

Flammability and Thermal Properties of Epoxy/Glass/MWNT Composites

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ABSTRACT: The aim of this work is to study the effect of nanotubes on flammability properties of epoxy/glass composites. Multiwalled carbon nanotubes (MWNT) and its functionalized derivative (amino functionalized nanotubes) were incorporated into epoxy resin. To disperse MWNTs in the epoxy resin, different ways were employed. Microscopic observations showed that, the best dispersion state was gained by using ultrasonication method and high shear flow simultaneously. Thermal resistance of cured epoxy resins containing various amounts of nanotubes (0.25–0.7 wt %), was investigated by thermo gravimetric analysis (TGA). Introducing MWNTs and amino-MWNTs to samples increased the initial thermal decomposition temperature for about 32 and 37°C, respectively. LOI measurements of composite samples showed an increase up to 32. Cone calorimetry test was carried out on epoxy/glass and epoxy/glass containing 0.5% MWNT. The results showed that, introducing 0.5% MWNTs decreases maximum average rate of heat emission for about 26%. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39849.

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INTRODUCTION

Fiber reinforced polymer composites have been widely used in many applications due to their light weight, high specific stiffness, and strength. Among various polymer matrices, epoxy resins have attracted interests because of their excellent mechanical performance, low shrinkage, and good impregnation and adhesion to fiber reinforcement. Flammability is the weakness of epoxy resin which forces the composite producers to use flame retardants in the resin matrix.¹ Various flame retardant fillers have been used for epoxy resins such as chemical compounds based on halogen, silicon,² nitrogen,³ boron, and phosphorus.⁴ Nanoparticles have recently been considered to be high potential filler materials for improving flame retardant properties in polymeric materials. Nanoclay,⁵ carbon nanotube (CNT),⁶ carbon nanofiber,⁷ and polyhedral oligomeric silsesquioxanes,⁸ are common nanoparticles used as fire retardants in polymers. These nanoparticles are environmental friendly and are more efficient compared with the conventional flame retardants.

For the first time in 2002, Beyer et al. discovered the potential of CNTs in reducing the flammability of ethylene vinyl acetate.⁹ In 2004, Kashiwagi et al. reported a mechanism for flame retarding of PP/MWNT nanocomposites.¹⁰ They attributed the flame retardant performance of the nanotubes to the formation of a network-structured floccule layer, which reemits much of the incident radiation back into the gas phase. Nanotubes have also been used as flame retardant filler in epoxy resins.^{11–15}

Rahatekar et al. studied flammability properties of epoxy/MWNT by means of a gasification apparatus. According to their results, introduction of 0.0025 mass fraction of MWNT to epoxy resin has decreased peak of mass loss rate for about 45%. They attributed this reduction, to high degree of exfoliation, which was gained due to use of highly aligned MWNTs instead of MWNTs. Highly aligned MWNTs are easily debundled compared with MWNT. This characteristic reduces the amount of MWNT, which is needed to reduce flammability and enhances the char integrity during combustion.¹¹ Katsoulis et al. studied the effect of different nanoparticles (nanoclay, nanosilica, and nanotube) on the thermal stability and fire properties of aerospace grade epoxy resins. They observed that double walled nanotubes (DWNTs) had thermal destabilization effect due to their poor dispersion.¹² Wladyke et al. used various functionalized nanotubes in epoxy resin matrix and studied fire reaction properties. They claimed that “a clear relationship between the CNT content in epoxy and its flammability is difficult to establish as well as the relation between the kind of nanotubes and the behavior of MWCNT nanocomposites. This is most likely associated with the dispersion degree of the nanotubes in the resin which needs further studies.”¹³

Different parameters affect the flame retarding performance such as loading of CNT, aspect ratio,¹⁶ uniformity of the char layer,^{6,15} and dispersion of nanotube in polymer matrix. Two main problems must be solved to prepare CNT-epoxy

nanocomposites: Dispersion of CNT in the resin and interfacial adhesion between CNT and matrix.^{17–19}

Various methods such as ultrasonication, mechanical mixing,^{20,21} dispersing agent, and surface functionalization have been used to disperse CNT in polymer matrix. Chemical functionalization is one of the most efficient methods to disperse CNT in matrix. Im et al. used fluorinated MWNT to reduce the flammability of epoxy resins.²² They observed that fluorination of nanotubes improves their dispersion by creating hydrophobic functional groups. These MWNTs reduced the degradation rate of the epoxy resin and increased the char yield. Limiting oxygen index (LOI) also increased from 21 to 26. Kuan et al. functionalized MWNT with a silane compound. They observed that introduction of 9% silanated-MWNT to epoxy resin increased LOI from 22 to 27 and the UL-94 changed from V-1 to V-0.²³

The main purpose of this investigation is to improve thermal and flame retardancy properties of epoxy/glass composites by introducing nanotubes. Although nanotubes have been used as flame retardant filler in epoxy resin and other polymeric matrices, rare reports on fire retardant application of nanotubes in epoxy/glass composites exist. Two strategies were employed to disperse nanotubes in the epoxy resin: Combination of ultrasonication method with high shear flow and functionalization of nanotubes. Flammability properties of epoxy/glass/MWNT composites were investigated by LOI and cone calorimeter tests.

EXPERIMENTAL

Materials

The nanotubes produced by chemical vapor deposition method were obtained from Neutrino (China). For this study, we used MWNTs and carboxylated MWNTs with 90–95% purity. The inner diameter of nanotubes varies from 5 to 10 nm and the outer diameter varies from 10 to 20 nm. The average length of nanotubes was $\sim 30 \mu\text{m}$. The COOH-MWNTs were prepared by UV/O₃ method²⁴ (MWNTs were ozonized under ozone stream at room temperature and atmosphere condition) and the density of carboxylic groups attached to nanotubes was about 2% (measured by the manufacturer).

Diglycidyl ether of bisphenol A (Araldite LY 564, Ciba Geigy) and polyamine hardener (HY 560, Ciba Geigy) were used to prepare composite samples. The epoxy equivalent was 5.7–6 eq/m². E-glass fabrics (200 g/m²) were used as reinforcement in epoxy/glass composites.

Amino Functionalization of MWNTs

COOH-MWNTs (500 mg) were added to 100 cc of 20 : 1 Thionyl chloride : Dimethylformamide solution and refluxed for 24 h at 70°C. After acylation, the solution was centrifuged and washed with 125 cc anhydrous tetrahydrofuran (THF) for five times (each time 25 cc of THF was used). The remaining solid was dried at 70°C under vacuum for 2 h.^{24–29}

Acyl-chlorinated MWNTs (100 mg) were refluxed with 50 cc ethylene diamine at 85°C for 48 h. After amidation the remained solid was centrifuged and washed with ethanol until pH of filtrate reaches to pH of ethanol.^{24–29} The remained solid was dried at 75°C under vacuum over night.

The functionalized MWNTs were characterized using Fourier Transform Infrared (FTIR). The functionalized nanotubes were dried in

Table 1. Condition of Different Methods Applied to Prepare Epoxy-Nanotube Suspension

Method number	Procedure	Nomenclature
1	Sonication	M1
2	Sonication + high shear flow	M2
3	Homogenizing + high shear flow	M3
4	Homogenizing	M4

the vacuum oven at 70°C for 12 h and then the KBr pellets were prepared from them. FTIR spectra (JASCO FTIR-680, Japan) were obtained between 400 and 4000 cm⁻¹ at 4 cm⁻¹ resolutions.

Preparation of Epoxy-Nanotube

To prepare epoxy/MWNT and epoxy/amino MWNT suspensions, four methods were employed. The suspensions were first mechanically stirred for 15 min at 600 rpm. In the first method, the suspension was ultrasonicated in an ice bath (UP 400S Hielscher) with 70% amplitude for 90 min. In the second method, the suspension was first ultrasonicated for 45 min and then dispersed using high shear flow (1200 s⁻¹) for 45 min. High shear flow was applied by means of a cylindrical apparatus containing a cup (outer cylinder) and a rotor (inner cylinder). The clearance between cup and rotor was 0.06 mm and the applied velocity was 512 rpm. In the third method after 45 min sonication, the suspension was dispersed with a homogenizer (Ultra-Turrax T 25 digital IKA, Germany) at 15,000 rpm for 30 min. To avoid structural damage of nanotubes, shearing was applied for 5 min and a rest time for about 5 min was given to the suspension. In other words, dispersion via homogenizing lasted for about 1 h; 30 min shearing and 30 min resting. In the fourth method, the suspension was only dispersed with the homogenizer at 15,000 rpm for 30 min. After preparation of each suspension, the hardener was added (27 parts curing agent and 100 parts epoxy by weight) and mechanically stirred at 400 rpm for 5 min. Finally, out gassing procedure was applied by vacuum chamber to remove bubbles inside the resin. Table I summarizes the condition applied in these methods.

To evaluate the dispersion state of nanotubes in the epoxy resins, the samples were broken in liquid nitrogen and the fracture surface was observed by a field emission scanning electron microscope (FE-SEM) (Hitachi S-4160, Japan). The samples were adhered onto the carbon tapes and sputtered with gold to avoid charging.

Fabrication of Epoxy/Glass/Nanotube Composites

Hand lay-up technique was used to impregnate and laminate the composite structures. In this technique, glass fabrics were wetted by a thin layer of pre-prepared epoxy suspension. First of all, the mold was coated with a thin layer of release agent. Then the layers of fabrics and resins were layed up. For LOI samples 12 layers and for cone calorimeter samples 16 layers were used. The excess resin was absorbed by an absorbing fabric. Samples were cured under vacuum at 80°C for 4 h.

Thermal and Flammability Analysis

Simultaneous differential and Thermogravimetric Analysis (DTA-TGA) was performed on cured neat epoxy resin and its

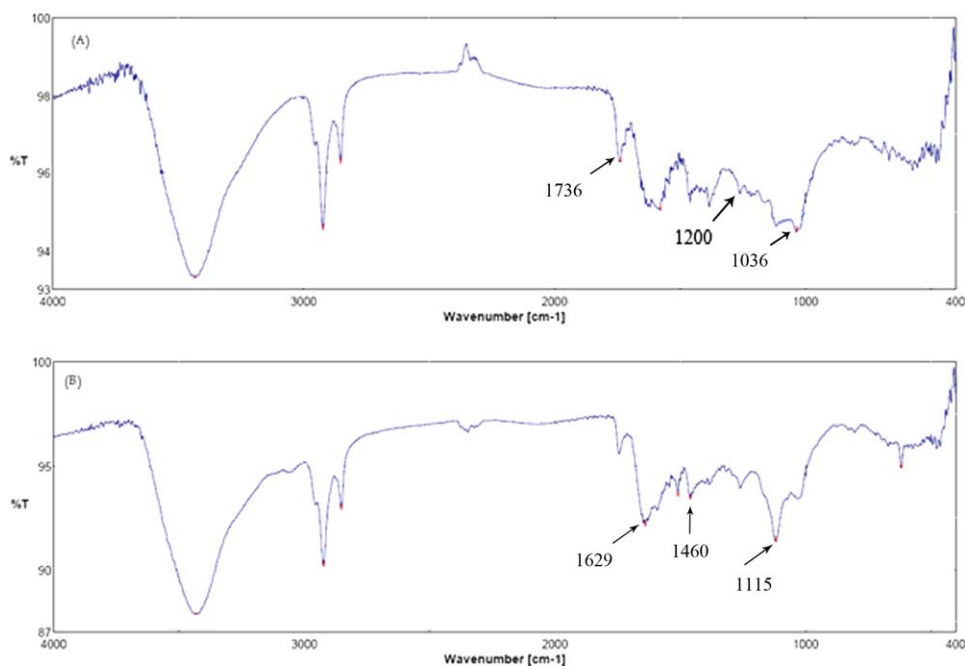


Figure 1. FTIR spectra of carboxylated MWNT (a) and amino functionalized MWNT (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nanocomposites to investigate thermal resistance of samples. The test was performed on TGA 1998 (Rheometric Scientific) using 15 ± 1 mg sample. Heating rate was set on $10^\circ\text{C}/\text{min}$ and the initial and final temperatures were 30 and 800°C respectively under atmosphere of nitrogen. The LOI for all composite samples ($100 \times 6.5 \text{ mm}^2 \times 3.2 \pm 0.2$) were measured according to ASTM D2863-00. At least five specimens were tested for each sample.

A cone calorimeter was used to study flammability characteristics of samples according to ISO 5660. All samples were wrapped with thin film aluminum foil without frame and grid and irradiated with a heat flux of $50 \text{ kW}/\text{m}^2$ (758°C). Three tests for each sample ($100 \times 100 \times 4.2 \pm 0.2$) were conducted.

RESULTS AND DISCUSSION

Amidation of Nanotubes

Figure 1 shows the FTIR spectra of carboxylated and amino functionalized MWNTs. The band at 3434 cm^{-1} is attributed to the presence of hydroxyl groups in carboxylic acids. The peaks at around 2852 and 2922 cm^{-1} are assigned to the C—H stretching mode associated with alkyl groups.²⁹ Formation of carboxylic groups on the MWNT surface can be confirmed by observation of these peaks [see Figure 1(a)]. The peaks at 1736 , 1200 , and 1036 cm^{-1} correspond to C=O, asymmetric and symmetric C—O—C, respectively.^{24,25}

The spectrum of amino functionalized MWNTs in Figure 1(b), shows the peaks at 1629 and 1115 cm^{-1} corresponding to amide C=O and C—O stretching, respectively.²⁴ The change of frequency from 1736 cm^{-1} in MWNT-COOH to 1629 cm^{-1} in amino functionalized MWNTs can prove the formation of amide linkage. The peaks at 1460 and 1300 cm^{-1} are also assigned to N—H and C—N vibration modes [Figure 1(b)]. Thus, amidation on the surface of MWNT has successfully been carried out.

Dispersion Evaluation

To evaluate dispersion state of nanotubes at the micron and millimeter scales, an optical microscope (Motic B3, magnification: $1000\times$) was employed. Figure 2 illustrates the epoxy-CNT suspensions after being sheared for various interval times. From this figure, it can be seen that shear flow can crush the agglomerates and improve dispersion. By comparing Figure 2(a) with Figure 2(f), it can be concluded that after 30 min shearing, the size of agglomerates has reduced and dispersion has improved. From Figure 2(a), it can be concluded that sonication is not efficient enough to disperse nanotubes [Figure 2(a)]. Combination of ultrasonication method and high shear flow can result in a good dispersion state [see Figure 2(f)]. For epoxy resin containing amino functionalized nanotubes, this trend was also held but the figures were almost the same as Figure 2. It can be concluded that at these scales the effect of shearing was more effective compared to the effect of amino functionalization.

Dispersion of nanotubes in polymer matrices is difficult because of their high surface area, nonpolar nature, and the Van der Waals forces between the tubes. Ultrasonication causes intramolecular vibrations, which forces the nanofillers to motivate and disperse. However, to crush the aggregates, sonication is not efficient enough. However, high shear forces can make the fillers to migrate and improve the dispersion.³⁰ Combination of ultrasonication method and high shear flow can result in a good dispersion state. Regarding to Table I, in method 2, epoxy/MWNT suspension was ultrasonicated for 45 min and then shear flow was applied for 45 min. Consequently, sonication or shear forces alone are not efficient enough, however, combination of them can result in a good dispersion state.

Figure 3(a–d) shows SEM micrographs of epoxy/MWNT (a,b) and epoxy/amino MWNT (c,d), each at two magnifications

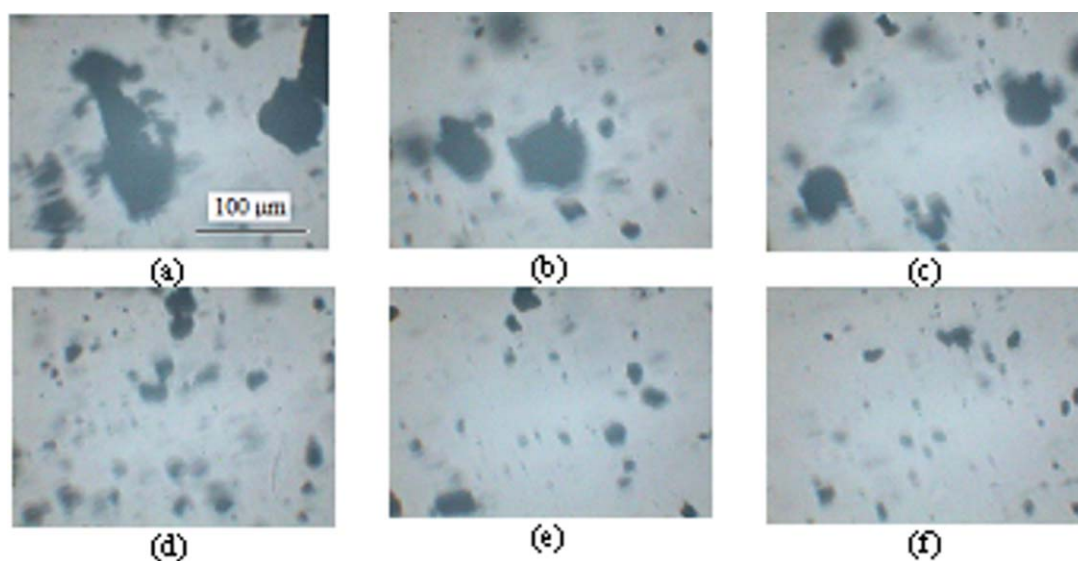


Figure 2. Optical micrographs of 0.25% CNT/epoxy suspension (a) before shearing, after shearing for (b) 10 min (c) 15 min (d) 20 min, (e) 25 min, and (f) 30 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

containing 0.5 wt % nanotubes. By comparing Figure 3(a) with Figure 3(c), it is observed that amino functionalization has reduced the size of agglomerate. The white spots in magnified images, Figure 3(b,d), show the tips of nanotubes. Amino functionalization has increased the distance between white spots, which means that epoxy resins has infiltrated into nanotubes. Consequently, nanotubes are better dispersed

and distributed when they have been functionalized. This occasion takes place when polar functionalities are set on the surface of nanotube.²² Amino groups on the surface of nanotube can interact physically and sometimes chemically with epoxy groups. They can act as amine curing agents (see Figure 4) as well as increasing hydrogen bonding with epoxy resin.

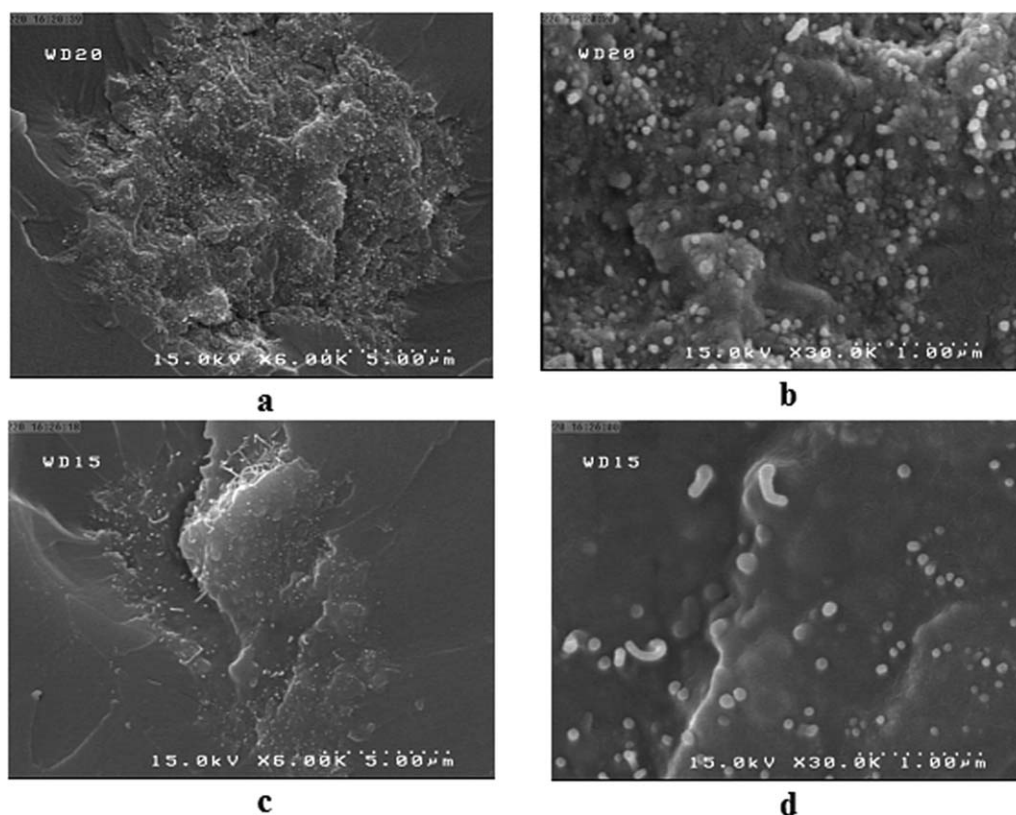


Figure 3. FE-SEM images of cured epoxy resin containing: MWNT (a,b), amino-MWNT (c,d), at two magnifications: 6000 \times (a,c) and 30,000 \times (b,d).

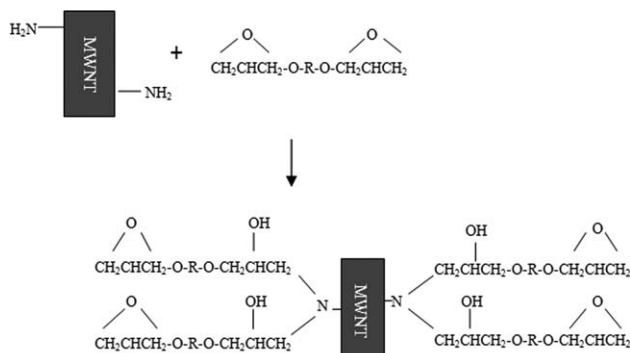


Figure 4. Linkage formation between amino-MWNT and epoxy resin.

Thermal Properties

Figure 5(a,b) shows thermal gravimetric analysis (TGA) results of nanocomposite samples compared with the neat epoxy resin. The data extracted from the curves in Figure 5 are presented in Table II. $T_{5\%}$ and $T_{10\%}$ show the temperatures at which 5 and 10% of weight loss has been occurred, respectively. $\Delta T_{5\%}$ shows the difference of $T_{5\%}$ between the nanocomposite and the neat resin. T_{\max} is a temperature at which thermal degradation rate reaches a maximum value. Another parameter, which is gained from TGA curves, is overall stabilization effect (OSE). This parameter is calculated via integration of the area under Δ mass% versus temperature curves of Figure 5(b). OSE is a useful parameter, which enables us to have a fair comparison between various samples (epoxy samples containing nanotubes). Positive OSE values mean that the composite samples are thermally more stable than the virgin polymer while the negative values confirm the destabilization effect of the filler.^{13,15,31}

$$\text{OSE} = \sum_{T=30}^{800} (\text{mass percent of nanocomposite at } T - \text{mass present of neat resin at } T)$$

Figure 6 compares the amount of OSE of the samples. Introducing 0.25 and 0.5% MWNT has increased $\Delta T_{5\%}$ for about 32 and 42°C, respectively. However, addition of 0.7% MWNT has decreased this value for 8°C (see Table II). From Table II, it can be seen that introducing 0.25 and 0.5% MWNT have increased T_{\max} from 426°C for neat resin to 468 and 469°C, respectively. However, for 0.7% MWNT this value has decreased to 416°C.

During heating of the samples in TGA test, the surface temperature increases until chain scission begins to occur. Chain scission produces free radicals, which are able to attack other chains. Nanotubes are believed to have scavenging effect because of their high electron affinity.²² Thus, the free radicals formed during degradation can be trapped by nanotubes. However, slowing down the rate of thermal degradation may be explained as follows.

Thermal degradation of epoxy resins at high temperature produces small molecules, which have the potential to accelerate thermal degradation. Introducing nanotubes can retard the diffusion and extravasations of these small molecules and consequently improve thermal stability.^{22,26}

Although nanotubes have the potential to improve thermal stability of epoxy resins, this improvement is greatly dependent on

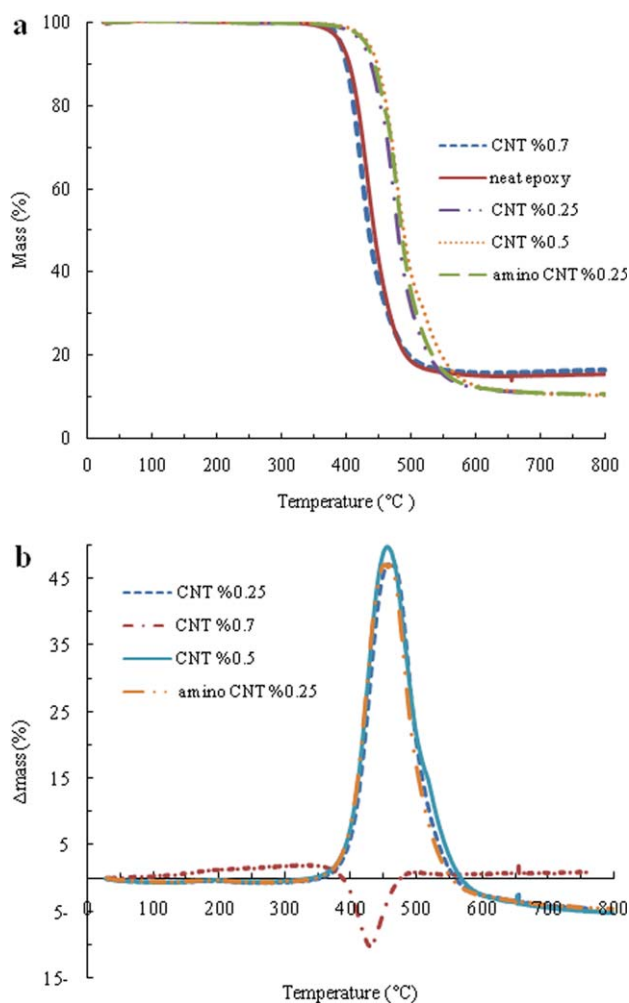


Figure 5. Thermal analysis of epoxy and its nanocomposites: (a) TGA mass-temperature (b) mass difference between a sample and epoxy-temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the dispersion state of nanotubes in the polymeric matrix. A good dispersion would obtain in a strong interaction with polymer chains and this would lead to the reduction of small molecule's extravasations.²⁶

As mentioned before by increasing nanotube loading up to 0.5%, both IDT and T_{\max} increase. More increase in nanotube loading (0.7%), leads to decrement in IDT and T_{\max} (see Table II). This can be attributed to bad dispersion of

Table II. LOI Results for Neat Epoxy/Glass Containing Nanotubes

wt % of Nanotube	Nanotube functionality	
	MWNT	amino MWNT
0	26.6	26.6
0.25	30	31.4
0.35	30.4	31.6
0.5	31.6	32
0.7	32	31.6

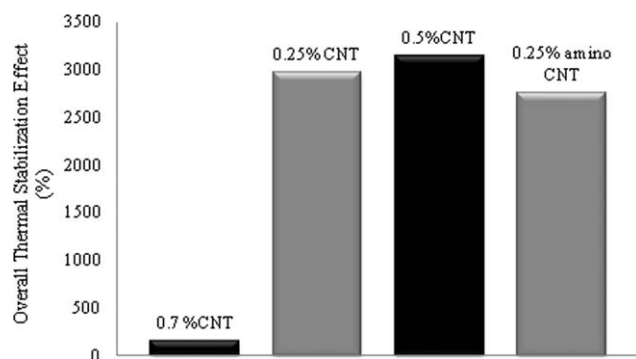


Figure 6. Overall thermal stabilization effect of various epoxy/nanotube nanocomposites.

nanotubes, which results in the formation of agglomerates. The agglomerates act as defect points in matrix and accelerate thermal degradation.²⁹ Ye et al. also gained similar results. They studied the effect of different MWNTs (non-functionalized and amino functionalized) with different contents (0.01–1%), on thermal properties of epoxy/MWNT nanocomposites. They also concluded that IDT of all samples containing 1% MWNT was lower than the corresponding samples containing 0.25% MWNT. They attributed this result to bad dispersion of nanotubes in epoxy resin, which causes bubbles and agglomerates in the matrix and quicken the thermal degradation.²⁹

To study the effect of nanotube functionality on thermal stability, the sample containing amino-MWNTs is compared with those of MWNTs at a constant loading (0.25%). IDT of the 0.25% amino-MWNT sample increases for 37°C, which is 5°C higher than 0.25% MWNT sample. This could be due to better dispersion of amino-MWNTs in the resin matrix.

OSE is used to compare thermal stability of all nanocomposite samples with neat resin (see Figure 6). A good correlation is found between OSE and IDT as well as T_{max} of the samples. The sample contained 0.5% MWNT has the highest OSE value, which stands for good thermal stabilization. By using the OSE parameter, we can choose the most thermally stable sample. Ye et al. studied the effect of various amino functionalized nanotubes on thermal stability of epoxy resin. According to their results, adding 0.25% amino-MWNT increased IDT for 30°C.²⁹ Wang et al. have also reported that adding 0.5% amino-MWNT to epoxy resin increased IDT for 57°C but MWNT and MWNT-COOH decreased this value for about 5 and 15°C, respectively.²⁶

Flammability Properties

LOI Results. The LOI values of epoxy/glass composites containing various amounts of nonfunctionalized and amino functionalized nanotubes are shown in Table III. Nanotube loading varies from 0.25 to 0.7%. LOI of the neat epoxy/glass is 26.6. The results show that by increasing the amount of nanotube, LOI value increases. It can also be seen that amino functionalized nanotubes have higher LOI value compared to nonfunctionalized nanotubes. For example, introducing 0.5% MWNT to epoxy/glass composite, has increased LOI from 26.6 to 31.6 while 0.5% amino-MWNT has increased this

Table III. TGA-DTA Data for Epoxy Resin and Its Nanocomposites

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$\Delta T_{5\%}$ (°C)	T_{max} (°C)	OSE
Neat epoxy	393	405	0	426	–
0.25% MWNT	425	439	32	468	2975
0.5% MWNT	435	448	42	469	3135
0.7% MWNT	385	395	–8	416	153
0.25% Amino MWNT	430	444	37	474	2758

value to 32. The higher LOI value means that the material needs more oxygen to sustain in a flame.³² Thus, introducing nanotubes (functionalized or nonfunctionalized) has reduced the ease of flammability.

Cone Calorimetry Results. According to results obtained by TGA and LOI tests, it can be concluded that introducing 0.5% MWNT can improve both thermal stability and LOI simultaneously. The criterion for thermal resistancy was the value of OSE. According to literature, at high nanotube loading, thermal resistancy, and flame retardancy decreases. This is also confirmed by OSE value of “0.7% MWNT,” which is almost 153. Although the sample containing 0.7% MWNT showed the highest LOI (32) but because of its low OSE value, this sample was not selected. According to Table III, it can be seen that aminofunctionality does not lead to a higher thermal resistancy. At a constant loading (0.25%), the amino functionalized sample had a lower OSE value although this sample had a higher LOI and IDT. The sample containing 0.5% MWNT had the highest OSE value and almost the highest LOI (31.6). Consequently, the sample with 0.5% MWNT was tested by cone calorimeter and the results have been compared with the reference sample (epoxy/glass). Figure 7(a–d) shows cone calorimetry results of epoxy/glass (ref) and epoxy/glass containing 0.5% MWNT (0.5% CNT). Figure 7(a) shows the heat released as a function of exposure time for the samples. It can be seen that introducing 0.5% MWNT has reduced the peak of heat release rate (pHRR) for about 10%. From this curve it can also be seen that time to ignition (TTI) has not changed remarkably (see also Table IV). TTI is a point at which the combustible gaseous mixture has reached to its critical concentration and the sample starts to ignite. Figure 7(b) depicts the total heat released (THR) during combustion which is calculated via integration of heat release curve over exposure time. THR is in correlation with fuel load of a material. Introduction of 0.5% MWNT has reduced this value for about 11%. As THR increases, fuel load increases and the material is more susceptible to burn. The reduction of THR value confirms that introduction of MWNTs can restrict fire development. Figure 7(c,d) show the amount of carbon monoxide and carbon dioxide generated during the test respectively. It can be seen that introducing 0.5% MWNT has reduced the amount of harmful gases, which are generated during combustion. The amount of toxic gases is an important factor for fire safety rankings.

Maximum average rate of heat emission (MARHE)³³ which is defined as the maximum value of cumulative heat release

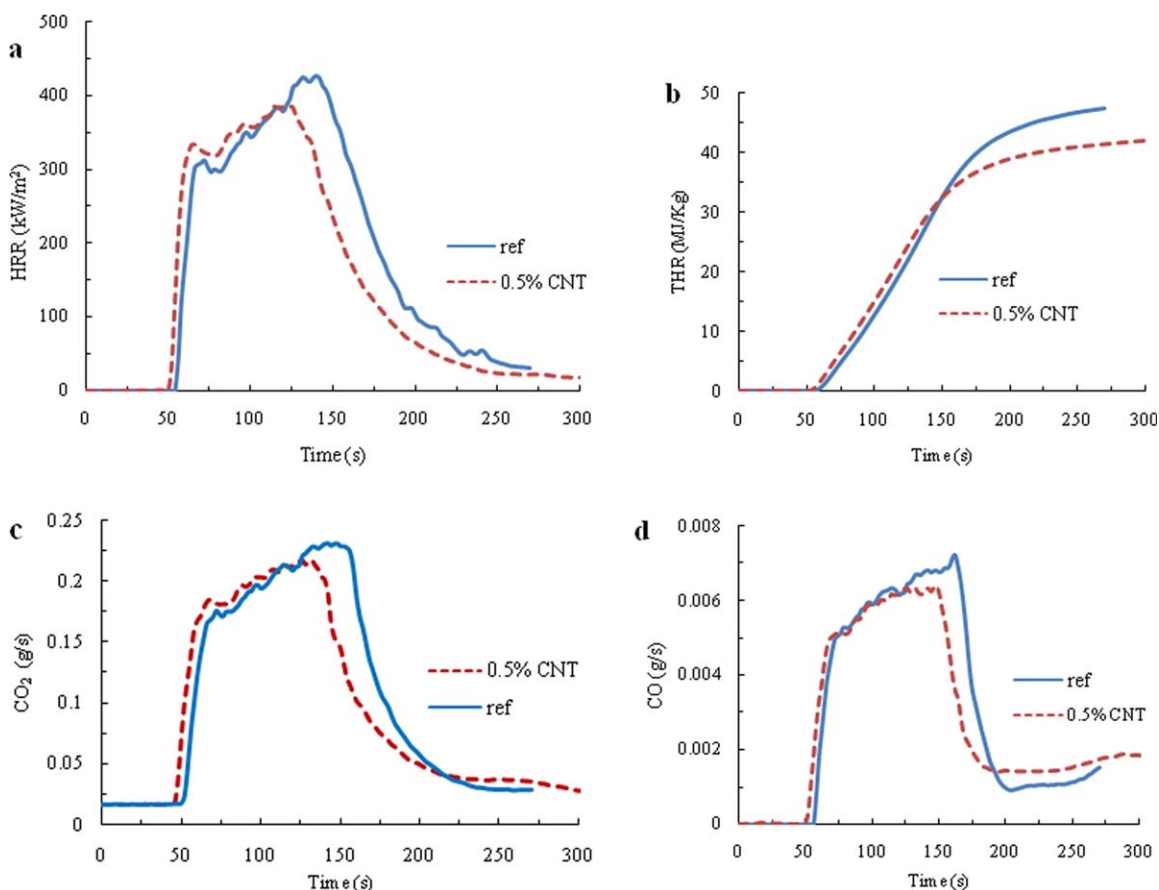


Figure 7. Cone calorimetric curves heat release rate (a), THR rate (b), CO₂ production rate (c), and CO production rate (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Main Parameters from Cone Calorimeter Curves

Sample	Thickness (mm)	TTI (s)	pHRR (kW/m ²)	THR (MJ/Kg)	MARHE (kW/m ²)	Maximum average of mass loss rate (g/m ² s)
Ref	3.4 ± 0.2	53 ± 2	428 ± 4	47.4 ± 1.1	219.52 ± 3	9.25
0.5% MWNT	3.2 ± 0.2	50 ± 2	386 ± 3	42.1 ± 0.9	162.11 ± 2	6.85

divided by time is a fire safety parameter and presented in Table IV. The amounts of other main parameters extracted from cone calorimetry are shown in this table. MARHE shows the flame spread ability of a material. 0.5% MWNT has decreased this value for about 26%. Maximum average of mass loss rate is another value gained by cone calorimetry test. A reduction for about 26% is observed, which means that introduction of MWNTs has prevented thermal degradation. These results are in agreement with those obtained by TGA.

Kashiwagi et al. scrutinized the flame retardancy mechanism of polymers containing nanofillers.³⁴ They claimed that: as the material starts to ignite, the temperature increases until thermal degradation of the polymeric chains initiates. The degraded products form, as the chain scission proceeds. Since the boiling points of the degraded products are lower than the thermal degradation point of polymer, once the products form, they become super heated. The bubbles of the super

heated products nucleate under the surface of polymer and grow as the amount of products increase. These bubbles move to the outer layer of polymer and help to form a solid like char. As reported by many researchers “the char layer produced by burning of polymeric matrix containing nanotube, acts as a radiation shield and reflects most of the combustion heat back into the gas phase.”^{10,11,15,16,22,34} Integrity of this char layer is an important factor which influences the flame retardancy. It is believed that a nonporous and crack-free char layer can reduce the diffusion of combustible gases and improve flame retardancy. Dispersion of nanotubes in the matrix is an important factor, which affects the integrity and crack density of char layer. Good dispersion results in a smooth char layer and in adverse, bad dispersion may not improve flame retardancy and sometimes can reduce it either, as reported by Wladyke et al.¹³ Katsoulis et al. compared the effect of various nanofillers (nanoclay, nanosilica, and nanotube) on thermal and flammability properties of epoxy resin

(LY5052). According to their results, introducing 0.5% DWNTs to epoxy resin, had destabilization effect on thermal resistance due to their bad dispersion. They also reported that LOI has decreased from 21.5 to 20.1 but, pHRR has increased for about 3%.¹²

CONCLUSION

The results obtained here confirm the improvement of flame retardancy of epoxy/glass composites by introducing CNTs. It is believed that improvement of the dispersion of nanotubes can improve thermal and flame resistancy. Thermal properties of epoxy/nanotube samples were investigated by thermo gravimetric analysis (TGA). Introducing 0.25%, 0.5% MWNTs and 0.25 amino-MWNTs to epoxy resin, increased the initial thermal decomposition temperature (IDT) up to 32, 42, and 37°C respectively. To study flammability properties of fiber reinforced composites, LOI was employed. The results showed that, introducing 0.7% MWNTs increases LOI from 26.6 to 32. Although the sample contained 0.7% nanotube, had maximum LOI, but did not show improvement in thermal resistance. However, 0.5% nanotubes improved thermal resistance and increased LOI from 26.6 to 31.6. Thus, the sample contained 0.5% MWNTs was selected to evaluate by cone calorimeter. The cone calorimetry results showed that, introducing 0.5% MWNTs decreases pHRR and THR to 10 and 11%, respectively. MARHE, which shows the flame spread ability of the material, has decreased for about 26%. The amount of CO and CO₂ generated during combustion has also reduced. The cone calorimetry results along with the results obtained from TGA and LOI tests show that MWNT had a positive effect on fire performance of epoxy/glass composites. The main purpose of this article was to improve flame retardancy of epoxy/glass composites by introducing CNTs. Dispersion of nanofillers as an important factor for improvement of flame retardancy was studied. Although there is other factors which improve flame retardancy as mentioned before such as: uniformity of char layer. The next studies will focus on these factors.

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