

Effect of silane treatment of carboxylic-functionalized multi-walled carbon nanotubes on the thermal properties of epoxy nanocomposites

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Abstract. The effect of silane treatment of carboxylic-functionalized multi-walled carbon nanotubes (COOH-MWCNTs) on the thermal properties of COOH-MWCNTs/epoxy nanocomposites was studied by comparing the research results on differential scanning calorimetry and thermogravimetric analysis data of silane treated COOH-MWCNTs/epoxy system with those of as-received COOH-MWCNTs/epoxy system. At the initial curing stage, silane treatment of COOH-MWCNTs does not change the autocatalytic cure reaction mechanism of COOH-MWCNTs/diglycidyl ether of bisphenol-A glycidol ether epoxy resin/2-ethyl-4-methylimidazole (COOH-MWCNTs/DGEBA/EMI-2,4) system, however, silane treatment of COOH-MWCNTs has catalytic effect on the curing process, which could help to shorten pre-cure time or lower pre-temperature. Then, at the later curing stage, silane treatment of COOH-MWCNTs promotes vitrification, which would help to shorten post-cure time or lower post-temperature. Therefore, overall, silane treatment of COOH-MWCNTs could bring positive effect on the processing of epoxy nanocomposites. Furthermore, it was also found that silane treatment of COOH-MWCNTs does not affect the thermal degradation pattern of COOH-MWCNTs/DGEBA/EMI-2,4 system, however, decreases the thermal stability of COOH-MWCNTs/DGEBA/EMI-2,4 nanocomposites.

Keywords: polymer composites, thermal properties, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA)

1. Introduction

The property enhancements of epoxy nanocomposites filled with carbon nanotubes (CNTs) are far below the expectations based on the excellent properties of CNTs. However, studies suggested that the properties can be further improved if better dispersion and more efficient interfacial adhesion can be achieved. One of the most promising approaches is to chemically modify the surface of CNTs before dispersing CNTs into epoxy [1–7]. Since silane coupling agent can act as a chemical bridge between hydrophilic CNTs and hydrophobic epoxy, silane treatment of CNTs will be efficient to

enhance CNTs/epoxy interfacial adhesion, as well as preventing the agglomeration of CNTs. Furthermore, functionalized CNTs are more desirable than non-functionalized CNTs since functionalized CNTs have more functional groups to form chemical bonding with coupling agent and/or epoxy. Therefore, in this study, we filled epoxy with γ -aminopropyl-triethoxysilane (A1100) treated carboxylic-functionalized multi-walled CNTs (COOH-MWCNTs).

Different chemical modification of CNTs would result in differences in the way the epoxy and/or the curing agent reacts with CNTs, which in turn, affect

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the cure reaction which determines the resulting properties. Recently some studies have been stimulated to address the effect of functionalized CNTs on the cure reaction of epoxy systems [7–12], however, few efforts have been made to address the effect of silane treatment of functionalized CNTs on the cure reaction of functionalized CNTs/epoxy systems. Furthermore, chemical modification of CNTs may also affect the thermal stability of epoxy nanocomposites [9], but hardly any published papers are available to date on the effect of silane treatment of COOH-MWCNTs on the thermal stability of COOH-MWCNTs/DGEBA/EMI-2,4 nanocomposites.

In this work, by comparing the research results on differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data of silane treated COOH-MWCNTs/epoxy system with those of as-received COOH-MWCNTs/epoxy system, the effect of silane treatment of COOH-MWCNTs on the thermal properties of COOH-MWCNTs/epoxy nanocomposites was studied. We do theoretical work, analyzing dynamic DSC data with an isoconversional kinetics method, to obtain the effect of silane treatment of COOH-MWCNTs on the curing kinetics of COOH-MWCNTs/DGEBA/EMI-2,4 nanocomposites. Particular emphasis is given to the study on the variation of activation energy E during the curing process, which is conducive to better understanding of the effect of silane treatment of COOH-MWCNTs on the cure behavior of nanocomposites, and thus will be valuable to provide guidance for choosing proper processing methods. This work is part of a wider investigation on high performance nanocomposites for more demanding applications, such as in nano-electronics applications.

2. Experimental

2.1. Materials

Epoxy resin used in this work was a nominally difunctional epoxy resin, Epon 828, supplied by Shanghai Resin Co. Ltd., Shanghai, China. Epon 828 is, basically, DGEBA with epoxy value of 0.48–0.52 mol/100 g. Curing agent, EMI-2,4, was offered by Beijing Chemical Reagent Co. Ltd., Beijing, China. COOH-MWCNTs were provided by Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, Chengdu, China. Details of

Table 1. Specification of as-received COOH-MWCNTs (supplied by the manufacturer)

	COOH-MWCNTs
Functionalized rate of surface carbon atom	8–10 mol%
Carboxylic group weight percentum	1–6 wt%
Purity	>95%
Color	black
Outside Diameter	50–80 nm
Inside Diameter	5–15 nm
Length	10–20 μm
Specific Surface Area	>40 m^2/g
Bulk density	0.05 g/cm^3
True density	2.1 g/cm^3
Making method	CVD

the as-received COOH-MWCNTs are summarized in Table 1. Before stored in desiccators, COOH-MWCNTs were dried at 110°C for 24 h in vacuum to eliminate the agglomeration caused by hygroscopic absorption, as well as removing surface water, which would hinder the interaction between coupling agent and COOH-MWCNTs. Amino silane coupling agent, A1100, was obtained from Shanghai Chemical Reagent Co. Ltd., Shanghai, China. Other agents utilized were analytically pure grade and supplied by Sinopharm Chemical Reagent Co. Ltd., Shanghai, China.

2.2. Silane treatment of COOH-MWCNTs

Silane treatment of COOH-MWCNTs using A1100 involved (a) making a silane-absolute ethanol solution at 0.001 g/ml concentration, and the amount of A1100 was 10% by weight of COOH-MWCNTs, (b) adding dried COOH-MWCNTs to the solution, stirring with a magnetic stirrer at 60°C for 30 min, then dispersing the solution by sonication for 1 h, (c) rinsing with absolute ethanol by filtration, then washing silane treated particles with absolute ethanol repeatedly, and (d) drying at 110°C for 1 h in vacuum. Before stored in desiccators, the dried silane treated COOH-MWCNTs were weighted and the amount of silane coupling agent introduced onto the surface of COOH-MWCNTs was about 7.3% by weight of COOH-MWCNTs.

In this study, silane treated COOH-MWCNTs, compared with as-received COOH-MWCNTs, go through an additional treatment of 30 min stir and 1 h sonication during the silane treatment process as introduced in the previous passage. This additional treatment may lead to some defects in the

nanotubes and a decrease of the aspect ratios of COOH-MWCNTs; therefore, besides the effect of functional groups of silane coupling agent, this additional treatment may also contributes to the final effect of silane treatment of COOH-MWCNTs on the thermal properties of epoxy nanocomposites.

Fourier-transform infrared (FTIR) spectra of as-received COOH-MWCNTs and silane treated COOH-MWCNTs are shown in Figure 1. It is obvious that there is a mass of OH, C=O groups on the surface of COOH-MWCNTs, while a lot of C–O–Si bonds are found to exist on the surface of silane treated COOH-MWCNTs, confirming that silane coupling agent has been covalently bonded to COOH-MWCNTs as expected. Characteristic vibrational bands of the functional groups are shown in the spectra. The intensity of the characteristic peak of OH group decreases with increasing extent of COOH-MWCNTs modification. According to Beer-Lambert Law, the characteristic peak of C=O group can be regarded as the internal standard, and then the extent of COOH-MWCNTs modification can be quantitatively calculated by Equation (1):

$$\eta = 1 - \frac{B'_{OH} / B'_{C=O}}{B_{OH} / B_{C=O}} \quad (1)$$

where B is the absorbance of as-received COOH-MWCNTs, B' is the absorbance of silane treated COOH-MWCNTs, and the OH and C=O subscripts represent OH and C=O groups, respectively. In this study, the extent of COOH-MWCNTs modification is calculated to be ~56%. Furthermore, the FTIR result (–CH stretching) shows that COOH-MWCNTs contain defects. These defects may be formed

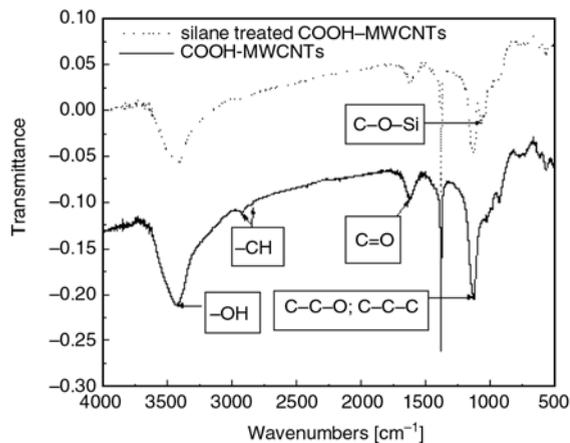


Figure 1. FTIR spectra of as-received COOH-MWCNTs and silane treated COOH-MWCNTs

during the COOH-MWCNTs manufacturing, and the silane treatment of COOH-MWCNTs has no obvious effect on the –CH peak, as shown in Figure 1.

2.3. Composites preparation

The COOH-MWCNTs/DGEBA/EMI-2,4 nanocomposites were prepared by solution blending and casting method, which involved (a) stirring

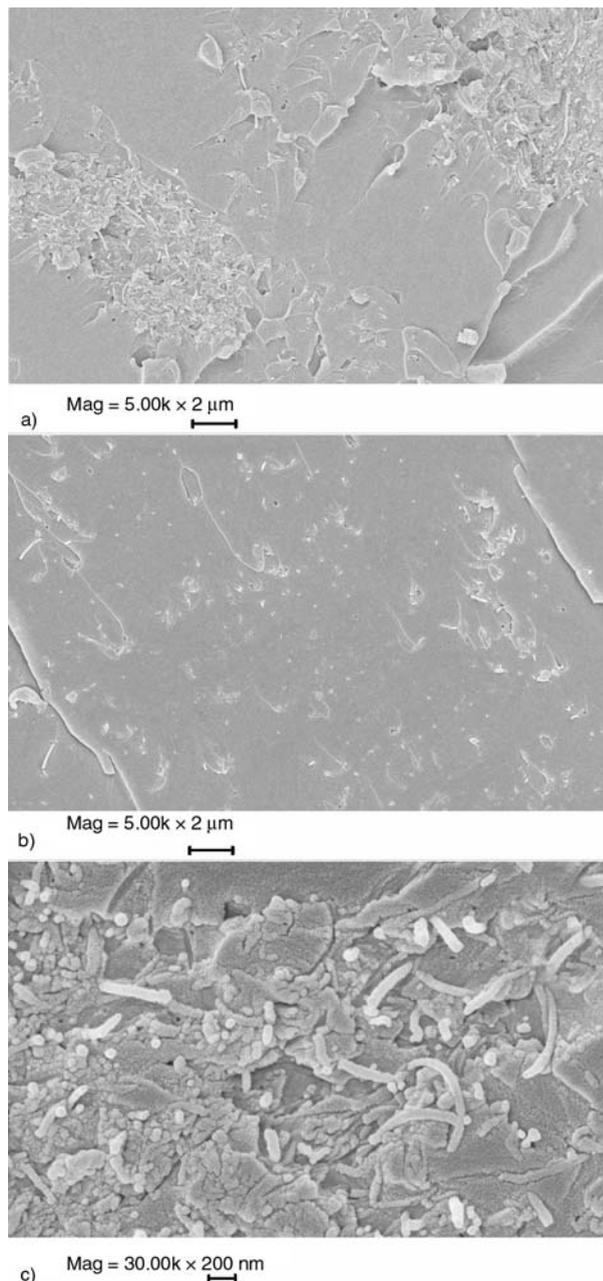


Figure 2. Micrographs of as-received 3%COOH-MWCNTs/DGEBA/EMI-2,4 nanocomposite (a) 5kx and silane treated 3%COOH-MWCNTs/DGEBA/EMI-2,4 nanocomposite (b) 5kx and (c) 30kx

DGEBA-absolute ethanol solution at 80°C with magnetic stirrer for 20 min, (b) adding appropriate amount of silane treated or untreated COOH-MWCNTs to the solution and continuing stir for 30 min, then sonicating the solution for 1 h to ensure good homogeneity, (c) cooling to 60°C, (d) adding EMI-2,4, which is 6% by weight of DGEBA, to the mixture and continuing stir for 10 min, (e) casting the mixture in mould, (f) repeatedly degassing the mixture in vacuum drying oven at 60°C until no air bubble appears on the surface of the mixture, (g) curing the mixture at 65°C for 1 h, 120°C for 1.5 h, and 160°C for 1.5 h, (h) cooling to room temperature, then demoulding.

Figure 2 shows the FE-SEM micrographs of 3%COOH-MWCNTs/DGEBA/EMI-2,4 nanocomposites. As shown in Figure 2a, as-received COOH-MWCNTs agglomerate severely, however, silane treated COOH-MWCNTs in Figure 2b are seen to be better dispersed and their distribution in matrix is relatively homogeneous, therefore silane treatment is indeed effective in improving the dispersion of COOH-MWCNTs in the epoxy matrix. Since silane treated COOH-MWCNTs' agglomeration still exists, as shown in Figure 2c, the dispersion of COOH-MWCNTs in the matrix still needs to be improved by some means in future work. Besides, naked nanotubes are observed on the fracture surface and some nanotubes are pulled out of the surface instead of being embedded and tightly held to the matrix, indicating interfacial bonding between the COOH-MWCNTs and epoxy also needs to be improved by some means in future work.

2.4. Characterization

FTIR spectra were recorded in KBr pellets on a VECTOR22 spectrometer (Bruker Co., Germany). Blank scanning was performed before measurements to eliminate the influence of water vapor and CO₂ in air.

The specimens with the compositions listed in Table 2 were prepared at ambient temperature. The base polymer formulation was prepared by mixing DGEBA and EMI-2,4 with a weight ratio of 100:6 for 15 min. A specified quantity of COOH-MWCNTs was added into the base polymer and the mixture was dispersed by sonication for 1.5 h. A sample of approximately 4 mg was weighted accurately into an aluminum DSC sample pan, and then covered with an aluminum lid.

Dynamic DSC measurements with a DSC-Q20 (TA Instruments, USA) system which was calibrated with an indium standard were performed at different heating rates of 10, 15 and 20°C/min over a temperature range of 30–300°C. The reaction was considered to be complete when the rate curve leveled off to a baseline. The exotherm was measured under a nitrogen flow rate of 10 ml/min. The exotherm baseline was corrected via data in the empty chamber. The cured sample was left in the DSC cell and cooled to 30°C, and then the cured sample was scanned at 20°C/min to determine the glass transition temperature (T_g) of the reacted product. The initial temperature of the heat flow step of the second diagram was taken to be the T_g . The total area under the exotherm curve, based on the extrapolated baseline at the end of the reaction, was used to calculate the heat of reaction, ΔH [J/g]. Morphological studies of the fracture surfaces of the nanocomposites were carried out using FE-SEM (LEO1550, LEO Electron Microscopy Ltd., Cambridge, UK). The nanocomposites were fractured in liquid nitrogen and then the fracture surfaces were coated with a thin gold layer before FE-SEM.

Thermal degradation studies were performed using TGA (STA-449C system, NETZSCH Instruments Co., Germany) at a scan rate of 10°C/min to 750°C in N₂ atmosphere. Five specimens from each system (neat epoxy, C3 and S3) were tested and the average was reported.

Table 2. Compositions of tested specimens (by weight)

System	DGEBA/EMI-2,4	COOH-MWCNTs	Silane treated COOH-MWCNTs
Neat epoxy	100/6	0	0
C1	100/6	1	0
C3	100/6	3	0
C5	100/6	5	0
S1	100/6	0	1
S3	100/6	0	3
S5	100/6	0	5

3. Results and discussion

It is known that activation energy E represents the potential barrier of cure reaction. The study on the variation of E during the curing process is conducive to better understanding on the effect of silane treatment of COOH-MWCNTs on the cure behavior of COOH-MWCNTs/epoxy nanocomposites. In this work, we use Friedman kinetics method, a differential isoconversional kinetics method which assumes that E is a function of fractional extent of conversion α , i.e., curing degree, to analyze dynamic DSC data for obtaining the variation of E during the curing process.

The curing mechanism of DGEBA/EMI-2,4 system involves two stages consisting of adduct and etherification reactions. The O/OH adducts are believed to be the catalyst that initiates the etherification reactions which cross-link the epoxy and determine the final properties. Previous work showed that the adduct formation is necessary prior to the etherification reactions [13–15]. Thus, low EMI-2,4 concentrations can be used to analyze the etherification reactions by suppressing the adduct formation. The objective criterion of meeting this specification is that the heat of reaction, ΔH , approaches a constant. It is shown that the variation amplitude of ΔH is small when the concentration of EMI-2,4 is between 3 and 10% by weight of DGEBA, as the cure reaction is incomplete when the content of EMI-2,4 is below 3 wt% [16]. In this work, the concentration of EMI-2,4 is 6 wt% which falls within the range of 3–10 wt%, therefore the heat of reaction for the etherification reaction peak is approximately the total heat of cure reaction. Furthermore, relative to the magnitude of ΔH , the heat released during the chemical reaction between amino silane coupling agent and epoxy is small, e.g., ΔH of S3 and C3 system are 355.7 and 345.6 J/g, respec-

Table 3. Total heats of reaction (ΔH) and exothermic peak temperatures (T_p) at 10°C/min heating rate, inflexions of the curves of E_α , and glass transition temperatures (T_g) of the cured systems

System	ΔH [J/g]	T_p [°C]	Inflexions of the curves of E_α	T_g [°C]
Neat epoxy	361.8	126.56	0.50	154
C1	357.2	113.74	0.50	144
C3	345.6	107.41	0.65	137
C5	343.9	104.82	0.70	131
S1	363.6	112.49	0.45	146
S3	355.7	104.64	0.60	141
S5	351.3	101.54	0.60	137

tively (as listed in Table 3). Thus, in this work, the etherification reactions dominate the curing process and ΔH can be considered as a constant over the whole cure reaction. Then, the rate of the cure reaction is $d\alpha/dt = (dH/dt)/\Delta H$ where dH/dt is the heat flow above the baseline.

Friedman kinetics method starts with the basic equation that relates $d\alpha/dt$ to some function of the concentration of reactants. For the thermosetting resins, $d\alpha/dt$ is usually expressed by Equation (2):

$$\frac{d\alpha}{dt} = A e^{-E/RT} f(\alpha) \tag{2}$$

where A is the frequency factor, E is the activation energy, $f(\alpha)$ is a function of the fractional extent of conversion α and is associated with a certain reaction mechanism, R is the gas constant and T is the absolute temperature at time t .

From Equation (2) Equation (3) is obtained:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A - \frac{E}{RT} + \ln f(\alpha) \tag{3}$$

Let $Af(\alpha) = F(\alpha)$, then from Equation (3) Equation (4) follows:

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E}{RT} + \ln F(\alpha) \tag{4}$$

From Equation (4), a plot of $\ln(d\alpha/dt)$ vs. $1/T$ at the same α from a series of dynamic DSC experiments at different heating rates would result in a straight line with a slope of $-E/R$. Repeating this procedure, E_α values corresponding to different α from the dynamic DSC curing curves can be obtained. Thus the relationship of E_α vs. α can be decided [17].

Figures 3–5 are the plots of $\ln(d\alpha/dt)$ vs. $1/T$ of neat epoxy, Ci and Si ($i = 1, 3, 5$) systems for various

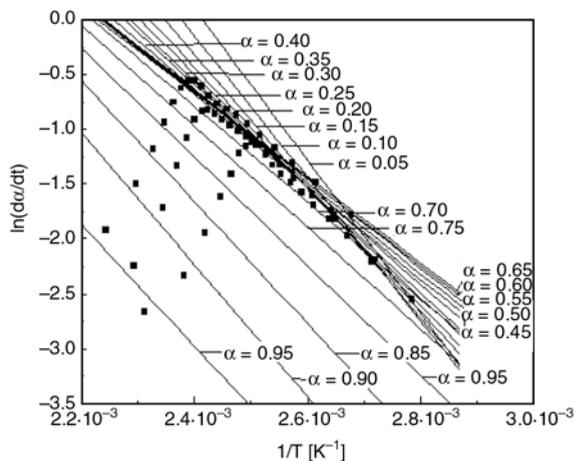


Figure 3. Plots of $\ln(d\alpha/dt)$ vs. $1/T$ of neat epoxy system

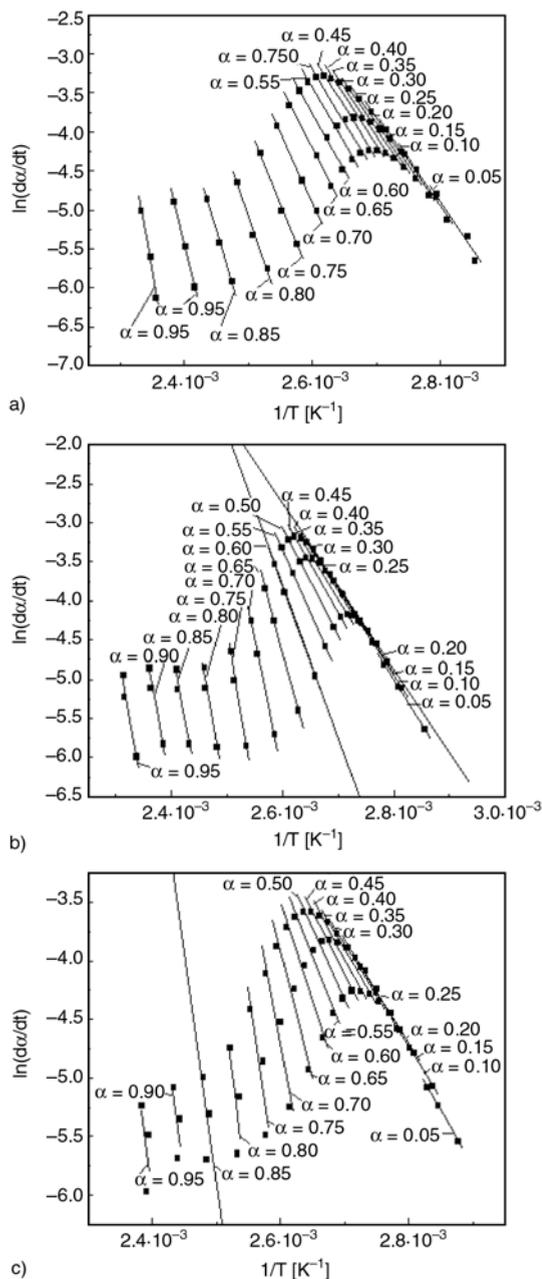


Figure 4. Plots of $\ln(d\alpha/dt)$ vs. $1/T$ of (a) C1, (b) C3 and (c) C5 systems

values of α ($\alpha = 0.05, 0.10, 0.15, \dots, 0.90, 0.95$) covering the experimental range, respectively. Fitting linear regression lines, the groups of E_α values of each system were obtained. Figure 6 shows the plots of E_α vs. α of neat epoxy, Ci and Si ($i = 1, 3, 5$) systems. It can be seen that, for all the studied systems, E initially decreases at low conversions, and then increases as the curing process proceeds. The cure reaction of DGEBA/EMI-2,4 system is autocatalytic. The O⁻/OH adducts are not consumed since they are continually regenerated during the following etherification reactions, it is

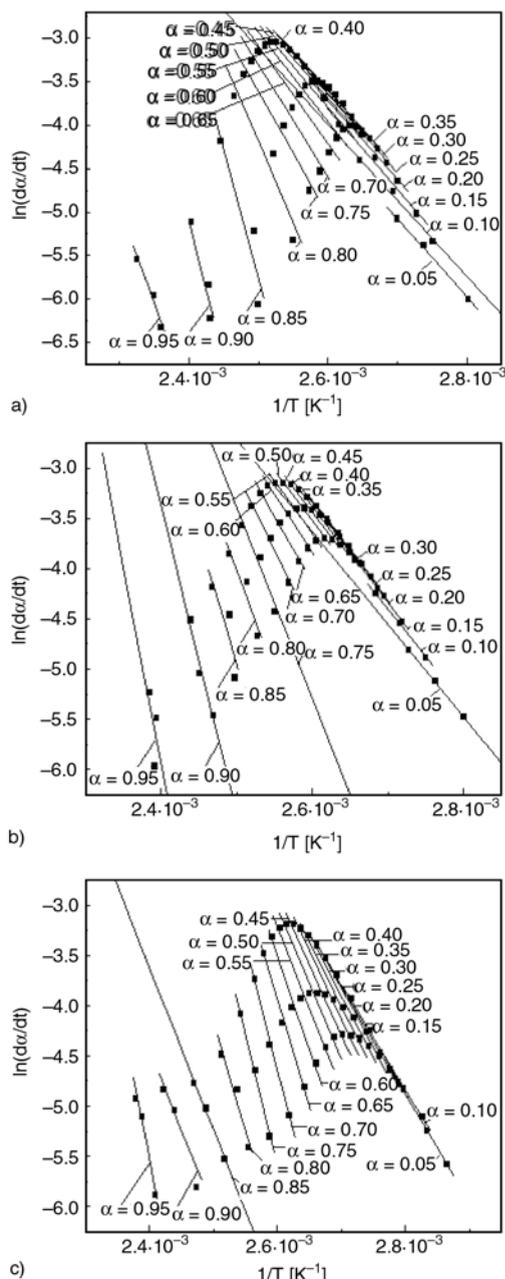


Figure 5. Plots of $\ln(d\alpha/dt)$ vs. $1/T$ of (a) S1, (b) S3 and (c) S5 systems

therefore reasonable to expect a decrease in E , as compared to the very beginning of the curing process where no autocatalyzed reaction occurs. As is shown in Figure 6, at the initial curing stage, values of E of all the studied systems decrease with increasing α , demonstrating that the introduction of COOH-MWCNTs does not change the autocatalytic cure reaction mechanism of DGEBA/EMI-2,4 system and silane treatment of COOH-MWCNTs also does not change the autocatalytic cure reaction mechanism of COOH-MWCNTs/DGEBA/EMI-2,4 system. Additionally, it can be seen that

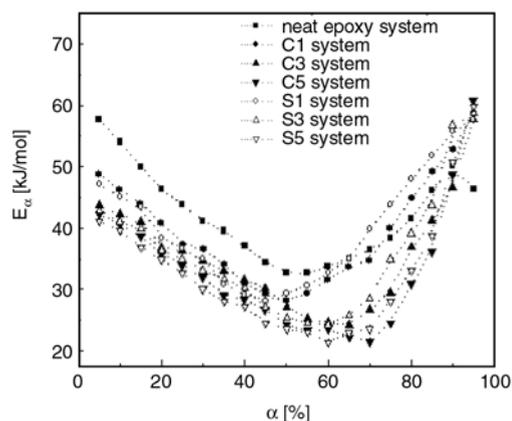


Figure 6. Plots of E_α vs. α of neat epoxy, C1, C3, C5, S1, S3 and S5 systems. Dotted lines are given only for showing the tendency.

increasing COOH-MWCNTs content and silane treatment of COOH-MWCNTs decrease E , so both COOH-MWCNTs and silane treatment of COOH-MWCNTs have catalytic effect on the initial curing process, which can also be evidenced by decreased exothermic peak temperature T_p , as shown in Table 3. Moreover, the decrease effect on E and T_p is already noticeable at the lowest content of COOH-MWCNTs investigated (1 wt%) with slightly further effect at higher concentrations, proving a saturation of catalyzing action at higher contents investigated (3 and 5 wt%), possibly due to the physical hindrance of COOH-MWCNTs to the mobility of epoxy monomers [18].

The catalytic effect of non-functionalized CNTs at the initial curing stage was also found in previous works [19–23] and the accelerating effect observed was primarily ascribed to the extremely high thermal conductivity of CNTs [22, 23]. In this study, besides the high thermal conductivity of CNTs, the catalytic effect of COOH-MWCNTs can also be attributed to the carboxyl groups ($-\text{COOH}$) which would function as O^-/OH adducts, exert a catalytic effect for epoxide ring opening, and react with the epoxide hydroxyl group creating the ether link, i.e., $\text{C}-\text{O}-\text{C}$ bonds. Furthermore, the catalytic effect of silane treatment of COOH-MWCNTs can be attributed to the amino group ($-\text{NH}_2$) end of the coupling agent which would function as EMI-2,4 and accelerate the cure reaction.

As the curing process proceeds, the system undergoes gelation (liquid-to-rubber) and vitrification (rubber-to-glass) transitions. As the glass transition temperature (T_g) increases over the curing tempera-

ture (T_c), the system vitrifies. At the glassy state, the small amount of free volume only allows local motions of the chain segments. To initiate translational motion of the segments, it requires a great degree of cooperativity between the chain segments, which is associated with a large energy barrier as reflected in the great value of E , so when the system vitrifies, the value of E begins to increase. It can be seen in Figure 6 and Table 3 that the inflexions of the curves of E , i.e., the fractional extents of conversion α where E begins to increase, increase with increasing COOH-MWCNTs content, so COOH-MWCNTs prevent from vitrification at the later curing stage, however, there is a slight reduction of inflexions for the Si ($i = 1, 3, 5$) systems in comparison with the Ci ($i = 1, 3, 5$) systems, so silane treatment of COOH-MWCNTs decreases the inflexions, implying that silane treatment of COOH-MWCNTs promotes vitrification.

The phenomena can be interpreted by Table 3 that T_{gs} of COOH-MWCNTs/epoxy systems decrease with increasing COOH-MWCNTs content, thus make it difficult for T_g to increase over T_c , consequently prevents from vitrification, on the other hand, there is a slight increase of T_{gs} for the Si ($i = 1, 3, 5$) systems in comparison with the Ci ($i = 1, 3, 5$) systems, so silane treatment of COOH-MWCNTs increases the T_{gs} of COOH-MWCNTs/epoxy systems, thus promotes vitrification.

Usually T_g decreases with decreasing crosslinking density and increased chain mobility [22]. The high COOH-MWCNTs/epoxy interface creates extra free volume and therefore extra chain mobility and lower T_g compared with neat epoxy. At higher loadings, the difficulty to disperse COOH-MWCNTs remarkably increases and agglomeration can occur. Agglomeration decreases the surface-to-volume ratio of the nanoparticles and therefore increases T_g , however, the final effect is that T_g of the COOH-MWCNTs/epoxy systems decreases with increasing loading, as shown in Table 3.

Silane treatment of COOH-MWCNTs improves the compatibility between COOH-MWCNTs and epoxy matrix, and thus results in a more ‘compact’ structure and increased T_{gs} , thereby resulting in promoted vitrification.

For the development of nanocomposites, the cure acceleration effect caused by COOH-MWCNTs and silane treatment of COOH-MWCNTs could bring positive effect on the processing of nanocom-

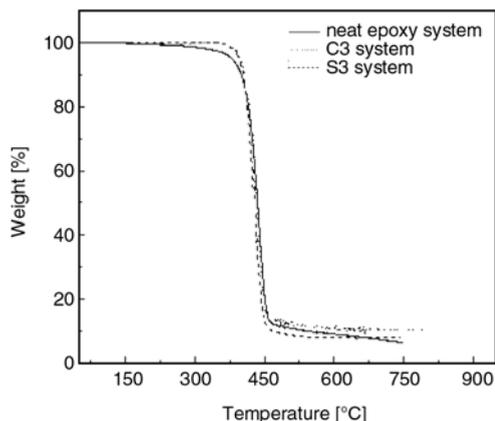


Figure 7. TGA curves of neat epoxy, C3 and S3 systems

posites since it needs shorter pre-cure time or lower pre-temperature, the hindrance effect to vitrification of COOH-MWCNTs would bring negative effect as it needs longer post-cure time or higher post-temperature, however, silane treatment of COOH-MWCNTs promotes vitrification, which would help to shorten post-cure time or lower post-temperature.

Since silane treatment of COOH-MWCNTs could bring positive effect on the processing of nanocomposites, silane treatment of COOH-MWCNTs on the thermal stability of the nanocomposites was also evaluated. TGA curves of neat epoxy, C3 and S3 systems are shown in Figure 7. The curves in Figure 7 are similar, indicating that the introduction of COOH-MWCNTs does not affect the thermal degradation pattern of DGEBA/EMI-2,4 system and silane treatment of COOH-MWCNTs does not affect the thermal degradation pattern of COOH-MWCNTs/DGEBA/EMI-2,4 system.

All the TGA curves have only one step degradation and it is a common practice to consider the peak degradation temperature as the thermal stability for such cases [24]. In this study, the thermal degradation onset temperature T_{onset} , determined from the intersection of two tangents at the first inflection point, and the char residual at 750°C were summarized in Table 4. The difference in T_{onset} of C3 and S3 is not noticeable, however, the difference in T_{onset} of neat epoxy and C3 is really noticeable and the addition of COOH-MWCNTs increases T_{onset} , so the addition of COOH-MWCNTs would delay the thermal degradation of DGEBA/EMI-2,4 system. In addition, the half-weight-loss temperature T_{half} was also summarized in Table 4. It is a common practice to consider T_{half} as an indicator for the

Table 4. Thermal stabilities of neat epoxy, C3 and S3 systems as determined from TGA curves

System	T_{onset} [°C]	T_{half} [°C]	Char residual at 750°C [%]
Neat epoxy	404.9±0.2	433.4±0.1	6.03±0.12
C3	410.8±0.3	434.9±0.2	10.23±0.13
S3	410.2±0.2	430.1±0.2	7.58±0.15

beginning of structural decomposition [24]. The difference in T_{half} of neat epoxy and C3 is not really noticeable, however, the difference in T_{half} of C3 and S3 is noticeable and silane treatment of COOH-MWCNTs decreases T_{half} , so silane treatment of COOH-MWCNTs decreases the thermal stability of COOH-MWCNTs/DGEBA/EMI-2,4 nanocomposites.

When COOH-MWCNTs are introduced into system, there would, on the one hand, result in a decrease in thermal stability, which can be due to the weakened Van der Waals interaction between polymer chains [25] and the lowered T_g shown in Table 3. On the other hand, the addition of COOH-MWCNTs can also increase the thermal stability due to their hindering effect to the thermal motion of polymer molecular chains [26]. However, the final result of COOH-MWCNTs on the thermal stability, arising from the antagonistic competition of these two effects, is that the addition of COOH-MWCNTs slightly improves the thermal stability of DGEBA/EMI-2,4 system.

Silane treatment of COOH-MWCNTs enhances the interactions between COOH-MWCNTs and epoxy, weakening Van der Waals interaction between polymer chains, resulting in decreased thermal stability, but its effect of enhanced T_g would lead to increased thermal stability, however, the final result is that silane treatment of COOH-MWCNTs decreases the thermal stability of COOH-MWCNTs/DGEBA/EMI-2,4 nanocomposites.

4. Conclusions

By comparing the research results on DSC and TGA data of silane treated COOH-MWCNTs/epoxy system with those of as-received COOH-MWCNTs/epoxy system, the effect of silane treatment of COOH-MWCNTs on the thermal properties of COOH-MWCNTs/epoxy system was obtained.

At the initial curing stage, the introduction of COOH-MWCNTs does not change the autocatalytic cure reaction mechanism of DGEBA/EMI-2,4 system and silane treatment of COOH-MWCNTs does not change the autocatalytic cure reaction mechanism of COOH-MWCNTs/DGEBA/EMI-2,4 system. Both COOH-MWCNTs and silane treatment of COOH-MWCNTs have catalytic effect on the curing process. Then, at the later curing stage, COOH-MWCNTs prevent from vitrification; however, silane treatment of COOH-MWCNTs promotes vitrification.

The cure acceleration effect caused by COOH-MWCNTs and silane treatment of COOH-MWCNTs could bring positive effect on the processing of epoxy nanocomposites since it needs shorter pre-cure time or lower pre-temperature, the hindrance effect to vitrification of COOH-MWCNTs would bring negative effect as it needs longer post-cure time or higher post-temperature, however, silane treatment of COOH-MWCNTs promotes vitrification, which would help to shorten post-cure time or lower post-temperature.

The introduction of COOH-MWCNTs does not affect the thermal degradation pattern of DGEBA/EMI-2,4 system and silane treatment of COOH-MWCNTs does not affect the thermal degradation pattern of COOH-MWCNTs/DGEBA/EMI-2,4 system. The addition of COOH-MWCNTs would delay the thermal degradation of DGEBA/EMI-2,4 system and silane treatment of COOH-MWCNTs decreases the thermal stability of COOH-MWCNTs/DGEBA/EMI-2,4 nanocomposites.

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