Fire performance of composite laminates embedded with multi-ply carbon nanofiber sheets

Jihua Gou [a,*], Yong Tang [a], Jinfeng Zhuge [a], Zhongfu Zhao [a], Ruey-Hung Chen [a], David Hui [b], Christopher Ibeh [c]

[a] Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, FL 32816, United States
[b] Department of Mechanical Engineering, University of New Orleans, New Orleans, LA 70148, United States
[c] Center for Nanocomposites and Multifunctional Materials Pittsburgh State University, Pittsburg, KS 66762, United States

ARTICLE INFO

ABSTRACT

In this study, free-standing carbon nanofiber sheets (CNS) were incorporated into glass fiber reinforced polyester composites through resin transfer molding (RTM) process. These sheets were made of vapor grown carbon nanofibers. The composite laminates consisted of eight plies of CNS and eight plies of glass fiber mats. The fire retarding performance of the laminates was evaluated with cone calorimeter tests with an external radiated heat flux of 50 kW/m^2. The test results indicated that there was significant improvement in the fire retardancy of composite laminates due to the incorporation of CNS. It was found that the CNS plies survived the test except the one on the top surface of the laminates. The formation of compact char materials was observed on the surface of the CNS residues. The improvement in fire retarding performance was achieved through the barrier and insulator effects of the CNS and charred materials by restricting the migration of flammable products to the top surface of the laminates and preventing the transmission of external heat to the underlying polyester resin.

1. Introduction

Nanoparticles have been extensively studied to improve the fire retardancy of polymers [1–10]. Among a variety of nanoparticles, clay, carbon nanotubes (CNT) and carbon nanofibers (CNF) have attracted considerable attention for their fire retardant performance. Compared to conventional fire retardants, they are environmentally friendly and highly efficient (below 10 wt% of loading). They also add to polymers other desirable properties such as improved mechanical strength, Young's modulus, and electrical conductivity. At present, clay/polymer nanocomposites have been extensively studied for a wide range of applications in many important sectors of industry such as aircraft, naval constructions, building, and offshore structures. However, their poor dispersability, the decomposition of the organic surfactants in the clay gallery, and the high viscosity of the polymer melt have limited their applications in polymer matrix. The efficiency of CNT is very good, but their price is surprisingly high. The CNF has much lower cost, but its efficiency is low and requires high loadings in the nanocomposites. Principally, these nanoparticles form a protective layer, serving as barriers to O_2 supply, the flammable pyrolysis products, and the external heat flux to underlying polymers [1,4–8].

Although these nanoparticles have achieved significant success in a variety of polymers, their applications in fiber reinforced polymer matrix composites have been much less explored. They are susceptible to combustion and fire damage as a result of changes in their chemical structures, causing the deterioration of their mechanical and structural strength. In order to increase their market penetration and meet current stringent aviation and other legislative requirements for safety [11–16], there is an urgent need to develop new concepts to improve their fire performance. In this study, CNF was used in the form of a free-standing carbon nanofiber sheet just like traditional fiber mats for fiber reinforced polymer composites. The pre-formed carbon nanofiber networks within the CNS played an important role in the fire retardancy of composites by changing the patterns of melt flow, heat transmission, and vapor fuel transportation. As the char formation is desirable for improving the fire retardancy of polymer composites, the char characteristics and morphology of the composite structures were studied for understanding of the fire retardation of CNS.

2. Experimental

2.1. Preparation of carbon nanofiber sheets and composite laminates

Vapor grown carbon nanofibers (PR19-PS) supplied from Applied Sciences, Inc. have a diameter of 100–200 nm and a length of 30—100 μm. The CNF was dispersed in distilled water with a high-intensity sonicator. The upper suspension was collected after settling overnight and filtered with high-pressure air to make the

CNS. The CNS had a density of $\sim 0.400\,g/cm^3$ and a thickness of ~0.25 mm. The resin transfer molding (RTM) process was used to fabricate three types of composite laminates, as shown in Table 1. The glass fiber mat with an aerial density of $800\,g/m^2$ and the unsaturated polyester resin (712–6117, Eastman Chemical Co.) were used in this study. The polyester resin was cured with MEK peroxide at a weight ratio of 100:1. The composite laminates were post-cured in an oven at 120 °C for 2 h. In the laminate labeled as CNS-8, eight plies of CNS were alternately laminated with eight plies of glass fiber mats with one ply of CNS on the top surface, as shown in Fig. 1. For comparison purposes, two reference laminates, labeled as CNS-0 and CNS-1, were made. The CNS-0 laminate was made without CNS and the CNS-1 laminate consisted of one ply of CNS on the top surface.

2.2. Characterization and evaluation

The fire retardant performance of these laminates was evaluated with cone calorimeter tests with an incident heat flux of $50\,kW/m^2$ in accordance with ASTM E1354/ISO 5660. All samples were cut into three circular disks with a diameter of 75 ± 0.1 mm using a water jet. The appearances of the samples are shown in Fig. 2. These samples were wrapped in an aluminum foil before the cone calorimeter test to allow the top surface to be exposed to the heat flux. All tests were conducted with the samples in a horizontal position. The data presented is the average of three specimens in each set of CNS-0, CNS-1 and CNS-8 samples. The heat release rate (HRR) and DTA data were obtained from the cone calorimeter tests.

The thermal gravimetric analysis was conducted using TA Q500 TGA from 100 °C to 1000 °C in a non-oxidizing pure N_2 environment with a heating rate of 10 °C/min on the residues of F1–F8, which consisted of the CNS and pyrolyzed products from the polyester resin. They were also characterized with scanning electron microscopy (JEOL 6400 F at 5 kV) to study their morphologies. The samples were sputtered with 10 nm of Au prior to imaging.

3. Results and discussion

3.1. Heat release rates

Fig. 3 shows the heat release rates (HRR) of test samples. Compared to the CNS-0, the peak heat release rate (PHRR) of the CNS-8 decreased by 8%. The time to ignition (TTI) decreased from 42 to 31 s. For comparison, published time to ignition for isophthalic polyester under $50\,kW/cm^2$ radiation is in the range of 35–42 s, and 69–85 s with unspecified levels and patterns of glass reinforcement [17]. It is of interest to note that the top ply of the CNS remained until the end of cone calorimeter test (at $t \approx 1000 - 1200\,s$). The PHRR of the CNS-1 is higher by 15% than that of the CNS-0 and the TTI is slightly shorter, which is about 32 s. During the RTM processing of the CNS-1 and the CNS-8 laminates, the polyester resin penetrated the CNS and formed a very thin polyester film, covering the top ply of the CNS. Carbon nanofibers on the skin surface, being darker in color shown in Fig. 2, could easily absorb the radiant heat flux and quickly heat up the polyester
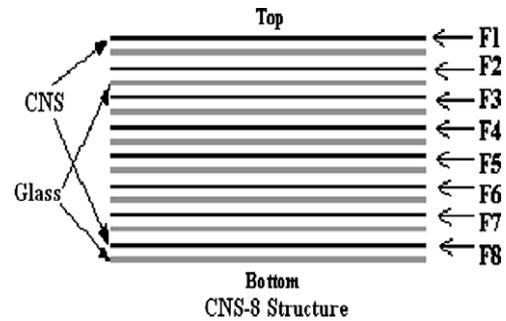

Fig. 1. Schematic of the CNS-8 laminate.

resin film. This phenomenon could be responsible for the early ignition of the CNS-1 and the CNS-8. To improve the resistance to ignition, the RTM process will need to be modified so that the polyester resin could not penetrate the top CNS ply.

The results from Fig. 3 show that for $t < 400\,s$ broad peaks of HRR with smaller heat release rates follow PHRR at ignition. This suggests that the fuel vapor accumulating over the top surface is rapidly consumed when ignition occurs (thus PHRR) and that further burning would have to rely on the fuel vapor supplied from within the depth of the polymer matrix composites. The broad peak values are in the order of CNS-1 > CNS-0 > CNS-8 and range approximately from $200\,kW/cm^2$ to $300\,kW/cm^2$. The reported mean value of HHR from ignition time to 180 s for polyester with external heat flux is $500\,kW/cm^2$. The current glass fiber reinforcement reduced HHR. Adding CNS was expected to further reduce HHR. However, adding only one ply of CNS led to a slight increase in HHR while adding eight plies slightly reduce HHR over that without any CNS (see Fig. 3). As discussed in the following section, the char formation on CNS within the depth appeared to be more effective in preventing vaporization and vapor flow than the CNS on the top surface. For $t > 400\,s$, the values of HRR for the three laminates rapidly decrease from a value of approximately $200\,kW/m^2$. This suggests that most of the heat release, mass loss and vaporization/pyrolysis occur during $t < 400\,s$.

3.2. Char formation in the composite laminates

After the cone calorimeter tests, the glass fiber mats were removed from the residue samples and were photographed. The results are shown in Fig. 4, where the numbers beside the samples indicate the sequence of the mats from the top (1) to the bottom (8). The char materials can be seen to have formed on some of the mats during tests, indicated by the dark color in Fig. 4. The CNS-0 appears to be free of any char. In the case of CNS-1, glass fiber mats 1–5 are free of chars and have clean surfaces while the bottom two plies (7 and 8) close to the bottom are dark. All the plies of glass fiber mats except the top one are dark in the CNS-8.

It is reasonable to postulate that during the cone calorimeter test there were temperature gradients within the laminates. The temperature decreased with an increase in the depth of the laminates. In the CNS-8 laminate, the CNS appeared to function as a barrier to both mass and heat transport. These sheets decreased the amount of heat penetration into the laminate and slowed down the release of the flammable vapor, which reduced the vapor flow to support the fire and thus the smaller HHR shown in Fig. 3 for $t < 400\,s$. They also reduced the local temperature, promoting char formation and decreasing the likelihood for CNS oxidation. As a consequence, more char materials were produced from the polymer resin and deposited on the surface of the CNS close to the bottom of the laminates, as can be seen from the results shown in Fig. 5.

Table 1
Identification and composition of composite laminates.

Laminate ID	Composition (wt%)			Thickness (mm)
	Glass fiber	Polyester resin	CNF	
CNS-0	53.12	46.88	–	7.37
CNS-1	54.17	45.38	0.45	7.21
CNS-8	50.07	46.54	3.39	7.89

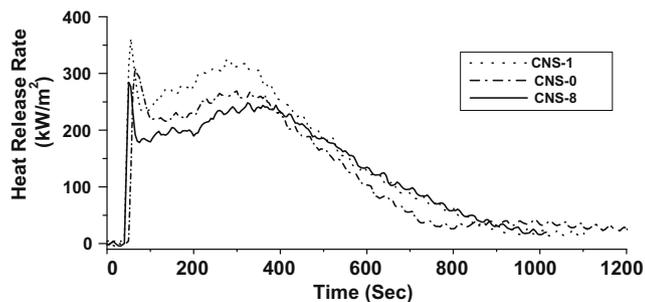**Fig. 2.** Original specimens for cone calorimeter test.

Fig. 3. HRR curves of CNS-0, CNS-1 and CNS-8 laminates.

Fig. 5 shows the plots of the CNS weight *vs* the sequence number from the top to bottom of the laminates. As noted in Fig. 5, a pristine CNS weighs 0.25 g. It is interesting to note that the weight of each ply of CNS increases after cone calorimeter test except for F1 and F2. The increase of the weight is due to the formation of char materials from the decomposed polyester resin, which deposited on the surface of the CNS. It is believed that CNS promotes char formation mainly due to its barrier and insulator effects. The char formation is favored at low temperatures and long residence time, and CNS provides such conditions from F2 and down. This is further supported by the fact that F3–F8 remained free-standing. Such increases are further demonstrated by the morphologies of CNS residues from the cone calorimeter tests in the following section. With such promising effects, it is desirable to understand thermo-physical mechanisms on the char formation with embedded CNS [18,19]. This merits further efforts in obtaining temperature profiles that would provide data on how fast and how deep the pyrolysis front would have penetrate the nanocomposites.

3.3. Morphologies of residues after fire damage

The morphologies of the CNS residues and pristine CNS were characterized with scanning electron microscopy (JEOL 6300 F, at 5 kV). Fig. 6a shows the morphology of the pristine CNS, where the uniform network consists of well-dispersed individual CNFs and some elliptical particles coming from the metal catalysts used for synthesizing CNFs. Although the CNS has much larger pore sizes and larger fiber diameters than the network of single-walled carbon nanotubes [7], its network has similar pore sizes and diameters of multi-walled carbon nanotubes [5,6]. The pre-formed network in the CNS on the top surface was expected to act as a barrier (or insulator) to protect the underlying polymer resin. However, its existence on the top surface actually increased the flammability of the laminates possibly due to its lower thermal

stability than multi-walled carbon nanotubes [20]. This might help explain the reduced time to ignition for CNS-1 and CNS-8 compared to that for CNS-0.

Depending on the distance to the top surface of the laminates, the CNS residues after cone calorimeter tests varied in their appearances, shapes of the floccules, and percentage of surface coverage by the floccules. In the F1 residue (not shown here), only red catalyst remained without any floccules. The F2 residue (see Fig. 6b) consisted of both CNS and some small floccules that are more or less evenly distributed throughout the image. Carbon nanofibers in the F2 residue are shorter than those of in the pristine CNS, suggesting burning or destruction of carbon nanofibers. The char floccules can be seen to cover about 85% of the CNS surface in the F3 residue (see Fig. 6c), where the underlying CNF network appears to remain intact until possibly these char floccules are burned out. In the F4 residue (see Fig. 6d), the entire CNS surface is covered with floccules. The F5–F8 residues (see Fig. 6e–h) have similar morphologies, with increased densities of the floccules as the images reveal smaller spacing between floccules. It is believed that such floccules are responsible for the weight increases of the F3–F8 residues (see Fig. 6). Based on above observations, it is believed that the CNS plies from F4 to F8 are increasingly more effective than F1, F2 and F3 as a mass and heat transport barrier. The temperature probably decreased significantly starting from F4 and down. More detailed studies will be conducted by using embedded thermal couples to measure the temperature variations throughout the depth of the laminate.

3.4. Thermal stability of residues after fire damage

Thermal gravimetric analysis (TGA) was conducted on the polyester resin, pristine CNS, and F2-F8 residues using a TA Instruments TGA Q500 at 10 °C/min from 100 °C to 1000 °C in an N_2 flow at 60 cm^3/min. Three sharp peaks of the pristine CNS at around 220 °C, 405 °C and 970 °C and a broad peak in the range of 500–800 °C were observed, as shown in Fig. 7a. At 220 °C, 405 °C and 970 °C, there are about 3%, 6% and 26% of weight loss, respectively. During cone calorimeter tests, the burning surfaces had temperatures in the range of 400–500 °C under the thermal radiation from an electrically heated element at a temperature of about 750 °C [6]. Therefore, the pristine CNS would have lost approximately 10% of its weight at the ignition temperature of 750 °C (see Fig. 7a) and would have lost thermal stability during cone calorimeter test. The DTA data shown in Fig. 7b suggest a rapid decomposition of the polyester resin prior to reaching 400 °C, which lead to its complete decomposition. This decomposition temperature is lower than that on the top surface (400–500 °C). One may very well expect the embedded CNS (those within the polyester resin) to
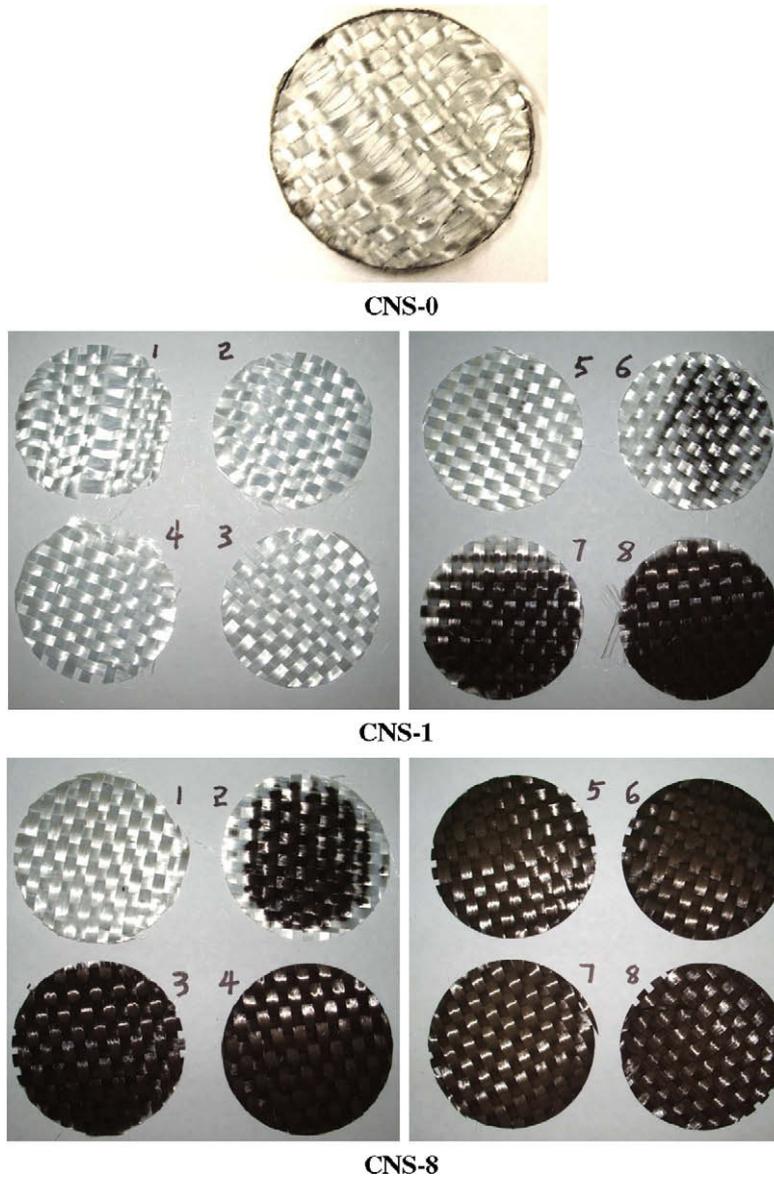
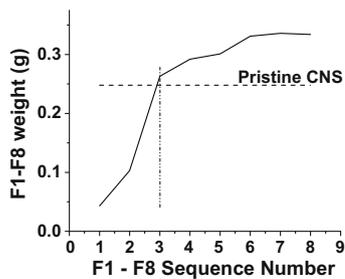**Fig. 4.** Char materials formed on glass fiber mats during cone calorimeter test.

Fig. 5. Weights of F1–F8 residues.

survive the cone calorimeter test. This reasoning is supported by the fact that CNS residues F3–F8 remained free-standing after the test.

It is clear that the fire retardancy of the CNS-8 laminate has been achieved through a mechanism different from forming one barrier layer through the accumulation of nanoparticles only on the burning surfaces [1,4–8]. It has been reported that the CNF could improve the fire retardancy of polymers through its continuous protective layer at relative high-loading. In this study, the top ply of CNS could not contribute to the fire retardancy of the CNS-8 due to the low thermal stability of the polyester film covering the top surface of the laminate. In addition, highly concentrated CNFs on the top surface could easily absorb heat flux and be rapidly heated up to the temperature of ignition, then quickly ignite the surrounding polymer resin [5–8]. The temperature of the test samples decreases from the top burning surface towards the bottom of the specimens. Although the underlying CNS could survive, the degradation of the polyester resin would take place. These degradation products could easily migrate up and fuel the combusting surface. However, the multiple plies of CNS in the laminates could limit or slow down their migration. These degradation products could deposit on the surfaces of CNS and form charred floccules with compact structure and higher thermal stability. Therefore, the CNS would work together with the charred materials as effective barrier and insulator limiting the upward migration of the flammable materials and the downward transmission of the heat flux.
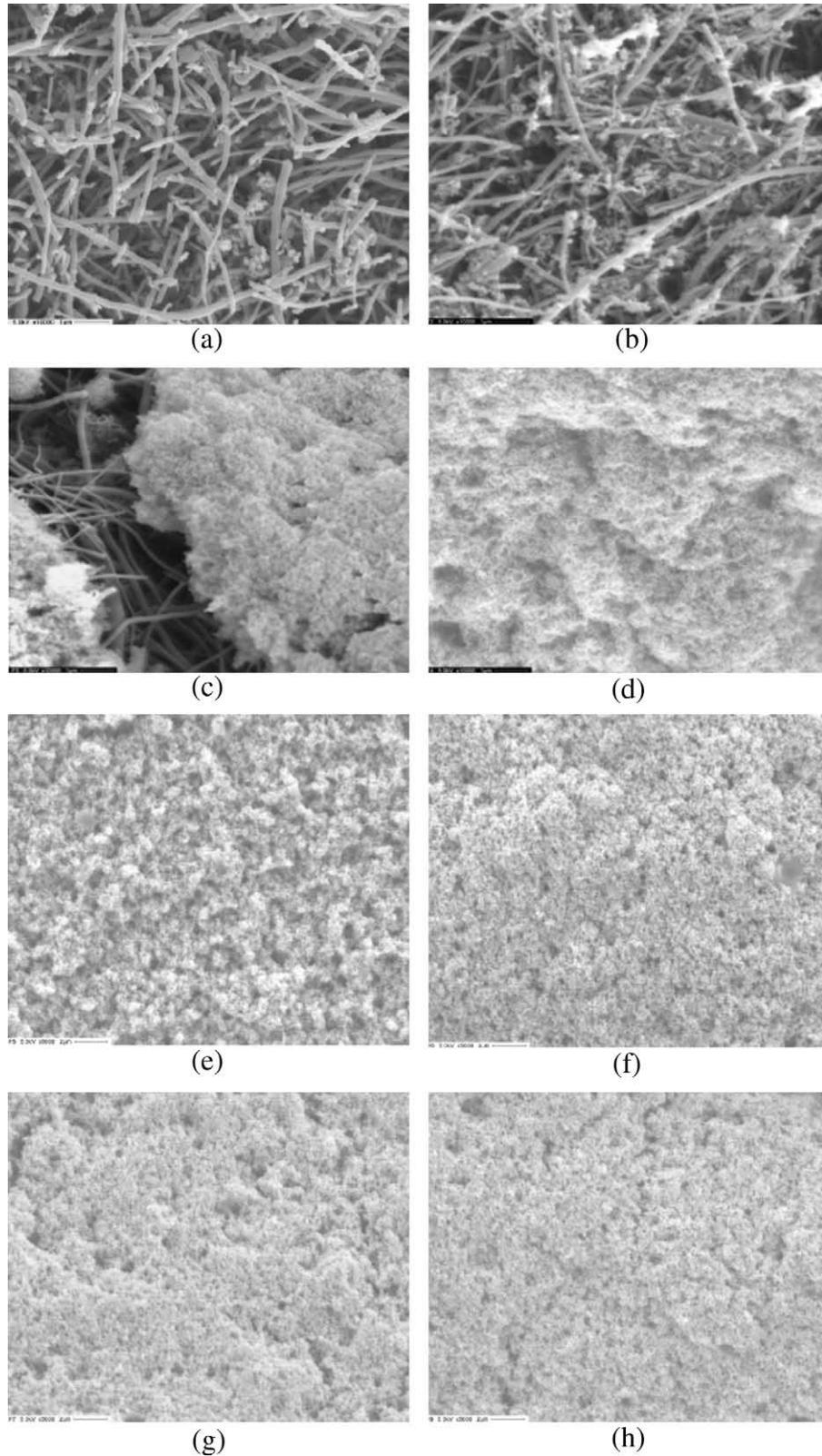
Fig. 6. SEM images of residues: (a) pristine CNS; (b) F2 residue; (c) F3 residue; (d) F4 residue; (e) F5 residue; (f) F6 residue; (g) F7 residue; and (h) F8 residue.

4. Conclusions

The carbon nanofiber sheets were successfully incorporated into the glass fiber reinforced polymer composites just like traditional glass fiber mats through resin transfer molding process.

The fire retardancy of the laminates was enhanced through the barrier effect of the embedded multi-ply CNS. However, the CNS on the top surface of the laminates was found not to contribute to the fire retardancy due to the low thermal stability of the polyester film covering on the top surface. The CNS residues and
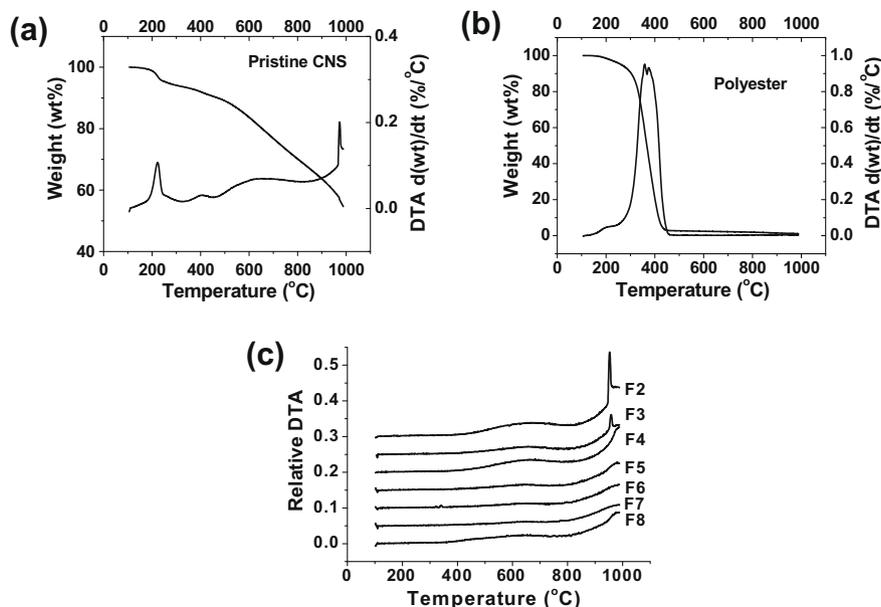
Fig. 7. TGA analysis of (a) pristine CNS; (b) polyester resin; and (c) F2–F8 residues.

charred materials obtained during cone calorimeter test varied in appearance, shape of the floccules, and area of the surface covered by the floccules depending on the distance from the top to bottom of the laminates. The synergistic interactions between the CNS and charred materials could restrict the melt flow and the migration of flammable vapor products to the top surface of the laminates, and prevent the transmission of the external heat to the underlying polyester resin. The ongoing work is to optimize the synergistic effect between CNF and other additives (such as polyhedral oligomeric silsequioxane, and ammonium polyphosphate), which will increase the char yielding and therefore enhance the fire performance.

Acknowledgements

References

[1] Tang T, Chen XC, Chen H, Meng XY, Jiang ZW, Bi WG. Catalyzing carbonization of polypropylene itself by support nickel catalyst during combustion of polypropylene/clay nanocomposite for improving fire retardancy. Chem. Mater. 2005;17:2799–802.
[2] Gilman JW. Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites. Appl Clay Sci 1999;15:31–49.
[3] Beyer G. Carbon nanotubes as flame retardants for polymers. Fire Mater 2002;26:291–3.
[4] Kashiwagi T, Harris R, Zhang X, Briber RM, Cipriano BH, Award WH, et al. Flame retardant mechanism of polyamide 6-clay nanocomposites. Polymer 2004;45:881–91.
[5] Kashiwagi T, Grulke E, Hilding J, Harris R, Awad W, Douglas J. Thermal degradation and flammability properties of polypropylene/carbon nanotube composites. Macrom Rapid Commun 2002;23:761–5.
[6] Kashiwagi T, Grulke E, Hilding J, Groth K, Harris R, Butler K, et al. Thermal and flammability properties of polypropylene/carbon nanotube nanocomposites. Polymer 2004;45:4227–39.
[7] Kashiwagi T, Du F, Winey KI, Groth K, Shields J, Bellayer S, et al. Flammability properties of polymer nanocomposites with single-walled carbon nanotubes: effects of nanotube dispersion and concentration. Polymer 2005;46:471–81.
[8] Kashiwagi T, Du FM, Douglas JF, Winey KI, Harris RH, Shields JR. Nanoparticle networks reduce the flammability of polymer nanocomposites. Nat Mater 2005;4:928–33.
[9] Zanetti M, Camino G, Mu¨lhaupt R. Combustion behaviour of EVA/fluorohectorite nanocomposites. Polym Degrad Stab 2001;74:413–7.
[10] Gilman J W, Harris Jr R H, Shields J R, Kashiwagi T, Morgan A B. A study of the flammability reduction mechanism of polystyrene-layered silicate nanocomposite: layered silicate reinforced carbonaceous char. Polym Adv Technol 2006;17:263–71.
[11] Kandola BK, Horrocks AR, Myle P, Blair D. Mechanical performance of heat/fire damaged novel flame retardant glass-reinforced epoxy composites. Compos: Part A 2003;34:863–73.
[12] Kandola BK, Akonda MH, Horrocks AR. Use of high-performance fibres and intumescents as char promoters in glass-reinforced polyester composites. Polym Degrad Stab 2005;88:123–9.
[13] Kandola BK, Horrocks AR, Myler P, Blair D. The effect of intumescents on the burning behaviour of polyester-resin-containing composites. Compos: Part A 2002;33:805–17.
[14] Sorathia U, Ness J, Blum M. Fire safety of composites in the US navy. Compos: Part A 1999;30:707–13.
[15] Mortaigne B, Bourbigot S, Le Bras M, Cordellier G, Baudry A, Dufay J. Fire behavior related to the thermal degradation of unsaturated polyesters. Polym Degrad Stab 1999;64:443–8.
[16] Le Lay F, Gutierrez J. Improvement of the fire behaviour of composite materials for naval application. Polym Degrad. Stab 1999;64:397–401.
[17] Scudamore MJ, Briggs PJ, Prager FH. Cone calorimetry – a review of tests carried out on plastics for the Association Manufacturers in Europe. Fire Mater 1991;15:65–84.
[18] Henderson JB, Weibelt JA, Tant MR. A model for the thermal response of polymer composite materials with experimental verification. J Compos Mater 1985;19:579–95.
[19] Asaro RJ, Lattimer B, Mealy C, Steele G. Thermo-physical performance of a fire protective coating for naval ship structures. Compos Part A 2009;40:11–8.
[20] Bom D, Andrews R, Jacques D, Anthony J, Chen B, Meier MS, et al. Thermogravimetric analysis of the oxidation of multiwalled carbon nanotubes: evidence for the role of defect sites in carbon nanotube chemistry. Nano Letter 2002;2(6):615–9.