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The effect of thermal stability of carbon nanotubes on the flame retardancy of epoxy and bismaleimide/carbon fiber/buckypaper composites

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Abstract Single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT) membranes (buckypaper) were incorporated onto the surface of epoxy and bismaleimide (BMI) carbon fiber composites. Their flammability behaviors were investigated by a cone calorimeter. The composites with buckypaper reduced the heat release rate (HRR) by more than 60% peak and smoke generation by 50% during combustion. The effects of different buckypaper on the flame retardancy of epoxy and BMI were compared and discussed. Our research team found that buckypapers acted as an effective flame-retardant shield to dramatically reduce the fire hazards of composites if they survived during fire combustion. Thermogravimetric analyses was used to compare the thermo-oxidation stability of the resins and buckypapers to explain the different effects of SWCNT and MWCNT buckypaper on flammability of epoxy and BMI carbon fiber composites.

Keywords Carbon nanotubes · Epoxy · Bismaleimide · Flame retardancy · Cone calorimeter

Introduction

Since Beyer initiated the use of carbon nanotubes in fire retardant polymeric materials [1], carbon nanoadditives, including carbon nanotubes, carbon nanofibers and carbon black, have been studied systematically as flame retardants by research group of fire research division at National Institute of Standards and Technology (NIST) [2–5]. They attribute the improved flame resistance to the formation of a protective, free-standing nanotube network structure that acts as a heat shield for composites. Consistent with this mechanism, the flame retardancy was found to improve with better dispersion and a higher interface area (aspect ratio) of the nanotubes at desired loading. However, the major hurdle remaining is ensuring proper homogenous dispersion of the CNTs to achieve maximum benefits. Experiments have indicated that failures in using nanocomposite materials are primarily due to poor nanoparticle dispersion.

In our previous work [6, 7], we developed a unique concept of manufacturing nanocomposites with carbon nanotube membranes. Single-walled carbon nanotube (SWCNT), multi-walled carbon nanotube (MWCNT) buckypaper and CNF paper as proposed fire shields were applied to the surface of epoxy carbon fiber composites. Their flammability behaviors were investigated by cone calorimeter. The thermo-oxidation stability and low gas permeability of buckypapers or CNF nanofiber are key roles in improving flame-retardant properties of composites. In the cone calorimeter test condition, the MWCNT-based buckypaper, due to its high thermo-oxidation and dense network, acted as an effective fire shield to reduce heat, smoke, and toxic gases generated during fire combustion. SWCNT-based buckypaper was burnt out after combustion in the Epoxy/IM-7/SWCNT-BP composite and did not affect the flammability of the composite. In the case of epoxy/IM-7/CNF paper composite, because of the big diameter of carbon nanofiber, the big pore size of the CNF paper network resulted in high gas permeability, which was a response for its low flame-retardant efficiency.

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However, another previous work in our lab showed SWCNT buckypapers also had dramatically improvement in polyhedral oligomeric silsesquioxane (POSS)/glass fiber composites [7]. Thermal stability of SWCNT and MWCNT buckypaper is another important fact in flame-retardant efficiency. The study of the differences in the thermal stability of SWCNT and MWCNT has been investigated by Pang et al. [8] and Silva et al. [9, 10]; however, the effect of thermal stability of SWCNT and MWCNT on flame retardancy of CNT composites has not been reported in the literature.

In this work, we explored the difference of flame retardancy of SWCNT in the different resins. Both SWCNT-based buckypapers and MWCNT-based buckypaper were studied as flame-retardant shields on the epoxy/carbon fiber and bismaleimide (BMI)/carbon fiber composites surface by cone calorimeter. Thermal gravimetry analysis (TGA) compared the thermo-oxidation stability of epoxy, BMI and buckypapers to discover the different effects of SWCNT and MWCNT buckypapers on the flammability of epoxy and BMI carbon fiber composites.

Experimental

Materials

HiPco SWCNTs were purchased from Carbon Nanotechnologies, Inc. MWCNTs were obtained from Thomas Swan, Inc. Nonionic surfactant Triton X-100 was supplied by Sigma-Aldrich. The epoxy matrix consisted of Epon 862 (diglycidyl ether of bisphenol F) with curing agent EPI-CURE W (diethylene toluene diamine, Miller-Stephenson chemical company, Inc). Modified bismaleimide resin (5250-4 RTM resins, from Cytec, Inc) was used as another matrix materials in this study. IM-7 carbon fiber fabrics (style 4178, Textile Products, Inc) were used as reinforcement.

Buckypaper preparation

SWCNTs or MWCNTs were grinded in a mortar with a small amount of de-ionized water and Triton X-100. After grinding, the mixture was subsequently sonicated using a probe sonicator to make a stable suspension of carbon nanotubes. Buckypapers were prepared by filtering a carbon nanotube suspension through a Nylon membrane on a home-made 22.8 cm × 22.8 cm funnel with the aid of a pressure pump [6, 11]. Following filtration, the buckypapers were washed with water to remove the surfactant. After air drying, buckypapers ~20 μm thick were peeled from the membrane. SWCNT and MWCNT buckypapers were self-supporting mats, appearing as uniform, smooth, and crack-free paper-like sheets.

Composite preparation

The epoxy/IM-7 composites with and without buckypaper skins were fabricated by processing the composites using hand lay-up followed by vacuum bagging. The composites were cured at 121 °C for 2 h and at 177 °C for an additional 2 h, then cooled to ambient temperature. The BMI/IM-7 composites with and without buckypaper skins were fabricated by lay-up BMI/IM-7 prepregs followed by curing at 177 °C for 6 h and at 227 °C for an additional 4 h under the pressure of 0.1 MPa in a hot press, then cooled to ambient temperature. For control composites, six layers of IM-7 carbon fiber fabrics were incorporated in the composite laminates. For composites with buckypaper skin, one piece of buckypaper was placed at the top and two pieces of buckypaper placed at the bottom of carbon fiber laminates on a mold. The bottom sides of the composites, with two pieces of buckypaper, were facing up during cone calorimeter test, since a conical radiant electrical heater uniformly irradiates the sample from above [12]. Compositions of different composite panels are presented in Table 1. Due to the high viscosity of BMI resin and the present of buckypaper skin, the content of BMI resin in composites is higher than that of epoxy composites.

Testing

Combustion tests were performed on 100 × 100 × ~2.5 mm specimens with a Cone Calorimeter, using the standardized cone calorimeter testing procedure (ASTM E-1354-02d). Tests were performed at 50 kW/m^2 external heat flux, and three tests for each sample were conducted. Thermogravimetric analyses were performed using a Q 50 thermogravimetric analyzer from TA instruments with a heating ramp of 10 °C/min from 50 to 800 °C under air atmosphere.

Table 1 Compositions of different composite panels

Sample	IM-7/g	Resin/g	Buckypaper or CNF paper/g	Sample mass/g
Epoxy/IM-7	24	12.6	0	36.6
Epoxy/IM-7/SWCNT-BP	24	13.0	0.4	37.4
Epoxy/IM-7/MWCNT-BP	24	12.7	0.5	37.2
BMI/IM-7	24	11.2	0	35.2
BMI/IM-7/SWCNT-BP	24	15.6	0.4	40.0
BMI/IM-7/MWCNT-BP	24	15.4	0.5	39.8

Table 2 Main parameters from cone calorimeter measurements

Sample	TTI/s	Peak HRR/ kW m^{-2}	Time to Peak HRR/s	THR/ MJ m^{-2}	TSR/ m^2 m^{-2}	Total CO yield/ kg kg^{-1}	MAHRE/ kw m^{-2}	FIGRA	Total mass loss/%
Epoxy/IM-7	46	568	84	23.2	1123.7	0.1	179	6.77	29.0
Epoxy/IM-7/SWCNT-BP	50	526	95	24.5	1180.1	0.08	151.8	5.64	28.9
Epoxy/IM-7/MWCNT-BP	64	258	94	13.2	526.1	0.08	82	2.75	16.7
BMI/IM-7	52	661	79	20.8	957.9	0.1	177	8.37	25.9
BMI/IM-7/SWCNT-BP	61	248	92	14.2	480.8	0.08	81	2.69	16.8
BMI/IM-7/MWCNT-BP	67	232	96	12.6	462.5	0.05	72	2.44	14.8

Results and discussion

Cone calorimeter test

Table 2 reports the main parameters for each material obtained from cone calorimeter measurements. The parameters, which will be addressed, include time to ignition (TTI), heat release rate (HRR), total heat released (THR), maximum average rate of heat emission (MAHRE), fire growth rate (FIGRA), total smoke released (TSR), CO and CO_2 yields, and mass loss during combustion.

Figure 1 shows a comparison of HRR curves for Resin/IM-7, Resin/IM-7/SWCNT-BP and Resin/IM-7/MWCNT-BP. In the case of Epoxy-based composites, the HRRs of the Epoxy/IM-7/SWCNT-BP composite was about the same as that of the Epoxy/IM-7 composite, whereas a remarkable reduction was observed for Epoxy/IM-7/MWCNT-BP. The peak HRR of the Epoxy/IM-7/MWCNT-BP composite was about 45% of that of the Epoxy/IM-7 composite. In the case of BMI-based composites, the peak HRRs of the BMI/IM-7/SWCNT-BP and BMI/IM-7/MWCNT-BP composites showed more than 60% reduction compared to the BMI/IM-7 composite. The different effects of SWCNT buckypaper on the HRR between Epoxy and BMI composites will be discussed later. The TTI for a Resin/IM-7/BP composite appears later with respect to the Resin/IM-7 composites. The Time-to-Peak HRR was 10 s longer for Resin/IM-7/BP composites compared to Resin/IM-7 composites. The value of THR, the integral of HRR curves over the duration of the experiment, of the Epoxy/IM-7/MWCNT-BP composite was 60% of that of the Epoxy/IM-7 composite, whereas THR value of the Epoxy/IM-7/SWCNT-BP was close to that of the Epoxy/IM-7 composite. For the BMI-based composites, both BMI/IM-7/MWCNT-BP and BMI/IM-7/SWCNT-BP composites showed much lower THR values than that of the BMI/IM-7 composites. The reduction of THR values indicates that the presence of buckypaper can restrict fire development. The mass loss during cone calorimetry test are listed in Table 2. A reduction in mass loss during the combustion was found in the Epoxy/IM-7/MWCNT-BP, BMI/IM-7/MWCNT-BP and BMI/IM-7/SWCNT-BP composites. The values of total mass loss provide positive evidence that the presence of buckypaper reduces the mass loss during the combustion, which is directly relative to the THR values. Test results show that the buckypaper layer acted as a mass transport barrier to slow combustible species released, which reduced the fuel to support a fire.

MAHRE (maximum average rate of heat emission) and FIGRA (fire growth rate) are the indices introduced to rank the hazard of developing fires. MAHRE is defined as the cumulative heat release from $t = 0$ to time t divided by time t. The MAHRE can best be thought of as an ignition modified rate of heat emission parameter, which is useful to rank materials in terms of ability to measure fire spread to other objects. A lower MAHRE value indicates a reduction in fire spread hazard. FIGRA is determined by dividing the peak HRR by the time to peak HRR. The FIGRA represents the rate of fire growth for a material once exposed to heat. A higher FIGRA suggests faster flame spread and possible ignition of nearby objects. Column MAHRE and FIGRA in

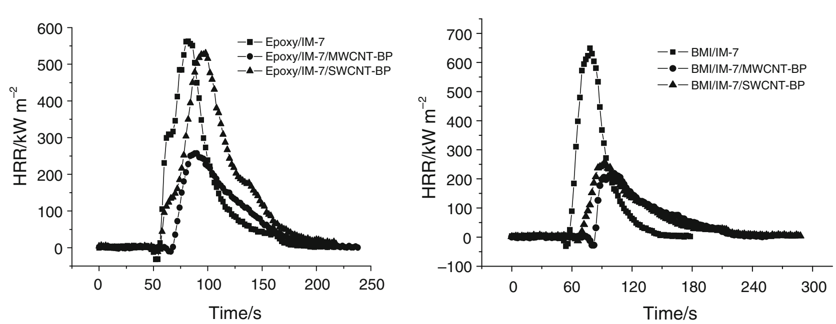

Fig. 1 Comparison of HRR curves for Resin/IM-7, Resin/IM-7/SWCNT-BP and Resin/IM-7/MWCNT-BP (*left* epoxy composites; *right* BMI composites.)

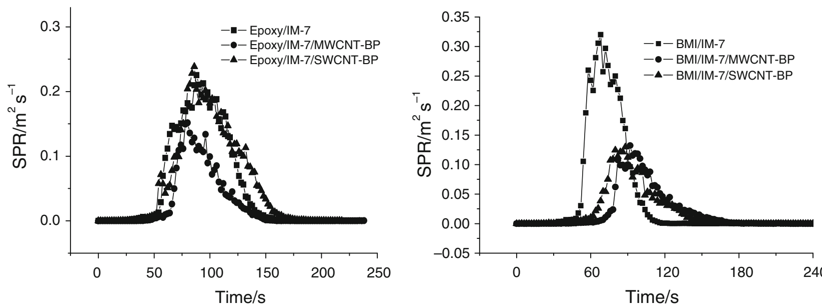

Fig. 2 Comparison of smoke production during combustion

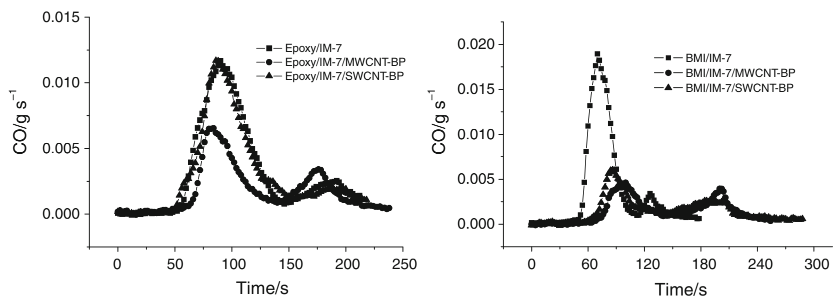

Fig. 3 Comparison of CO productions during combustion

Table 2 shows that the presence of buckypaper on the surface of Resin/IM-7 composites dramatically reduced the values of MAHRE and FIGRA, especially for the Epoxy/IM-7/MWCNT-BP, BMI/IM-7/MWCNT-BP and BMI/IM-7/SWCNT-BP composites. The reduction of MAHRE or FIGRA was greater than 55 or 60%, respectively.

Smoke and toxic gases generated during combustion are the other two important factors concerning fire safety: heavy smoke can hinder escape and toxic gases act as one killer during the fire hazard. Figure 2 and Table 2 report smoke production parameters. Except for the Epoxy/IM-7/SWCNT-BP composite, the values of the smoke production rate (SPR) and total smoke released (TSR) of the Resin/IM-7/Buckypaper composites were reduced by more than 50% compared to the Resin/IM-7 composites. The smoke production is ascribed to the thermal decomposition of resins, which leads to aromatic volatiles in the flame. The presence of MWCNT buckypaper accumulated the poly-aromatic hydrocarbons and prevented them from pyrolysis and subsequent oxidation/combustion. The lower smoke production is also related to the lower mass loss during the combustion test. Figure 3 shows the CO production significantly decreased in CO yield due to the buckypaper skin.

Morphological structure of the composite residues

Figure 4 shows photographs of residues collected after combustion. IM-7 carbon fiber fabrics from the Resin/IM-7 composites were totally exposed after combustion. However, the residues from Resin/IM-7/MWCNT-BP composites were covered by buckypaper. The residues from the Epoxy/IM-7/SWCNT-BP and the BMI/IM-7/SWCNT-BP composites are different. The SWCNT buckypaper on the surface of Epoxy/IM-7 composites were burned out with the red iron catalyst residue left on the surface. However, SWNT buckypaper partially remained on the surface of the BMI/IM-7/SWNT-BP composite after combustion. This may explain the different effect of SWNT buckypaper on the fire behaviors between the Epoxy/IM-7/SWCNT-BP and BMI/IM-7/SWCNT-BP composites.

Thermo-oxidation stability of materials

The thermo-oxidation stability of buckypaper indicates that the buckypaper can act as an effective fire shield on the composite surface if the buckypaper can survive during the flame combustion. Thermo-oxidation stability of the resin and buckypaper was evaluated by TGA considering that the surface temperature of materials in cone calorimeter at 50 kW/m^2 external heat fluxes can reach around 500 °C [13]. Figure 5 shows the TGA curves in air. The onset degradation point of SWCNT buckypaper and epoxy are approximately the same temperature or ~400 °C. During the cone calorimeter tests, SWCNT-buckypapers were burned with epoxy together due to their similar low thermo-oxidation stability, which is why SWCNT buckypapers cannot act as a flame-retardant shield in the Epoxy/IM-7/SWCNT-BP composites. In the case of BMI/IM-7/SWCNT-BP composite, the initial degradation onset temperature of BMI was ~450 °C, and the second mass loss step, which is related to the degradation of carbonaceous char formed during the first mass loss step, started at ~520 °C. The

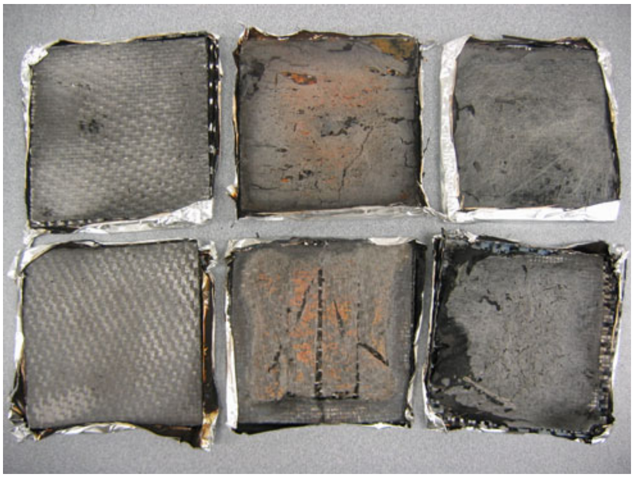

Fig. 4 Cone calorimetry test residues: BMI/IM-7 (*up left*); BMI/IM-7SWCNT-BP (*up middle*); BMI/IM-7/MWCNT-BP (*up right*); Epoxy/IM-7(*bottom left*); Epoxy/IM-7/SWCNT-BP (*bottom middle*); Epoxy/IM-7/MWCNT-BP (*bottom right*)

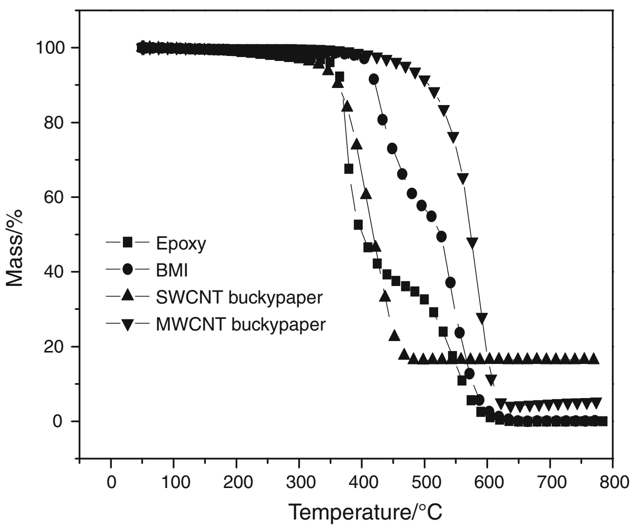

Fig. 5 The thermal gravimetric analysis results of epoxy, BMI, SWCNT Buckypaper, and MWCNT Buckypaper in air

carbonaceous char from BMI decomposition remained on the surface of SWCNT buckypaper and reduced the thermo-oxidation of SWCNT buckypaper. The surviving SWCNT buckypaper can reduce the flammable volatiles release from the bulk, due to its dense structure and restricted gas permeability [6, 14, 15]. MWCNT buckypaper survived after fire tests due to its high thermo-oxidation degradation onset temperature ($\sim$550 °C) and acted as the fire shield to delay and reduce the flammable specimen release. This may explain why the presence of MWCNT buckypaper on the composites resulted in the improvement on the all flame-retardant performance of the composites. The smaller diameter nanotubes are believed to oxidize at lower temperature due to higher curvature strain [16]. The SWCNTs are more exposed to oxidative damage during the fire, which can therefore destroy the protective network as the nanotubes are oxidized away through the walls of the tubes. MWCNT on the other hand, has multiple layers which have to be "burned through" before the tube is broken which might account for why this network holds together better under fire conditions and therefore provides better fire protection.

Conclusions

The enhanced flame retardancy of epoxy or BMI carbon fiber composites was achieved by incorporating buckypaper on the surface of composites. The thermo-oxidation stability of buckypaper played a key role in improving flame-retardant properties of composites. In the cone calorimeter test condition, the MWCNT-based buckypaper, due to its high thermo-oxidation, survived and acted as an effective fire shield to reduce heat, smoke and toxic gases generated during fire combustion. SWCNT-based buckypaper was burned out after combustion in the Epoxy/IM-7/SWCNT-BP composite and did not affect the flammability of the composite. In the case of BMI/IM-7/SWCNT-BP composite, due to the synergistic effect between BMI and SWCNT buckpaper, the buckypaper partially survived, which indicates the SWCNT buckypaper can act as fire shield to retard the fire development during the combustion.

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