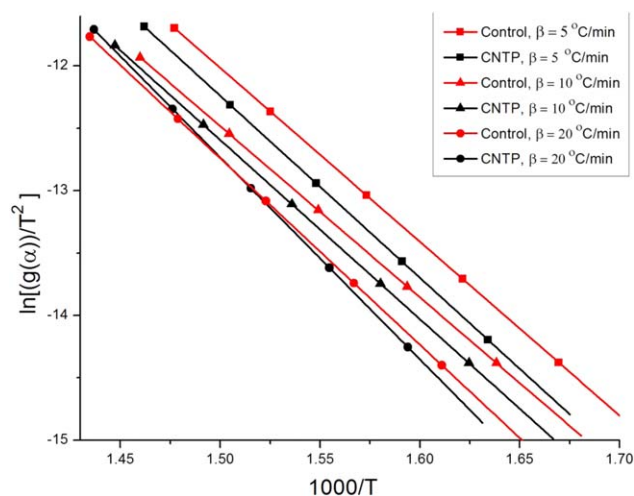
**Figure 6.** Linear fitted graph plots of $\ln[g(\alpha)/T^2]$ versus $1000/T$ for control and MWCNT/polyol modified epoxy to calculate the activation energy by Coats–Redfern method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Calculated Activation Energy of Degradation for Control and MWCNT/Polyol Modified Epoxy Composites by Coats–Redfern Method

Heating rate β ($^{\circ}\text{C}/\text{min}$)	Sample	Activation energy E (KJ/mol)	Correlation coefficient, R^2	% Increase w.r.t. control
5	Control epoxy	115.8	0.9086	-
	MWCNT/polyol/epoxy	121.2	0.8552	4.7
10	Control epoxy	114.1	0.8675	-
	MWCNT/polyol/epoxy	119.3	0.8792	4.6
20	Control epoxy	124.1	0.9006	-
	MWCNT/polyol/epoxy	134.6	0.8626	8.4

According to free volume theory, a plasticizer significantly increases the number of ends and thus enhances free volume in the epoxy systems. According to the gel theory of plasticization, plasticizers hinder polymer molecules from interacting with each other by breaking the attachments along the chains. Hence, plasticizer reduced the self-crosslinking density of epoxy. However, when amino-MWCNTs were added along with polyol, the crosslinking density increased again as a result of covalent bond formation between amino and epoxide groups. During the polymerization process, polyol phase separates as it becomes less miscible with the epoxy matrix. SEM micrographs show the dispersed tiny polyol particles as voids in epoxy structure (Figure 8). In TEM micrograph (Figure 9), polyols are seen as white circular regions distributed within epoxy matrix. From TEM micrograph, MWCNTs can also be seen to be quite well dispersed in epoxy matrix.

In case of control epoxy sample, hydrogen atoms in amine groups of DETA molecule (hardener) react with the epoxide group of DGEBA resin molecules and forms crosslink between DGEBA molecular chains. However, as NH_2 -MWCNTs were mixed with epoxy and polyol before addition of curing agent in nanophased samples, there might be an interfacial reaction taking place. The interfacial reaction can increase the adhesion of nanoparticles with the polymer matrix resulting in higher degrees of dispersion, which, in most cases lead to substantial enhancement of thermal decomposition properties.⁷ On mixing of Part-B of epoxy resin, hardener reacts with DGEBA in similar manner to the control SC-15. However, it is very difficult to prove whether MWCNTs were particularly responsible for formation of amino groups as both hardener and nanotubes are responsible for formation of this group by reacting with part A of SC-15. Thus reaction between amine functional groups of CNTs and epoxide groups of DGEBA and epoxy terminated polyol may have resulted in a ring opening reaction followed by a crosslinking reaction.⁶ NH_2 -MWCNTs were possibly responsible for promoting the crosslink density of epoxy composites due to the presence of reactive NH_2 functionalization and

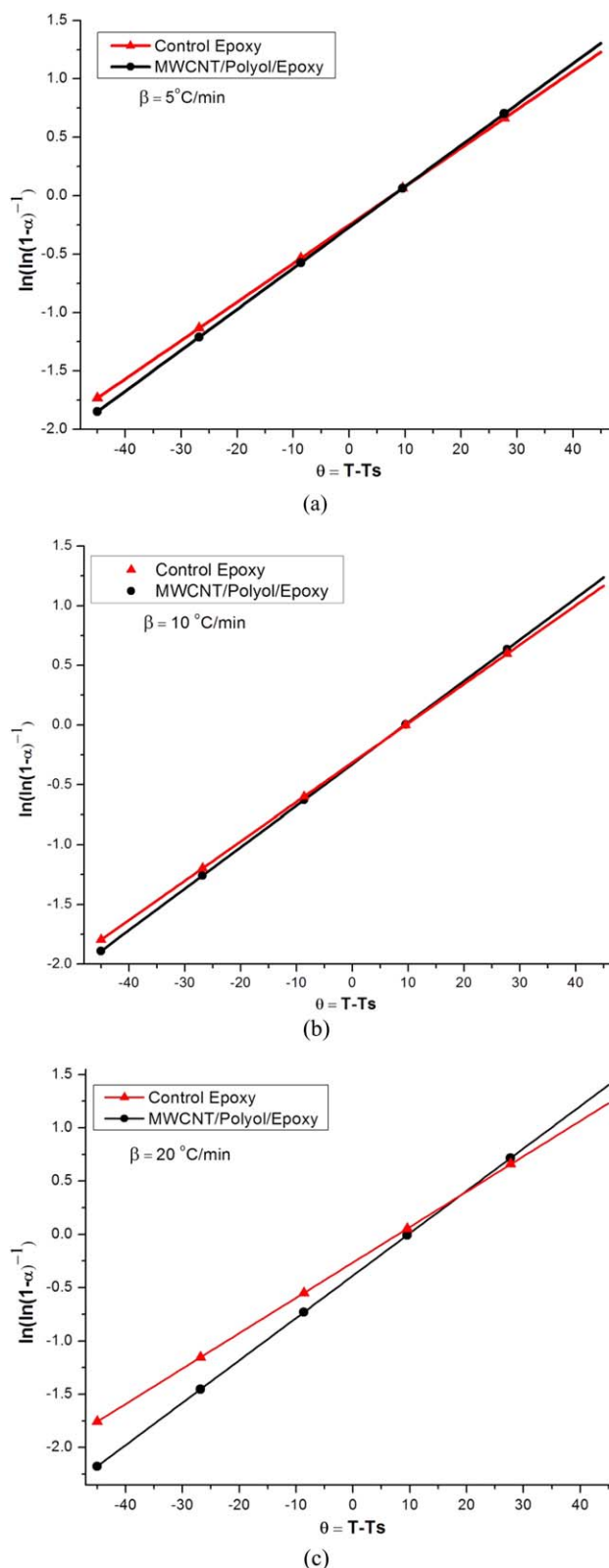
**Figure 7.** Linear fitted graph plots of $\ln(\ln(1-\alpha)-1)$ versus $T - T_s$ at a) $5^{\circ}\text{C}/\text{min}$, b) $10^{\circ}\text{C}/\text{min}$, and c) $20^{\circ}\text{C}/\text{min}$ heating rates for calculating activation energy by Horowitz–Metzger method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VI. Calculated Activation Energy of Degradation for Control and MWCNT/Polyol Modified Epoxy Composites by Horowitz–Metzger Method

s	Sample	Activation energy E (KJ/mol)	Correlation coefficient, R^2	% Increase w.r.t. control
5	Control epoxy	107.3	0.9924	-
	MWCNT/polyol/epoxy	119.9	0.9868	11.8
10	Control epoxy	114.2	0.9867	-
	MWCNT/polyol/epoxy	121.5	0.9814	6.5
20	Control epoxy	117.7	0.9899	-
	MWCNT/polyol/epoxy	141.4	0.9845	20.1

induced restricted mobility in the system due to the formation of covalent bonds. This reduction in mobility led to an increase in degradation activation energy and improved thermal stability.

CONCLUSIONS

Thermal stability and kinetics of degradation of NH_2 -MWCNTs/Polyol modified epoxy system were examined using thermogravimetric analysis (TGA) and compared with control

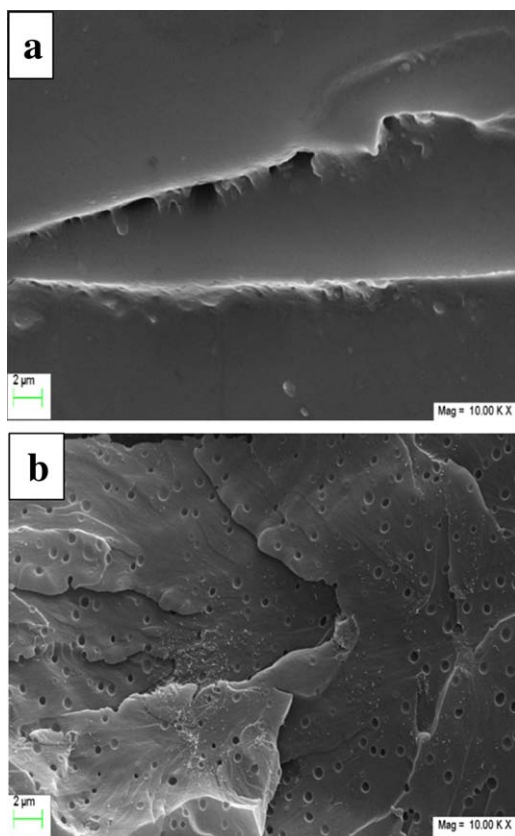


Figure 8. SEM micrographs (a) control epoxy, b) MWCNT/polyol/epoxy at a magnification of $\times 10,000$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

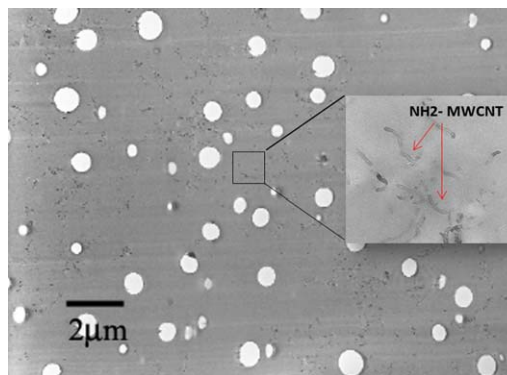


Figure 9. TEM micrograph showing quality of dispersion of polyol and NH_2 -MWCNTs in epoxy resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

or unmodified epoxy. Based on the analysis, following conclusions were drawn:

- Addition of MWCNTs/Polyol in epoxy resin slowed down thermal degradation of epoxy composite. The initial degradation temperature and peak degradation temperature for modified sample were higher than control epoxy at all heating rates while the final decomposition temperature was not affected.
- IPDT increased for modified samples indicating improved thermal stability.
- Calculated values of activation energy of modified samples from all four methods are higher than that of control epoxy. However, the methods that use multiple heating rates showed greater increase compared to the methods that use single heating rate.
- Among the methods based on multiple heating rates, activation energy for modified samples calculated by Kissinger method was found to be almost 34% higher than control sample while from Flynn–Wall–Ozawa method it was found to be around 36 to 55% higher at different conversion rates.
- Among the methods based on single heating rate, activation energy for modified samples calculated by Coats and Redfern method was found to be around 5 to 9% higher than control sample at different heating rates. However, from Horowitz–Metzger method it was found to be around 7 to 20% higher at different heating rates.

From these results, it can be concluded that thermal stability of epoxy composite improved with addition of MWCNT–Polyol making the modified sample a good candidate for use in high temperature applications.

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