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Study on the effect of phenol anchored multiwall carbon nanotube on the curing kinetics of epoxy/Novolac resins

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ABSTRACT

Multiwall carbon nanotube was functionalized by introducing ylide groups containing anchored phenol structures on the surface. The influence of functionalized carbon nanotube on the curing kinetics of diglycidyl ether of 4,4′-bisphenol-epoxy mesogenic resin was studied by non-isothermal differential scanning calorimetry at various heating rates. Novolac and triphenyl phosphine were used as a curing agent and activator, respectively. Differential scanning calorimetry peak of the pristine and functionalized carbon nanotube filled epoxy/Novolac resin shifts to the higher temperature indicating its influence on the curing reaction. The activation energy calculated by Kissinger method clearly depicts the autocatalytic reactions.

1. Introduction

Due to its unique mechanical, electrical and thermal properties, carbon nanotubes (CNTs) have attracted extensive research attention widely [1,2]. Some previous investigations have revealed that the introduction of carbon nanotubes as a structural element in polymer matrix can improve their mechanical properties [3–5], and electrical conductive property of polymers [6]. Thus introduction of carbon nanotubes into polymers may improve their applications in the fields of reinforcing composites, electronic devices and more.

The recent researches have extensively focused on the epoxy resin-based carbon nanotube composites because of their wide applications in the electronics, aeronautics and astronautics industries [7], Xu et al. [8] obtained about 20% increase in elastic modulus of epoxy by addition of 0.1% carbon nanotube. Approximately, 100% increase in elastic modulus was obtained by the addition of only 1% carbon nanotube [9]. Loading of carbon nanotube in epoxy matrix significantly improves the toughness [10] and prevents the crack propagation by bridging them [11]. However, the potential applications of epoxy/carbon nanotube composites are limited due to the poor adhesion between carbon nanotube and the matrix and poor dispersion. Normally, CNTs tend to cling to each other and making CNT composites with uniform dispersion has been reported to be tedious. Carbon nanotube pullout from the polymer matrix has been reported by several researchers [12].

Several recent studies have investigated the curing kinetics of CNT/epoxy nanocomposites [13–15]. Abdalla et al. studied the effect of carboxylated and fluorinated multiwalled carbon nanotubes (MWCNT) on the cure behavior under isothermal condition and suggested that cure mechanism of carboxylated MWCNT/epoxy was different compare to fluorinated MWNT/epoxy and neat epoxy [13]. Puglia et al. reported catalytic effect of carbon nanotubes, which resulted in shift of reaction peak to lower temperature [14].

Recently surface modification has being adopted by various researchers to enhance the adhesion between carbon nanotube and polymer matrix and thereby fine dispersion of nanotube in the polymer matrix. Surface functionalization of carbon nanotube has been done by oxidation or chemical functionalization of CNTs and covalent attachment of polymer chains to the CNTs that lead to strong interfacial bonding between the CNTs and the polymer. In our laboratory, we are successful in functionalizing the single and multi walled carbon nanotube by introducing azomethine ylide groups with anchoring phenol structures [16].

In this work, surface functionalization of multiwall carbon nanotube was carried out by introducing phenol anchored azomethine ylide groups on the surface followed by the characterization using Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy. The phenol anchored carbon nanotubes were then incorporated in epoxy/Novolac resin and its influence on the curing kinetics was investigated.

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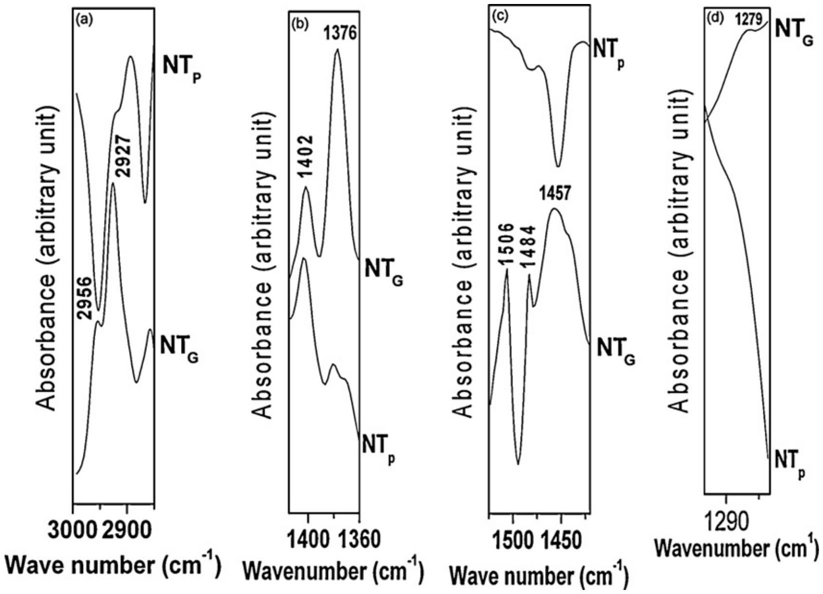

Fig. 1. FT-IR spectra of pristine (NT$_P$) and functionalized (NT$_G$) MWCNT.

2. Experimental

Difunctional epoxy resin (YD 118) supplied by Kukdo Chemicals Co. Ltd. YD 118 is diglycidyl ether of bisphenol A (DGEBA) with the epoxy value of 0.48–0.52 mol/100 g. The curing agent used was Novolac type phenolic resin (PN, KPE-F2000) obtained from Kolon chemicals Ltd, Korea. Multiwall carbon nanotube diameter 30–60 nm, length 2–15 μm was obtained from Il Jin Nanotech (Korea).

Surface functionalization of multiwall carbon nanotube was done by 1,3 dipolar addition reaction following the procedures reported by Georgakilas et al. [16]. Multiwall carbon nanotubes were suspended in dimethyl formamide (DMF), together with formaldehyde and N-(4-hydroxy)phenyl glycine. The heterogeneous reaction mixture was heated at 150 °C for 5 days with the frequent addition of DMF. The reaction was stopped after 5 days and the brown solid obtained was washed with dimethyl formamide (DMF). Pristine and azomethine ylide functionalized carbon nanotubes were designated as NT$_P$ and NT$_G$, respectively.

DGEBA, Novolac resin and carbon nanotube were mixed in a 100:100:1 weight ratio, then the mixture was dissolved in acetone and subjected to stirring for 1 h at 80 °C. The solution was cooled down and 1 wt% of TPP was added. The mixture solution was stirred and subsequently evaporating the solvent at room temperature under vacuum for 24 h. The samples were designated as EPN$_0$ (epoxy/Novolac); EPN$_T$ (pristine carbon nanotube filled epoxy/Novolac); EPN$_G$ (functionalized carbon nanotube filled epoxy/Novolac).

Curing kinetics was characterized using Perkin-Elmer DSC-7 system. Approximately 10 mg of sample was weighed into an aluminum sample pan and then covered with an aluminum lid. The entire operation was carried out by using in a dry chamber. The high purity indium was used as the reference material. Dynamic experiments were carried out under a nitrogen flow rate of 50 ml/min and performed in the range 30–250 °C at various heating rates of 5, 10, 15 and 20 °C/min. Curing kinetics was investigated by non-isothermal method at different heating rates and analyzed using Kissinger isoconversional method. The activation energy of the curing reaction (ASTM E 698-79) is calculated from the plot $\ln(\beta/T_m^2)$ against $1/T_m$, where T_m are the temperatures corresponding to peak maxima at different heating rates [17].

3. Results and discussion

Surface chemical functionalization of multiwall carbon nanotube was carried out by introducing azomethine ylide groups containing anchored phenol structures, generated by condensation reaction of an N-(4-hydroxy)phenyl glycine and formaldehyde [16]. The brown solid obtained by functionalization of carbon nanotubes were characterized using FT-IR and Raman spectroscopy.

Fig. 1 shows the specific regions in FT-IR spectra of NT$_P$ and NT$_G$ with anchored phenol structures. The new peaks at 2956 and 2927 cm^{-1} corresponds to the –CH stretching vibrations (Fig. 1(a)) of phenolic ring and –CH$_2$ groups present in the azomethine ylides groups. The two sharp peaks at 1506 and 1484 cm^{-1} in NT$_G$ corroborates the presence of phenolic rings on the surface of the carbon nanotubes (Fig. 1(c)). The peaks at 1457 and 1402 cm^{-1} that corresponds to –CH bending vibration present in azomethine ylides and phenol rings further supports the above facts (Fig. 1(b)). The formation of azomethine ylides is further confirmed from the peak at 1376 cm^{-1} (Fig. 1(b)) and a small hump at 1279 cm^{-1} (Fig. 1(d)) that are due to –CNC stretching and –CN stretching of tertiary amine group.

Raman spectroscopy is a powerful tool used to characterize the functionalized CNTs. As shown in Fig. 2 (514.5 nm excitation), the

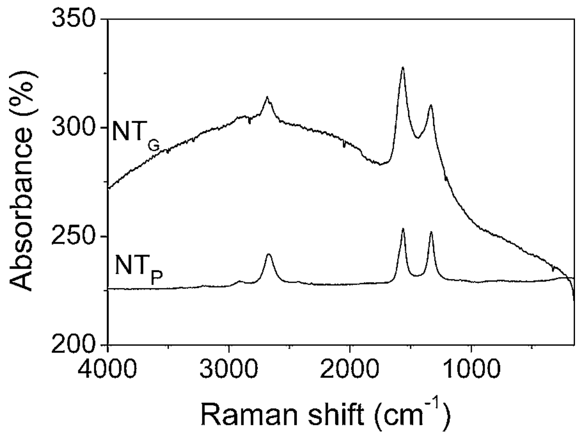

Fig. 2. Raman spectra of pristine (NT$_P$) and functionalized (NT$_G$) MWCNT.

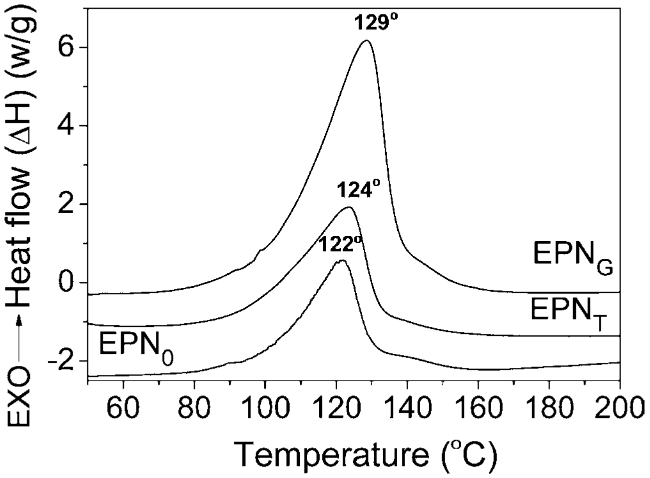

Fig. 3. DSC thermodiagrams of epoxy/Novolac (EPN_0) and epoxy/Novolac/MWCNT (EPN_T, EPN_G) nanocomposites.

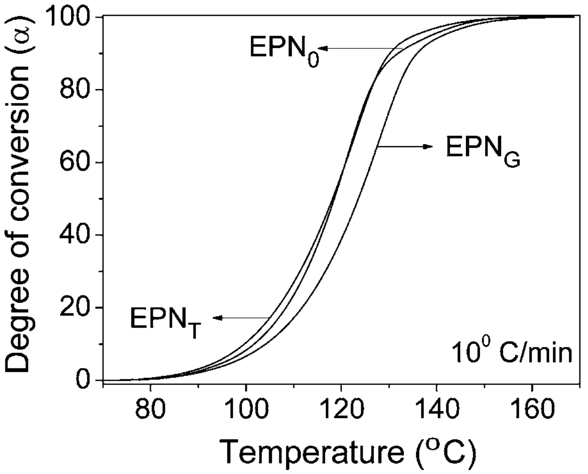

Fig. 4. Degree of conversion of epoxy/Novolac (EPN_0) and epoxy/Novolac/MWCNT (EPN_T, EPN_G) nanocomposites.

D- and G-bands at about 1329 and 1561 cm^{-1} are clearly observed for both NT_P and NT_G and those are attributed to the defects and disorder-induced modes and in-plane E_{2g} zone-center mode [18]. The D- to G-band intensity ratio (I_D/I_G), which tells about the defects on carbon nanotube surface, is 0.79 for NT_G, whereas it is 0.92 for NT_P. From the results, it is clear that the surface functionalization by introducing the azomethine ylides on the surface does not affect the crystal domain size. Also it is interesting to note that the band frequency blue shifted to about 4 cm^{-1} for NT_G. For the functionalized CNTs, the attached groups lead to coverage over the surface. This coverage with anchored phenol structures leads to the charge transfer between the anchored phenols or change in electronic property of carbon nanotubes. From the decrease in the intensity ratio (I_D/I_G), it is expected that the azomethine ylide functionalized carbon nanotubes possess excellent electronic property.

Epoxy/Novolac resin composites filled with NT_P and NT_G are prepared as discussed in Section 2. Curing of epoxy with Novolac type phenolic resin, making use of the reaction between phenolic –OH and epoxy groups, appears to be the simplest way to design addition-cure phenolic system. Although less preferred, polyphenols are used as curatives for epoxies, since the addition-curing results in void-free products, which are comparatively tougher due to the formation of flexible ether network [19]. The phenol-epoxy reaction is less facile than amine-epoxy reaction, and is usually performed in the presence of catalyst such as triphenyl phosphine (TPP).

The non-isothermal thermograms of unfilled (EPN_0) and carbon nanotube filled epoxy/Novolac resins (EPN_T and EPN_G) measured at a heating rate of 10 °C/min are shown in Fig. 3. EPN_0 shows a single exotherm with an onset (T_i) and peak temperature (T_P) at 92 and 122 °C. Incorporation of 1 wt% of pure CNT in epoxy-Novolac resin (EPN_p) slightly increases the onset and peak temperatures ($T_i = 94$ °C and $T_P = 124$ °C), while incorporation of 1 wt% of phenol functionalized carbon nanotube (EPN_G) shifts the onset and peak temperatures ($T_i = 99$ °C and $T_P = 129$ °C) significantly. This means that the addition of CNT retards the initiation of reaction and it becomes significant for functionalized CNT. However, more heat of reaction for epoxy/pure carbon nanotube system (EPN_T) and epoxy/ylide functionalized carbon nanotube system (EPN_G) reveals the better curing characteristics in comparison to pure epoxy system. The heat of reactions for EPN_0, EPN_T and EPN_G are observed to be 59.71, 85.71 and 108.1 J/g, respectively.

Fig. 4 compares the degree of conversion at a heating rate of 10 °C/min for EPN_0, EPN_T and EPN_G. It is quite clear that there is no significant variation in the degree of conversion for EPN_T, while it shifts significantly to the higher temperature for EPN_G and it confirms its influence on the curing kinetics of epoxy/Novolac resins.

Fig. 5 shows the representative graphs of $d\alpha/dt$ versus α of EPN_G at different heating rates. All systems exhibit $\alpha = 0$ at initial and final stage of the cure indicating that the curing reaction is autocatalytic. The rate of conversion is low at lower heating rate (5 °C/min) with the maximum rate of conversion at around $\alpha = 0.7$ for EPN_G. However, with increasing heating rate, maximum rate of conversion shifted to lower α value ($\alpha = 0.56$ at the heating rate of 20 °C/min). Similar trend is observed for EPN_0 and EPN_T indicating the cure reaction mechanism is autocatalytic in nature.

To understand these observations, activation energy of the curing reaction was calculated at different conversions using Kissinger method. Shown in Fig. 6 is the representative plot of $\ln(\beta/T_m^2)$ versus $(1000/T_\alpha)$ for EPN_G. Isoconversional plots at different heating rates exhibits a linear curve over the range of α with the R equals to 0.992. From the slope of the linear plots, activation energy of the curing reaction is calculated. From Fig. 7, it is quite evident that the trend of activation energy change is quite different for each curing systems. At early stage of curing ($\alpha = 0.05$), activation energy is high for EPN_0 ($E_a = 71.5$ kJ/mol), which decreases progressively with the degree of conversion and it tends to level off at about $\alpha = 0.9$. This variation of activation energy with degree of conversion clearly

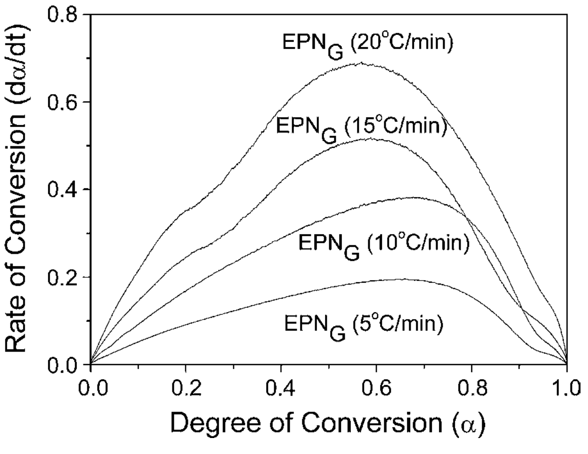

Fig. 5. Conversion rate vs. conversion of epoxy/Novolac/functionalized MWCNT (EPN_G) at various heating rates.

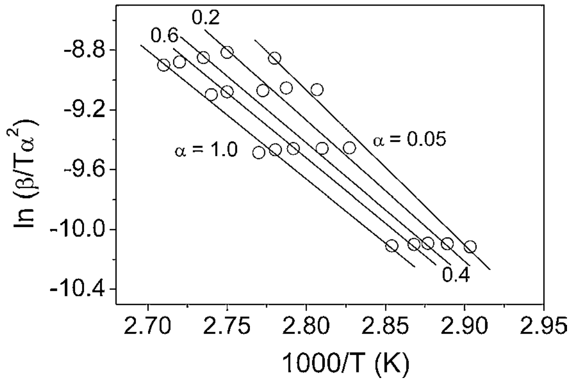

Fig. 6. Isoconversional plot of epoxy/Novolac/functionalized MWCNT (EPN_G) nanocomposite.

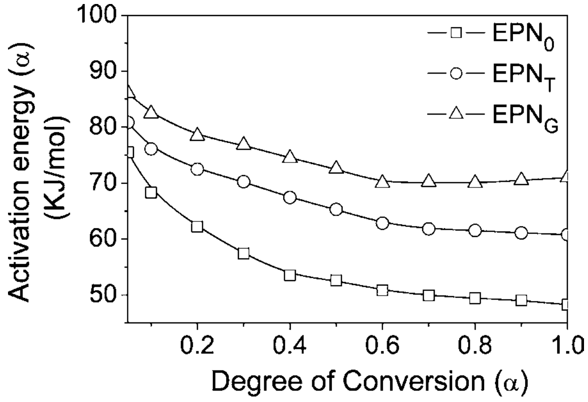

Fig. 7. Activation energy of nanocomposites as a function of conversion.

reveals the autocatalytic reaction [20]. At the initial stage of curing, the phenol hydroxyls addition is predominant. Etherification occurs only at elevated temperatures once most of the hydroxyl groups are exhausted. Therefore, the higher E_a value at lower conversion is attributed to the phenol hydroxyl reactions [20]. Because hydroxyl groups are formed during the curing facilitated ring opening, it is reasonable to expect a reduction in E_a in comparison with that at the very beginning of the cure. Interestingly, the activation energy at the early stage of curing ($\alpha = 0.05$) is very high for EPN_T and relatively higher for EPN_G in comparison to EPN_0. This is corroborated by the high E_a value at lower conversion ($\alpha = 0.05$) for EPN_T ($E_a = 81.2$ kJ/mol) and EPN_G ($E_a = 86.2$ kJ/mol) signifying the phenol hydroxyls addition. The activation energy decreases progressively with degree of conversion and remains constant at higher α value for all the systems indicating the autocatalytic mechanism. Earlier reports reveal that the generation of –OH groups on the surface of carbon nanotube, which is being introduced during purification by acid treatment [21]. This delays the etherification and increases the curing temperature for EPN_T. Similarly, significant amount of phenol groups introduced on the surface of carbon nanotube by azomethine ylide functionalization delays the etherification reaction and thereby shifts the peak temperature to the higher value. Presence of the excess amount of phenolic –OH groups leads to the formation of more secondary hydroxyl groups and thereby delays the onset of curing conversion in the case of EPN_G. The higher activation energy for EPN_T and EPN_G over the range of conversion may be attributed to the increase in the viscosity of the polymer due to the addition of nanotubes. In the previous work [22], a diffusion control process is observed for a conventional bisphenol A epoxy/amine system at the final stage of curing ($\alpha > 0.6$), where the activation energy started to decrease deeply. However, in the present cases, activation energy almost constant at higher conversion in contrast to conventional epoxy/amine system, which may be attributed to the formation of liquid crystalline, phases in all

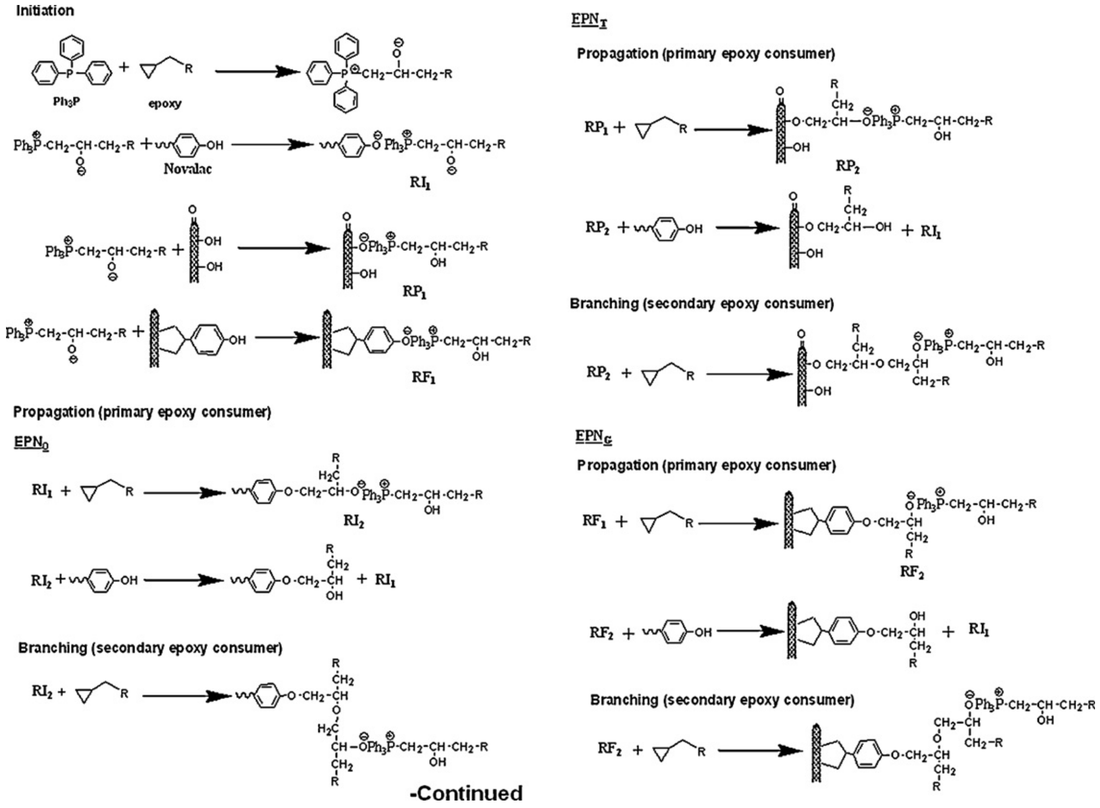

Fig. 8. Proposed reaction mechanism of various nanocomposite systems.

Table 1
Activation energy with various α values for epoxy/Novolac resins.

Sample	Degree of conversion (α)	Activation energy (E_a) (kJ/mol)		
		EPN_0	EPN_T	EPN_G
1.	0.05	75.7	81.2	86.1
2.	0.20	62.2	72.5	79.0
3.	0.40	53.3	67.5	74.6
4.	0.60	50.9	62.7	69.8
5.	0.80	49.5	61.2	69.6
6.	0.90	48.2	60.4	70.3

the systems. It has been reported that the liquid crystalline phases facilitates the reduction in viscosity (e.g. retarding gelification) [23].

According to the cure mechanism proposed by earlier researchers, the chainwise polymerization mechanisms of epoxy/Novolac resins can be divided into three main steps: initiation, propagation and branching [20]. In the initial stage of curing, TPP opens the epoxy ring by generating a zwitter ion as shown in the reaction mechanism (step 1, Fig. 8). In the presence of phenol group, a rapid proton transfer from the phenol to the secondary hydroxyl ion (RI_1) takes place (step 2, Fig. 8). The phenol hydroxyl-epoxy reaction is predominant at this stage until most of the phenol hydroxyls are exhausted. Similar reaction mechanism can be expected in EPN_T and EPN_G (Fig. 8). However, in the latter cases (both in NT_P and NT_G), zwitter ions react actively with both Novolac phenolic –OH groups (RI_1) and the phenolic –OH groups present in the carbon nanotube surface (RP_1 and RF_1). Since more active phenol groups exist in EPN_G, it delays the curing reaction as observed in Fig. 4. Once after completion of phenol hydroxyl-epoxy reaction, propagation of the curing reaction takes place as shown in Fig. 8. In the propagation step, the primary epoxies are consumed quickly resulting in greater number of secondary hydroxyl groups (RI_2) facilitating ring opening reaction (chain propagation, 1st step). However, in the case of EPN_T, the propagation step of curing reaction is activated by both RI_1 and RP_1 leading to the formation of RI_2 and RP_2. Similarly, the propagation step of curing reaction is activated by both RI_1 and RF_1 for EPN_G. These results in the decrease of the activation energy compared with the very beginning of the cure where non-autocatalytic reaction occurs [20]. This can be visualized in Table 1, which gives the information about the activation energy for selective α value. E_a value for EPN_0 decreases from 75.7 kJ/mol ($\alpha = 0.05$) to 62.2 kJ/mol ($\alpha = 0.2$). Similarly E_a decreases from 81.2 kJ/mol ($\alpha = 0.05$) to 72.5 kJ/mol ($\alpha = 0.2$) for EPN_T and it decreases from 86.1 kJ/mol ($\alpha = 0.05$) to 79.02 kJ/mol ($\alpha = 0.2$) for EPN_G. In the second step of chain propagation, generated secondary hydroxyl ions (RI_1) consume the unreacted Novolac phenolic –OH groups leading to the formation of RI_2. Similarly, EPN_T and EPN_G generate RP_2 and RF_2 along with RP_1 and RF_1 (Fig. 8). Hence, the progressive decrease in activation energy is expected at this stage until the active hydroxyl groups of the phenolic –OH group are consumed completely [20]. Final stage of curing reaction of epoxy/phenolic resin (EPN_0, EPN_T and EPN_G) is influenced by the branching of the chains which takes place, when the secondary epoxy groups started reacting with the new hydroxyl groups that came from the primary epoxy as shown in the reaction scheme (Fig. 8). The above mechanism is further supported by the delay in the onset of curing reactions as observed in Fig. 3.

4. Conclusions

Surface functionalization of multiwalled carbon nanotube has been done by introducing phenol anchored azomethine ylide groups on the surface. FT-IR and Raman spectroscopic studies reveal the effective functionalization of carbon nanotubes. Dynamic DSC was used to explore the role of functionalized carbon nanotube on the curing reactions of epoxy/Novolac resin. Functionalized carbon nanotube results in the shifting of peak temperature to the higher value signifying its influence on the curing reactions. In all the samples, early stage of cure is controlled by primary epoxy addition followed by the autocatalytic process. Higher activation energy for the filled epoxy/Novolac composites is attributed to the increase in viscosity of the composites due to the addition of carbon nanotubes.

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