

Effect of type and aspect ratio of different carbon nanotubes on cure behavior of epoxy-based nanocomposites

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Abstract Effect of incorporation of carbon nanotubes (CNTs) into diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin (HY5052/LY5052 system) on cure reaction was investigated via thermal analysis. Keeping their length constant, CNTs of different diameters were chosen. Samples based on epoxy resin and different type and content of CNTs were prepared and characterized. The cure behavior of epoxy matrix in the presence of CNTs was studied in both glassy and rubbery states. The results indicated that the final cure characteristics of epoxy nanocomposites were controlled by the competition of viscosity-increasing effect and heat-sink effect of CNTs. Isothermal analysis showed that accelerating or decelerating effect of CNTs on the cure process depends on CNT content, its aspect ratio and temperature of isothermal cure. The presence of the CNTs physically hindered the mobility of the epoxy and hardener monomers preventing the cure reaction (viscosity-increasing effect). In contrast, inherent high thermal conductivity of CNTs can act as a heat sink to accelerate the heat absorption of the epoxy (heat-sink effect). Below glass–rubber transition temperature (T_g), heat-sink effect of CNTs was dominant due to the restricted mobility of polymer chains in glassy state, whereas at temperatures higher than T_g , viscosity-increasing effect was dominant. CNTs physically hindered the mobility of reactive species despite the inherent tendency of polymer chains for long-range molecular motions.

Keywords Nanocomposites · Epoxy resin · Cure kinetics · CNT dimensions · Aspect ratio

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Introduction

Recently, the proper dispersion of CNT in polymer matrix has been the most critical issue for achieving appropriate properties of CNT/polymer composites [1–3]. Furthermore, it has been already reported in the literature that the choice of optimal dimensions and content of CNTs are a promising approach to improve the efficiency of CNTs as reinforcing/conductive nano-filler [4–6].

Wu et al. [7] studied the effect of CNTs with two aspect ratios (length-to-diameter, $A = l/d$) including high aspect ratio (HAR) and low aspect ratio (LAR) on network structure of the CNTs in biodegradable polylactide (PLA) matrix. They concluded that the composites with HAR CNTs present a higher modulus than that of the LAR CNT composites owing to the mesoscopic dispersion structure of CNTs which directly depends on the aspect ratio [7]. Zhang et al. [8] observed that the fatigue crack growth rates of epoxy matrix can be significantly reduced by increasing the aspect ratio of multi-walled carbon nanotubes (MWNT). Zhang et al. [9] also showed that longer nanotubes produce a higher toughening efficiency in polypropylene/CNT nanocomposites than the shorter ones. In contrast, Dubnikova et al. [10] reported that increase in the MWNTs aspect ratio reduces their efficiency due to the low flexibility and less entanglement of thick (LAR) nanotubes. Ayatollahi et al. [4] proposed a correction factor based of MWNT's dimensions to modify the predictions of Halpin–Tsai theory for modulus of epoxy nanocomposite. Hernandez-Perez et al. [11] pointed out that epoxy/HAR mixture presented higher viscosity which does not favor CNT's proper dispersion.

From a macro-kinetic point of view, the study of cure kinetics of polymers as a function of the processing and material parameters is of a great importance in the analysis

and design of processing operations [12]. Many studies have verified that introduction of carbon nanotubes can affect the cure behavior of epoxy resins [13–15].

Lau et al. [16] dispersed CNTs into epoxy matrix incorporating various solvents and found that even small traces of residual solvent had a significant impact on the cure reaction of epoxy resin. Puglia et al. [17, 18] demonstrated that incorporation of carbon nanotubes increased the rate of cure reaction and the thermal degradation of diglycidyl ether segment of the DGEBA epoxy matrix. The findings on cure kinetics and thermal degradation of the epoxy nanocomposites can be correlated to the ultrahigh thermal conductivity of CNTs and the ability of the epoxy resin to disperse the CNTs, providing a larger surface area for heat propagation. The effects of different grades of single-walled carbon nanotubes (SWNTs) on the curing behavior of epoxy were studied via a differential scanning calorimetry (DSC) method. It was observed that CNTs initiate the curing process of epoxy at lower temperatures, whereas the overall cure reaction was slowed down [19].

DSC was used to elucidate differences in the cure behavior of DGEBA epoxy originated from the surface chemistry of CNT. The comparison of the results hinted that the cure mechanisms of nanocomposites containing fluorinated CNT are similar to those of the neat resin, but different from that of the nanocomposites with carboxylated CNT [20]. Higher extent of reaction was reported for the composite obtained using the plasma-fluorinated SWNTs due to the covalently attached amine groups on CNTs [21].

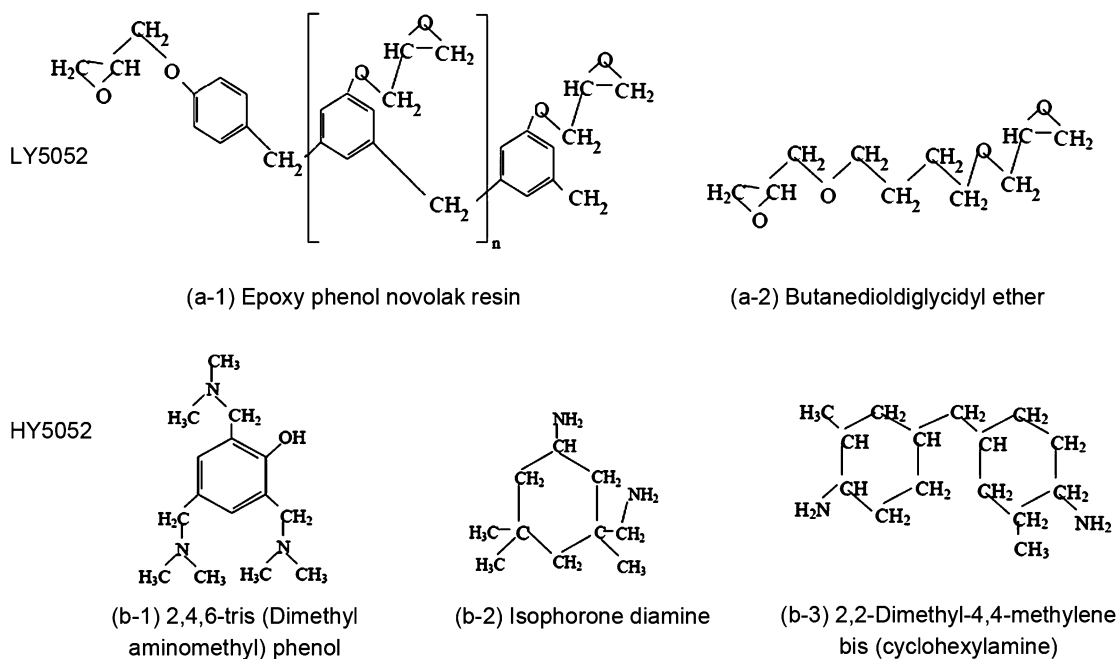
In another study, the accelerating effect of CNTs functionalized by liquid crystal epoxy resin (ef-CNTs) on cure of epoxy matrix was demonstrated [22].

As mentioned, a number of studies have been conducted on the cure reaction of epoxy system versus CNT content, but scarcely any published papers have been available to date on the influence of CNT aspect ratio on the cure kinetics of the epoxy system. The novel target of this study is to seek the influence of CNT aspect ratio on the cure kinetics of epoxy resin. Also, the purpose of this work is to provide a comprehensive understanding about the key role of temperature in the cure kinetics of epoxy. Particular emphasis is given to the glass–rubber transition temperature (T_g) and the experimental work has been elaborated to explain the influence of T_g on the cure kinetics of epoxy system for the first time.

Experimental

Materials

The polymer matrix (Araldite LY 5052/Aradur HY 5052, Huntsman, Switzerland) was used as a standard low viscosity epoxy [23] along with a hardener based on modified cycloaliphatic amines (HY5052). The chemical structures of the epoxy resin system are shown in Scheme 1 [24]. Different types of nanotubes were employed and their corresponding dimensions are listed in Table 1.



Scheme 1 Chemical structures of Araldite LY 5052/Aradur HY 5052 epoxy resin systems

Table 1 Different types of CNTs employed in the present study

Category	Diameter range (nm)	Length range ^a (μm)	Average aspect ratio (l/d)
SW	2–6	10–30	6,250
DW	6–10	10–30	3,125
MW-A	20–30	10–30	1,000
MW-B	40–60	10–30	500

SWNT single-wall carbon nanotube, DWNT double-walled carbon nanotube, MWNT-A multi-walled carbon nanotube: type A, MWNT-B multi-walled carbon nanotube: type B

^a According to the datasheet, the average length was assumed to be 25 μm

Preparation of nanocomposites and neat epoxy specimens

In the preparation of nanocomposites, CNTs were sonicated in the hardener for 30 min prior to curing. Afterward, the epoxy was mixed with a hardener and stirred in a water–ice bath at 100 rpm to avoid bubbles and curing. The mixture was poured into a rectangular cavity silicone mold and subject to 24 h of cure at room temperature followed by 4 h of post-cure at 100 °C.

Characterization

The overall quality of the CNTs' dispersion in epoxy matrix was determined via observing their cryo-fractured surfaces under a Vega/Tescan (Czech Republic) scanning electron microscope (SEM). A priori, the SEM specimens were prepared by fracturing the samples in liquid nitrogen. The dynamic thermo-mechanical tests were carried out on a cured sample using single cantilever bending fixture on a dynamic mechanical analyzer (DMA-TRITON, Tritec 2000 DMA, Lincolnshire, UK) according to ASTM-E 1640. The curing cycle was 24 h at ambient temperature followed by 4 h at 100 °C. The heating rate and frequency were set at 10 °C/min and 1 Hz, in the temperature range from 25 to 170 °C. Isothermal calorimetric tests were performed on a differential scanning calorimeter (DSC) Netzsch 200F3 (Germany) coupled with an intercooler. The procedure performed in isothermal scans was as follows. Samples of about 22 mg were heated from ambient temperature to isothermal temperatures (110, 120, 130 °C) at a scan rate of 70 °C/min. Dynamic scan was then carried out on the same specimen to make sure that the heat of reaction required to complete the cure process (post-cure heat or residual heat) was zero (not shown here).

Theoretical concept

The characteristics obtained from DSC thermograms are given in the following equation:

$$H_{\text{tot}} = H_{\text{iso}} + H_{\text{res}} \quad (1)$$

where H_{tot} , H_{iso} and H_{res} are the total heat of the reaction, the heat evolved during an isothermal scanning at the desired temperature and the residual heat obtained via dynamic scanning, respectively [18]. The degree of cure (α) is defined as follows:

$$\alpha = \frac{H_t}{H_{\text{tot}}} \quad (2)$$

where H_t is the partial area under the DSC isotherm trace up to time t [17]. The general curing kinetic mechanism is described as follows:

$$\frac{d\alpha}{dt} = k(T) \times f(\alpha) \quad (3)$$

where $k(T)$, $f(\alpha)$ and $\frac{d\alpha}{dt}$ are the Arrhenius rate constant at temperature T (1/s), the reaction model and reaction rate (1/s), respectively [25]. The curing kinetics of epoxy resins can be classified in two main groups: n th order and autocatalyzed. The former obeys the general form given by Eq. (4) [26]:

$$f(\alpha) = (1 - \alpha)^n, \quad (4)$$

and the latter has the following form:

$$f(\alpha) = \alpha^m \times (1 - \alpha)^n, \quad (5)$$

where n and m are reaction orders [27]. The activation energy (E_a , J/mol) and exponential factor (Z , 1/s) are calculated from Eq. (6) (R is the gas constant) as follows:

$$k(T) = Ze^{\frac{-E_a}{RT}}. \quad (6)$$

Results and discussion

Surface fracture morphology

The two main critical issues in the preparation of epoxy/CNT nanocomposites are adequate dispersion of the CNTs within the matrix and strong interfacial adhesion between the CNT and epoxy matrix [20, 28]. Several research works have recently been devoted to investigate the effect of CNT's aspect ratio on dispersion of CNTs in the epoxy matrix [4, 11, 16]. They observed that the higher aspect ratio of CNTs promoted tube agglomeration.

Due to the mentioned fact, the epoxy sample filled with 0.5 wt% of SWNTs was chosen for morphology studies. Figure 1a shows the cryo-fractured surface morphology of the 0.5 wt% epoxy/SW sample. It is observed that SWNTs were effectively dispersed in the epoxy resin matrix. It can be concluded that the employed mixing process is beneficial to obtain a good dispersion of SWNTs in the epoxy

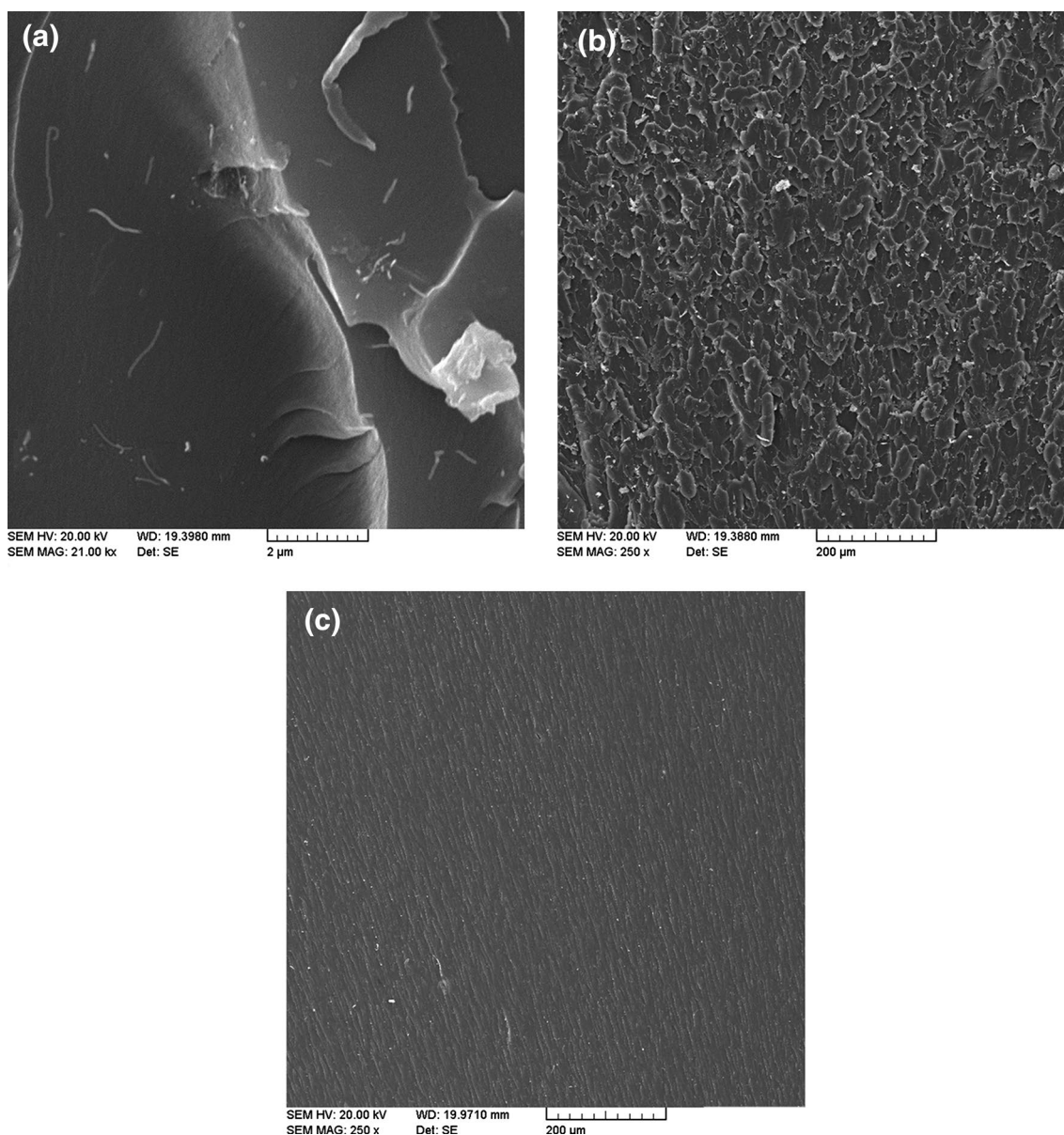


Fig. 1 SEM micrographs of the fracture surface of the epoxy nanocomposites with 0.5 wt% loading of SWs (a, b) and neat epoxy (c)

resin. Interaction between SWNTs and epoxy resin was clearly witnessed by comparison of SEM micrographs in Fig. 2b, c. The nanocomposites (Fig. 1b) showed a rough fracture surface characterized by the presence of thick river patterns [29], whereas, the fracture surface of a neat epoxy resin (Fig. 1c) appears typically cleavage like [30].

As seen, the fracture surface of the nanocomposite is very rough, suggesting that the failure phenomenon occurred through a plastic deformation. Increasing surface roughness causes the path of the crack front to deviate when it interacts with SWNTs, which makes crack propagation more difficult. On the contrary, the smooth fracture surface of neat epoxy indicates that brittle failure

is dominant. These observations are in agreement with the surface morphology reported by others [28].

Isothermal curing kinetics

CNTs' content effect

Isothermal curing studies were accomplished with the aim of determining the kinetic parameters of the curing reactions in epoxy nanocomposites. A priori, DMA tests were performed to determine the glass–rubber transition temperatures (T_g) of neat epoxy resin and its nanocomposites to obtain an appropriate temperature range for the isothermal cure test.

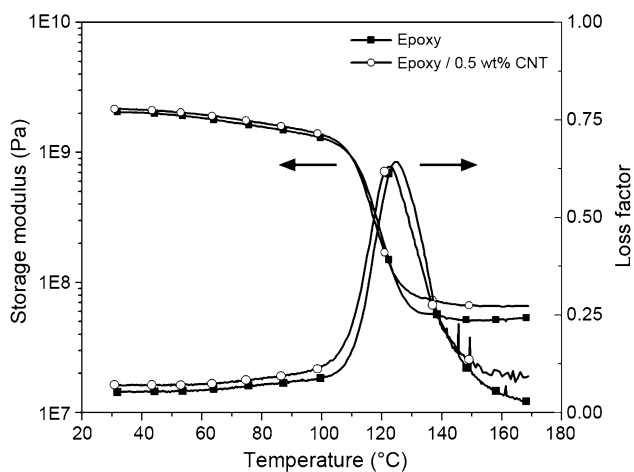


Fig. 2 Variation of storage modulus (E') and loss factor ($\tan \delta$) of the neat epoxy and its nanocomposite with 0.5 wt% loading of m-CNTs

The storage modulus (E') and loss factor ($\tan \delta$) of the nanocomposites were measured by DMA as a function of temperature for neat epoxy and the sample with 0.5 wt% of mixed CNTs (m-CNTs), which are given in Fig. 2. Mixed CNTs were generally prepared by physical mixing of equal weights of the four CNT types given in Table 1. Over the whole range of temperature, the epoxy nanocomposite exhibits a higher storage modulus than the neat epoxy. Although the addition of m-CNTs to the epoxy matrix slightly affected (8 % increase) the storage modulus in the glassy region, there was a considerable enhancement (25 % increase) in rubbery region storage modulus. This behavior could be associated with an improved interfacial interaction due to the extensive special surface area (SSA) of the CNTs [31]. Increasing trend of modulus at higher CNT contents has been reported previously [32]. This interfacial interaction hinders the mobility of the epoxy matrix segments in the vicinity of the CNTs and leads to an observable increase in E' value [33, 34].

Table 2 shows a summary of values of storage modulus, both in glassy and rubbery states for the neat epoxy and its nanocomposite. Also, the peak of $\tan \delta$ corresponding to α -relaxation was reported as glass to rubber transition temperature (T_g). Besides the influence on E' , introduction of m-CNTs into the epoxy matrix results in a shift of T_g toward lower temperatures. This effect has also been reported by other authors, although several causes are suggested for the occurrence of this phenomenon. It might be initiated due to lack of stoichiometry generated by the preferential adsorption of any of the reactive constituents onto the hollow CNTs which may lead to inhibition of cross-linking reaction between the epoxy and hardener [35, 36].

Another possibility is that CNTs can act as high-quality plasticizers and interact strongly with the epoxy matrix.

Table 2 Comparison of storage modulus and T_g in neat epoxy and its nanocomposite with 0.5 wt% loading of m-CNTs

Sample	E'_G (Pa)	E'_R (Pa)	T_g ($^{\circ}\text{C}$)
Epoxy	1.8×10^9	5.2×10^7	124
Epoxy/0.5 wt% m-CNTs	1.95×10^9	6.5×10^7	122

T_g glass to rubber transition temperature, E'_G glassy storage modulus at 60 $^{\circ}\text{C}$, E'_R rubbery storage plateau modulus at 160 $^{\circ}\text{C}$

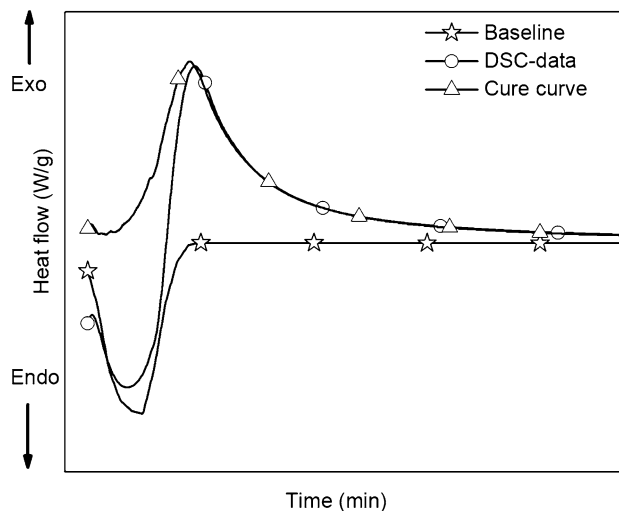


Fig. 3 Schematic showing the approach used to calculate the accurate cure thermogram of heat flow versus time

They can create an interphase region, restraining the epoxy system from exchanging energy with the surroundings [35]. For both the examined materials, the loss factor ($\tan \delta$) shows a sharp peak around 120 $^{\circ}\text{C}$ corresponding to T_g of the epoxy system. According to the datasheet of LY5052/HY5052 by Huntsman Inc. [23], the maximum attainable T_g for this epoxy system is about 130 $^{\circ}\text{C}$. Thus, based on the datasheet and DMA result presented in the manuscript, the authors are almost sure that at 110 $^{\circ}\text{C}$ the system is in its glassy state. Therefore, taking into account DMA data, isothermal curing tests were carried out at different temperatures in the range of 110–130 $^{\circ}\text{C}$ to investigate cure reaction at both glassy and rubbery states. To avoid any effect of CNTs' dimensions, m-CNTs (a mixture of all four types of CNTs mentioned in Table 1) were used in the study of the effect of CNTs' content on cure kinetics of the epoxy resin.

To exclude the endothermic heat flow required to raise the temperature of a substance to a given isothermal temperature, the following procedure was employed. The heat flow versus time thermogram of non-reacted epoxy resin and amine hardener (exactly at the same weight ratio) was used as baseline to calculate the cure thermogram of epoxy

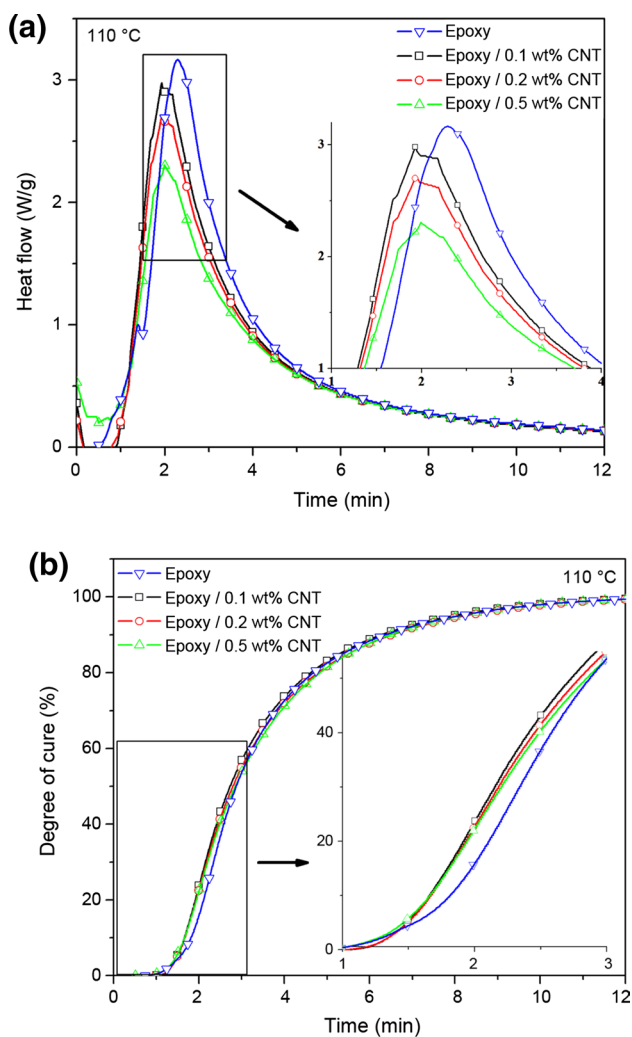


Fig. 4 Isothermal DSC curves for LY5052/HY5052 epoxy system and its nanocomposites. **a** Heat flow and **b** degree of curing versus time at 110 °C with different m-CNT contents

and its nanocomposites. In other words, the heat flow curve of the non-reacted epoxy/hardener system was subtracted from the heat flow curve of the samples obtained from DSC to extract the accurate exotherm of the cure process. For a clearer conception, a schematic of the approach is shown in Fig. 3.

The effect of CNT content on the cure of epoxy resin extracted from the DSC isotherm is shown in Figs. 4, 5, 6. All degree of cure curves present a sigmoidal form, indicative of an autocatalytic kinetics, due to the structural and molecular variations that occur during the cure process via amine–epoxide reaction [33, 37]. It is obvious from the cure curves that maximum reaction rates are attained at time $t > 0$. Thus, the n th order kinetics becomes invalid pointing to the autocatalytic model. The n th order kinetic model is suitable only if the maximum reaction rate occurs at $t = 0$. But in the autocatalytic model, the rate shows a

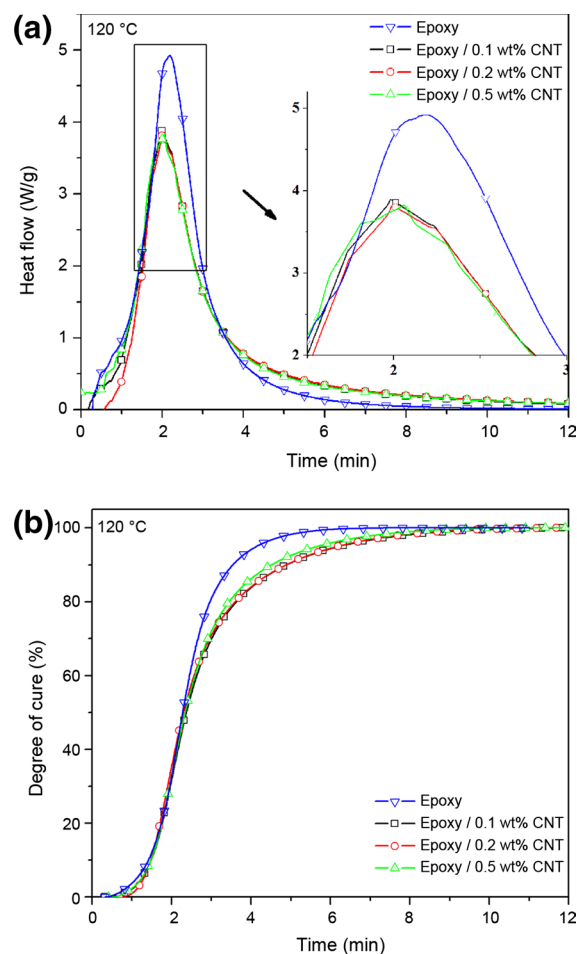


Fig. 5 Isothermal DSC curves for LY5052/HY5052 epoxy system and its nanocomposites. **a** Heat flow and **b** degree of curing versus time at 120 °C with different m-CNT contents

maximum at an intermediate conversion [36]. Frequently, “autocatalytic” behavior, explicitly with a maximum reaction rate at non-zero times, was reported for epoxy systems [14, 38]. The cure process includes initially the “gelation” process, increasing the viscosity of resin due to a progressive free volume reduction [39], since “gelation” followed by diffusion-controlled effects take place by the “vitrification” process [14].

The total area under the thermogram, based on the non-reacted LY5052/HY5052 composite, was calculated as the total heat of cure reaction. The maximum of the exotherm peak (t_p) and the total heat of reaction (H_{tot}) as a function of the m-CNTs’ content are reported in Table 3. Namely, the introduction of m-CNTs does not affect the overall cure mechanism of epoxy resin. However, exothermic peaks and total heat of reaction of epoxy/m-CNT nanocomposites were found to be smaller than that of the neat epoxy which has also been reported by others [13, 14, 20].

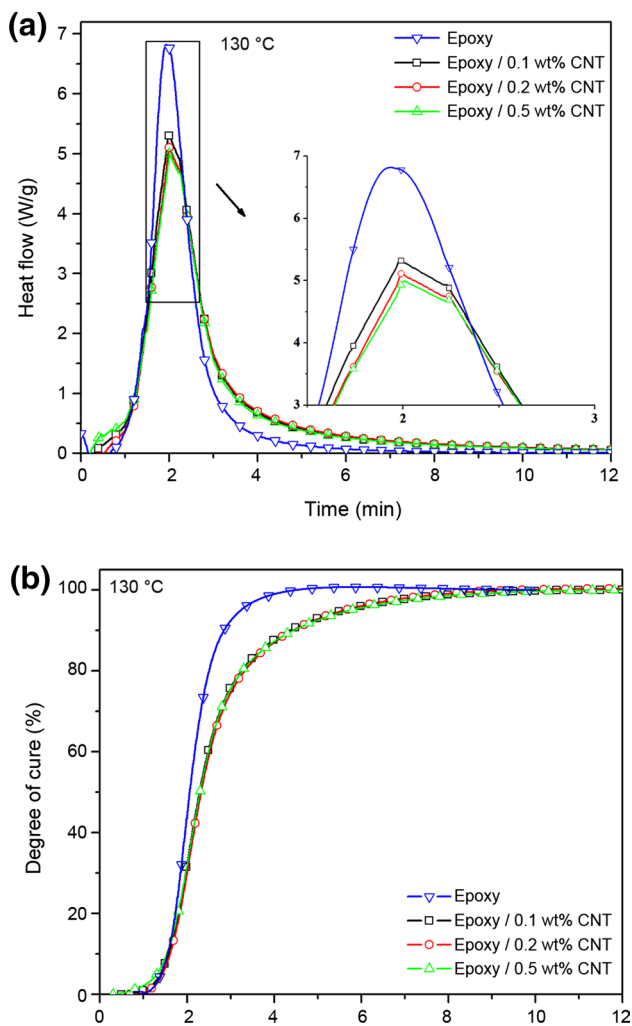


Fig. 6 Isothermal DSC curves for LY5052/HY5052 epoxy system and its nanocomposites. **a** Heat flow and **b** degree of curing versus time at 130 °C with different m-CNT contents

The values of isothermal enthalpy (H_{tot}) increased by increasing the isothermal cure temperature. This is related to the fact that the increase in isothermal reaction temperature for exothermic reactions generates heat in a higher proportion than the heat generated by the reaction itself [20]. For a given reaction temperature, the enthalpy of epoxy/CNT nanocomposites decreased relative to the neat resin. The decrease of H_{tot} with increasing m-CNT content can be directly attributed to the proportional decrease of epoxy concentration in the nanocomposite [14]. Furthermore, this suggests that the presence of the nanotubes causes an increase in viscosity which lowers the mobility of the reactive species and results in a lower enthalpy [20].

As known, the activation energy is the extent of energy barrier for a reaction [22]. Therefore, increase in viscosity which hinders the curing process is expected to raise activation energy. At elevated temperatures, thermal energy

Table 3 Comparison of isothermal DSC scan results for epoxy filled with different types and contents of CNTs

T_{iso} (°C)	Sample	CNT content (wt%)	T_{peak} (min)	H_{tot} (J/g)
110	Epoxy	0	2.29	411.48
	Epoxy/0.1 wt% m-CNT	0.1	2.01	387.71
	Epoxy/0.2 wt% m-CNT	0.2	2.03	367.78
	Epoxy/0.5 wt% m-CNT	0.5	2.07	319.64
	Epoxy/SW	0.01	2.23	415.02
	Epoxy/DW	0.01	2.25	402.90
	Epoxy/MW-A	0.01	2.25	383.90
	Epoxy/MW-B	0.01	2.29	380.22
120	Epoxy	0	2.12	458.22
	Epoxy/0.1 wt% m-CNT	0.1	1.97	419.04
	Epoxy/0.2 wt% m-CNT	0.2	1.98	399.03
	Epoxy/0.5 wt% m-CNT	0.5	2.03	396.92
	Epoxy/SW	0.01	2.12	447.89
	Epoxy/DW	0.01	2.21	432.83
	Epoxy/MW-A	0.01	2.21	404.47
	Epoxy/MW-B	0.01	2.25	427.25
130	Epoxy	0	1.84	493.49
	Epoxy/0.1 wt% m-CNT	0.1	1.99	462.45
	Epoxy/0.2 wt% m-CNT	0.2	1.99	456.28
	Epoxy/0.5 wt% m-CNT	0.5	2.00	452.71
	Epoxy/SW	0.01	1.91	482.21
	Epoxy/DW	0.01	2.04	459.44
	Epoxy/MW-A	0.01	2.05	460.55
	Epoxy/MW-B	0.01	2.07	470.88

becomes comparable to or higher than the energy barrier, which make it easier to overcome the heights of potential barriers [40]. This is consistent with the observed fact that the increase in isothermal temperatures decreases the total enthalpy difference between neat epoxy and epoxy/CNT samples. It can be concluded that the potential barrier of cure behavior (activation energy) has a range of validity at low temperatures, but are gradually be washed out as the temperature is raised. A similar effect was observed by Abdalla et al. [20]: by increasing temperature for a DGEBA/carboxyl-modified MWNT nanocomposite, the difference between the total heat of neat epoxy and epoxy/CNT decreased.

The maximum of the exothermic peaks of the neat epoxy resin is located around 2.29, 2.12 and 1.84 min at 110, 120 and 130 °C, respectively. A similar trend with increasing isotherm temperature was also observed for m-CNT-filled epoxy nanocomposite. This small decrease of the maximum of the exotherm peak is expected to be due to an increase in the isotherm cure temperature that can accelerate the cure reaction. Another notable observation is the slight shift of t_p for epoxy nanocomposites which depends

on the temperature of isotherm cure. On detecting the early stage of cure reaction, one can observe that at 110 °C the cure reaction of m-CNT-filled epoxy resin accelerates at the initial stage, whereas the opposite behavior is observed at higher temperatures at (130 °C).

Earlier reports revealed that there were several factors such as the thermal properties of CNTs [29], reduced molecular chain mobility [38], increased viscosity of epoxy in the presence of CNTs [41] and chemical species on CNTs' surfaces [34] that can influence the cure kinetics of epoxy resin. In the case of unmodified CNTs, two competitive effects arose from the presence of CNTs: (a) accelerating effect due to high thermal conductivity of CNTs, and (b) decelerating effect due to the restriction in molecular mobility imposed by CNTs (or increased viscosity). Accelerating effect of CNTs due to their high thermal conductivity might be dominant at 110 °C compared to 130 °C, owing to restricted motion of polymer chains leading to lower t_p values. Thus, the high thermal conductivity of the CNTs enhances the cure kinetics at high temperatures (130 °C) even at low m-CNT content. Although the change in t_p value of isotherm curing process is evident at the lowest CNT content, there is a negligible change with further increase of m-CNT content.

Tables 4, 5 summarize the activation energy and reaction order for the neat resin and nanocomposites using the autocatalytic model (Eq. 5). When the autocatalytic equation is employed for epoxy/amine system, the overall order of the reaction is 2, with $m + n \approx 2$. The higher activation energy of the nanocomposites compared to that of the neat resin is reported in the literature [33, 42].

As known, during the cure reaction, the system undergoes gelation and vitrification transitions. Intensive cross-linking occurring in the region between the above transitions restricts molecular mobility, causing the cure reaction to change from a kinetic-controlled mechanism to a diffusion-controlled regime [25]. The accelerating effect of CNTs due to their high thermal conductivity and decelerating effect of CNTs due to the restriction in molecular mobility imposed by CNTs (or increased viscosity) are predominant in diffusion-controlled and kinetic-controlled regimes, respectively. The K parameter governs the autocatalytic reaction after the initial autocatalytic stage [43], i.e., between gelation and vitrification transition. It is found that the cure temperature shows a positive effect on the K value, similar to that observed for epoxy/carboxylated CNT system [20]. With increasing temperature, vitrification occurs faster and the diffusion-controlled regime is extended. Thus, the accelerating effect of CNTs owing to high thermal conductivity can overcome the decreasing effect of CNTs due to increase of viscosity. The decreasing effect of CNTs is gradually washed out by increasing the

Table 4 Values of cure parameters of LY5052/HY5052 system and related nanocomposites with different types and contents of CNTs

T_{iso} (°C)	Sample	CNT content (wt%)	$k(T)$ (min ⁻¹)	m	n
110	Epoxy	0	2.15	0.81	1.92
	Epoxy/0.1 wt% m-CNT	0.1	1.34	0.52	1.65
	Epoxy/0.2 wt% m-CNT	0.2	1.28	0.52	1.66
	Epoxy/0.5 wt% m-CNT	0.5	1.31	0.59	1.67
	Epoxy/SW	0.01	1.86	0.76	1.75
	Epoxy/DW	0.01	2.35	0.97	1.88
	Epoxy/MW-A	0.01	2.02	0.91	1.80
	Epoxy/MW-B	0.01	1.88	0.84	1.79
	120	Epoxy	0	3.48	1.11
Epoxy/0.1 wt% m-CNT		0.1	3.01	0.94	1.65
Epoxy/0.2 wt% m-CNT		0.2	2.53	0.77	1.78
Epoxy/0.5 wt% m-CNT		0.5	2.84	0.91	1.70
Epoxy/SW		0.01	3.13	1.00	1.59
Epoxy/DW		0.01	2.98	1.00	1.83
Epoxy/MW-A		0.01	2.82	1.04	1.59
Epoxy/MW-B		0.01	3.09	1.08	1.64
130		Epoxy	0	4.29	0.92
	Epoxy/0.1 wt% m-CNT	0.1	4.06	0.98	1.87
	Epoxy/0.2 wt% m-CNT	0.2	3.68	0.92	1.83
	Epoxy/0.5 wt% m-CNT	0.5	4.81	1.13	1.97
	Epoxy/SW	0.01	3.53	0.89	1.35
	Epoxy/DW	0.01	4.30	0.98	1.91
	Epoxy/MW-A	0.01	3.98	1.06	1.86
	Epoxy/MW-B	0.01	3.52	0.87	1.64

Table 5 Activation energies and pre-exponential factors for each epoxy/CNT nanocomposites

Sample	E_a (kJ/mol)	Z
Epoxy	5.94	15.15
Epoxy/0.1 wt% m-CNT	9.01	27.5
Epoxy/0.2 wt% m-CNT	9.14	25.2
Epoxy/0.5 wt% m-CNT	11.07	55.66
Epoxy/SW	5.33	11.18
Epoxy/DW	5.70	13.84
Epoxy/MW-A	6.27	14.56
Epoxy/MW-B	5.26	10.95

temperature of curing. Diminishing decelerating effect of CNTs is more obvious at high content of CNTs (the sample with 0.5 wt% of CNTs), which show a higher value of K than neat epoxy.

It is interesting to observe that by increasing the curing time, in the last stage of cure reaction there is a significant influence of the presence of CNTs. At the last stage of cure reaction after vitrification transition, T_g plays a key role

in cure behavior of epoxy resin. Considering the vitrification phenomenon, the cure is mainly diffusion controlled at times above 6 min. Below T_g (110 °C), insignificant modification in the last stage of cure reaction is expected by addition of CNTs due to the scarce molecular motion after vitrification. Above T_g (130 °C), the effect of CNTs on cure behavior becomes clear due to the possible molecular motion of the epoxy matrix.

CNTs' aspect ratio effect

In spite of changing the cure kinetic parameters of epoxy, by increasing the CNT content, the overall cure mechanism of epoxy remains unchanged. To minimize the effect of CNT content, a very low content of every type of CNTs (0.01 wt%) was chosen for further investigation on the effect of CNTs' aspect ratio on cure kinetics. Increasing the length over diameter ratio (l/d) of CNTs initiates numerous phenomena in the epoxy matrix, which can cause opposite effects on the curing behavior as well as other mechanical [43], electrical [4] and thermo-mechanical [11] properties. Among these different issues, increase in thermal conductivity and viscosity of epoxy resin upon increasing l/d were found to affect epoxy nanocomposite cure behavior significantly.

Increasing thermal conductivity (λ , W/mK) of nano-fillers with increasing aspect ratio is the result of two facts: (a) the inherently higher individual thermal conductivity of CNTs which possesses higher l/d ratio ($\lambda_{SW} \geq \lambda_{DW} \geq \lambda_{MW-A} \geq \lambda_{MW-B}$) [44] and (b) easier formation of heat-conductive network in epoxy matrix, e.g., thermal percolation threshold (φ_C and wt%) for CNTs with higher aspect ratio [45].

Percolation threshold [46] characterized by a sharp drop of several orders of magnitude in thermal resistivity decreased with increasing aspect ratio of CNTs. Depending on the aspect ratio of CNTs and processing procedure, percolation thresholds between 0.0025 and 10 wt% have been experimentally observed for epoxy/CNT nanocomposites. Diffusion processes and particle–particle interactions in a matrix of low viscosity filled by nano-particles play a key role in the agglomeration and network formation [45]. Decreasing thermal percolation threshold of nano-fillers with increasing aspect ratio can be interpreted by some analytical models such as excluded volume theory [47]. The concept of excluded volume is a reliable approach to estimate the percolation threshold of nanocomposites containing randomly dispersed non-spherical nano-particles including CNTs [48]. A conducting network may be formed if the excluded volumes of two conductive nano-particles overlap. As the excluded volume reduces, the percolation threshold decreases which means a conductive network is formed at lower concentrations of conductive

nano-particles [4]. The increase of aspect ratio of conductive nano-particles has proven to be effective in reducing the excluded volume [49]. Therefore, with higher aspect ratio, more heat-conductive CNTs are definitely expected. Furthermore, the presence of CNTs causes an increase in viscosity of the epoxy matrix at the expense of lowering the mobility of reactive species of the curing reaction [20]. The introduction of high aspect ratio CNTs causes a viscosity increase of epoxy monomers markedly compared to that of low aspect ratio CNTs, due to their higher specific area [35].

Heat flow and degree of cure versus time (t) curves obtained at different isothermal temperatures for HY5052/LY5052/CNT nanocomposites for different CNT dimensions are reproduced in Figs. 7, 8, 9. The results of the neat epoxy and the analogous nanocomposites t_p and H_{tot} with the same CNT content for different types of CNT are summarized in Table 3.

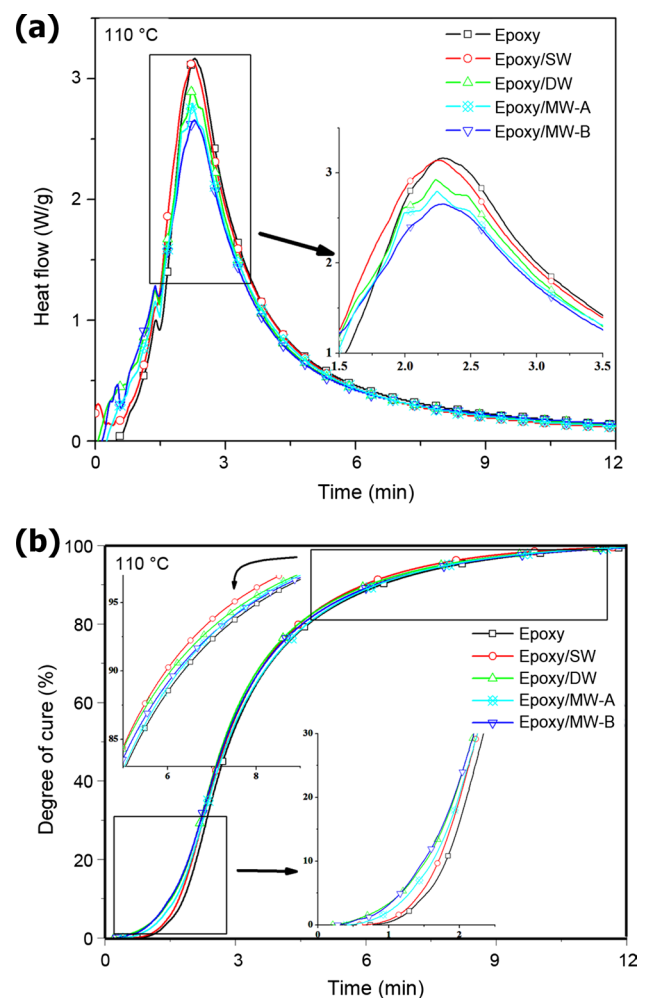


Fig. 7 Isothermal DSC curves for LY5052/HY5052 epoxy system and its nanocomposites. **a** Heat flow and **b** degree of curing versus time at 110 °C with different CNT types

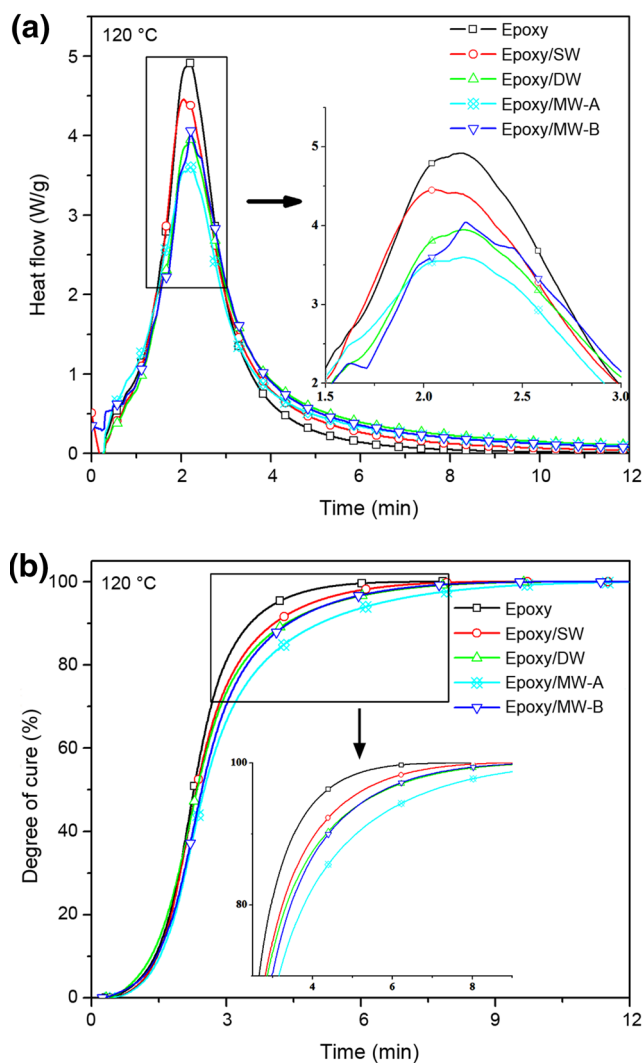


Fig. 8 Isothermal DSC curves for LY5052/HY5052 epoxy system and its nanocomposites. **a** Heat flow and **b** degree of curing versus time at 120 °C with different CNT types

Below T_g in glassy region (at 110 °C), in general, one can say that the addition of small amount of SWNTs and double-walled carbon nanotubes (DWNTs) significantly increased the cure rate in the initial stage of cure reaction, whereas MWNTs did not significantly influence the first 3 min of curing. The comparison of the results in Fig. 7b leads to an overall picture which opens new perspectives in modifying the thermal conductivity of polymer matrix systems via introduction of CNTs. The reported thermal conductivity for SWNT and MWNTs at room temperature is 6,600 and 200–3,000 W/mK, respectively [50].

According to the literature [51], a certain enhancement of the thermal conductivity of epoxy nanocomposites, by incorporation of CNTs with high ld may be expected. It is also expected that a low percolation threshold could be obtained by dispersing SWNTs in an epoxy matrix.

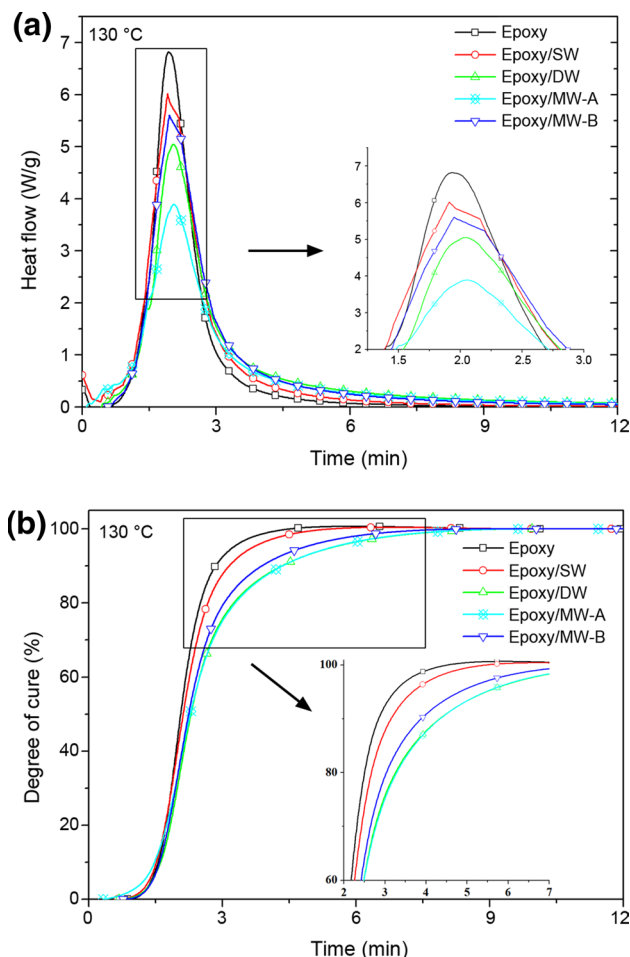


Fig. 9 Isothermal DSC curves for LY5052/HY5052 epoxy system and its nanocomposites. **a** Heat flow and **b** degree of curing versus time at 130 °C with different CNT types

Therefore, the accelerated cure of epoxy in the presence of the high aspect ratio CNTs (SWNTs and DWNTs) can be associated with high thermal conductivity of the epoxy nanocomposites. It has been proven that introduction of SWNT can improve the thermal stability and accelerate the heat absorption of the epoxy (heat-sink effect) [16]. But the stronger catalytic effect of MWNTs compared to that of SWNTs in the early stage of the cure process (the first 3 min of curing process) still needs to be investigated in depth

This inconsistency may be solved when looking at the relative surface area of CNTs. Compared to SWNTs and DWNTs, MWNTs showed the highest potential for the efficient enhancement of initial cure reaction. This is due to the relatively lower surface area of MWNTs which decreases their ability to adsorb curing species on their surfaces [50]. In addition, lower H_{tot} can be accounted for by the fact that the presence of the CNTs subordinates the mobility of the reactive species of cure reaction.

Above T_g , it can be seen that epoxy/CNTs nanocomposite exhibits a longer t_p and larger H_{tot} values. From Fig. 9b, it is evident that the acceleration effect of CNTs on the early stage of curing is not noticeable at high temperatures. This may be due to the fact that above T_g , an increase in viscosity reduces the mobility of reactive species. Here, large segments of the molecules can start to wiggle around, whereas below T_g the polymer molecules are frozen. In addition, rapid molecular motions above T_g negatively affect the initial cure rate of epoxy by suppressing the formation of high thermal-conductive network of CNTs, as a prerequisite for accelerating epoxy cure.

Application of least squares method to autocatalytic equation gives values of empirical parameters m , n and k listed in Table 4. Activation energies and pre-exponential parameter obtained by nonlinear regression are given in Table 5. Since CNTs can hinder curing reactions by influencing the molecular diffusivity, it is expected that pure CNTs show a negative effect on cure reaction and increase its activation energy. But in this case, due to a very low CNT content, some high thermal-conductive CNTs such as SWNTs can partially compensate this effect and reduce the activation energy of cure reaction. A slight uneven change in activation energy is correlated to competition between heat-sink and viscosity-increasing effects of CNTs of various aspect ratios. As shown above, the key points here are effect of both content and dimensions of CNT on the cure reaction of epoxy which are determined by isothermal DSC measurements below or above the T_g value.

Conclusion

Investigation of isothermal curing using DSC indicates that the effective parameters of CNTs in curing reaction of epoxy are (1) specific surface area, (2) aspect ratio (l/d) and (3) thermal conductivity. These parameters are correlated to heat-sink and viscosity-increasing effects of CNTs on cure process. It was observed that H_{tot} decreased on introducing a small quantity of CNTs. This is followed by a further significant decrease with increasing CNT loadings which can be directly attributed to the proportional decrease in reactive species concentration. Furthermore, below T_g , t_p is hastened with introduction of CNTs into the epoxy matrix, but above T_g the peak is somehow delayed compared to that of the neat epoxy. The shift of t_p is well apparent at the lowest CNT content, but there is no significant change in t_p with further increase in CNT content. DSC results focusing on the effect of CNT dimensions indicated that the composite cure is influenced not only by the viscosity-increasing effect of CNTs, but also by the heat-sink effect. The competition between these two factors determines the final cure characteristics of epoxy nanocomposites. The increased

thermal conductivity (heat-sink effect) induced by high aspect ratio CNTs and its effect on initial cure is more obvious at the low isothermal temperatures. Increasing l/d of CNTs at high isothermal temperatures does not produce any relative accelerating effect, suggesting a predominant viscosity-increasing effect of CNTs against the heat-sink effect. It was observed that CNTs were able to change the cure process of the epoxy system depending on the temperature of isothermal cure. In the glassy state, the accelerating effect of CNTs due to their high thermal conductivity is dominant owing to restricted motion of polymer chains. In the rubbery state, the decelerating effect of CNTs is predominant due to their viscosity-increasing effect.

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