Fire retardancy of clay/carbon nanofiber hybrid sheet in fiber reinforced polymer composites

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ABSTRACT

In this paper, two kinds of clay/carbon nanofiber hybrid sheets containing 0.05 wt% and 0.20 wt% of Cloisite Na$^+$ clay, were fabricated through a high-pressure filtration system. These sheets were integrated onto the surface of laminated composites like traditional continuous fiber mats through vacuum-assisted resin transfer molding process. The fire performance of the laminated composites was evaluated with cone calorimeter tests under an external radiant heat flux of 50 kW/m^2. Their residues were analyzed with scanning electron microscopy and thermal gravimetric analyses. It was found that the clay/nanofiber hybrid sheets survived on the combustion surface of composites and significantly reduced the heat release rate by ~60.5%. The protective clay layer reduces the heat release rates and the nanofiber network reinforces the clay layer against the air bubbling and melt flow of the products degraded from the polymer resin. The clay/carbon nanofiber hybrid sheet combines the barrier and insulator effects of the clays with the re-emitting heat effect of carbon nanofibers on the combustion surface of composites.

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1. Introduction

A variety of nanoparticles have been used to fabricate fire retardant nanocomposites with improved mechanical and functional properties. The common nanoparticles used for fire retardants include nanoclay, single-walled carbon nanotubes, multi-walled carbon nanotubes, carbon nanofibers, and polyhedral oligomeric silsesquioxanes (POSS). These nanoparticles provide an alternative to conventional fire retardants to reduce the flammability of polymer resin. Compared to conventional fire retardants, they are environmentally friendly, highly efficient, and capable of imparting polymers other properties.

Gilman [1] first reported that the presence of montmorillonite clay in the polymer matrix could substantially improve the fire performance. The fire retardancy of clay/polymer composites with a variety of polymer resins has been demonstrated. Wilkie and co-workers [2,3] reported that even when the fraction of clay was as low as 0.1%, the peak heat release rate in a cone calorimeter was lowered by 40%. The physical mechanism is the formation of a protective clay layer to lower the heat release rate and hinder the combustion of polymers. However, the poor dispersion of clay, the decomposition of the organic surfactant in the clay gallery, and the high viscosity of polymer melt limit the application of clay in fire retardant nanocomposites. In addition, such a clay layer

could be significantly affected by the melt flow and the bubbling of degraded products near the sample surface. Previous studies reported the fire retardant performance of carbon nanotubes in the polymers [4–7]. The efficiency of carbon nanotubes is very high and a much lower loading level of nanotubes (1–2 wt%) can form a relatively uniform network without any cracks or gaps. Very few literatures reported the fire retardant performance of carbon nanofibers due to the low efficiency in forming the nanofiber network when directly mixing them with the polymers [8]. In order to achieve an equivalent fire retardant effectiveness of carbon nanotubes, a higher loading level of carbon nanofibers is required. However, the use of carbon nanofibers is much more cost-effective than carbon nanotubes.

Fiber reinforced polymer matrix composites have become attractive engineering materials to replace conventional metallic materials in many important sectors of industry such as aircraft, naval constructions, ships, building and offshore structures. However, these materials are susceptible to combustion and fire damage due to their chemical structures. Although the nanoclay, carbon nanotubes, carbon nanofiber, and POSS have been used to enhance the fire retardancy of polymer nanocomposites, their applications have been limited in fiber reinforced polymer matrix composites. Very few studies have been reported on the fire retardant application of nanopartciles or additives in fiber reinforced polymer matrix composites [9–13]. In our work, one specialty of sheet (carbon nanofiber sheet, CNS) was developed by filtering well-dispersed carbon nanofibers under well-controlled processing

conditions [14–16]. The freestanding nanofiber sheet has a uniform network structure due to the entanglement of nanofibers with each other. Our research results show that the existence of carbon nanofiber sheet on the surface of laminated composites was not effective to improve the fire performance of composites due to a relatively low thermal stability of carbon nanofiber sheet. In this paper, we developed a freestanding clay/carbon nanofiber hybrid sheet, in which the clay particles and the nanofiber network penetrated into each other with strong physical strength due to their inter-reinforcing. Such a hybrid sheet was incorporated onto the surface of glass fiber reinforced polyester composites through vacuum-assisted resin transfer molding process. The flammability properties of the composites were evaluated with cone calorimeter tests. The residues were analyzed with scanning electron microscopy and thermal gravimetric analyses.

2. Experimental

2.1. Materials

Vapor grown carbon nanofiber (Pyrograf® III PR19-PS) was supplied from Applied Sciences Inc., Cedarville, Ohio. The nanofiber has a diameter of 50–150 nm and a length of 30–100 μm. The Cloisite Na$^+$ clay, one kind of organically modified clay (Cloisite 20A) was supplied from Southern Clay Products, Inc. The glass fiber was supplied from Composites One, Inc. with a surface density of 800 g/m^2. The unsaturated polyester resin supplied from Eastman Chemical Company was used as polymer matrix for laminated composites with the MEK peroxide as hardener at a weight ratio of 100:1.

2.2. Processing of clay/carbon nanofiber hybrid sheets and nanocomposites

The carbon nanofibers were received in powders from Applied Sciences, Inc. The nanofibers were grinded in a mortar with a small amount of de-ionized water. After grinding, they were transferred into 500 ml glass beaker and 400 ml water was added. The mixture was subsequently sonicated using a high intensity sonicator (Sonicator 3000 from Misonix Inc.) for 20 min to make a suspension of carbon nanofibers. After the suspension and the probe were cooled down to room temperature, the suspension was sonicated for another 20 min under the same condition. The suspension of 300 ml at the upper level of the beaker was used and mixed with the solution of clay. The mixture was sonicated for 10 min prior to being filtered through 0.4 μm polycarbonate membrane under high air pressure. The as-prepared sheet (clay/carbon nanofiber sheet, CCNS) was then dried in oven at 120 °C for 2 h. In this study, two kinds of sheets, CCNS5 and CCNS20 were prepared with 0.05 wt% and 0.20 wt% clay, respectively.

Vacuum-assisted resin transfer molding process was used to manufacture laminated composites. The CCNS or CNS sheet had good mechanical strength and flexibility to allow for handling like traditional glass fiber mat during making the composites. The sheet was laid on the surface of an aluminum mold and sealed along the edges. In the next step, eight plies of glass fiber mats were then stacked on the mold layer by layer. After applying all the fiber mats, vacuum bagging arrangements were made by applying release film, flow media, and bagging materials. The resin was then sucked into the bag under vacuum. After being cured at room temperature, the composite panel was post-cured at 120 °C for 2 h. Several composite panels were made and their compositions are listed in Table 1. For the panels of GE-CNS-1-20A and GE-CNS-0-20A, the polyester resin was compounded with 0.05 wt% Cloisite Na$^+$ clay. There was one ply of nanofiber sheet on the surfaces of GE-CNS-1 and GE-CNS-1-20A. No carbon nanofiber sheets were on the surfaces of GE-CNS-0 and GE-CNS-0-20A.

2.3. Characterization and measurements

The flammability of the composite panels was evaluated with cone calorimeter tests according to ASME E1354/ISO 5660. An external radiant heat flux of 50 kW/m^2 was applied. All of the panels were cut as circular disk with a diameter of 75 mm using a water jet. They were placed on a horizontal position and wrapped with a thin aluminum foil. The thermal gravimetric analysis was conducted using a TA Instruments TGA Q 500 from 100 °C to 1000 °C in N$_2$ with a heating rate of 10 °C/min on the CNS, CCNS and their residues. They were also characterized with scanning electron microscopy (JEOL 6400F at 5 kV). The samples were sputtered with 10 nm of Au prior to imaging.

Table 1
Compositions of different composite panels.

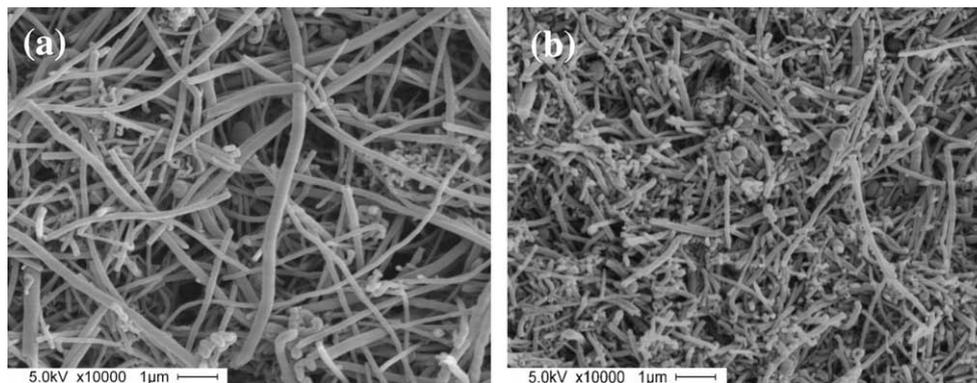| Sample ID	Composition (wt%)			
	Glass fiber	Polyester resin	Cloisite Na$^+$ clay	Carbon nanofiber
GE-CCNS20	53.22	45.68	0.20	0.88
GE-CCNS5	53.41	45.66	0.05	0.87
GE-CNS-1	54.60	44.96	0	0.84
GE-CNS-0	53.12	46.88	0	0
GE-CNS-1-20A	53.50	44.72	0.91	0.87
GE-CNS-0-20A	53.02	46.04	0.94	0

Fig. 1. SEM images of pristine CNS: (a) top surface and (b) bottom surface.

3. Results and discussion

3.1. Morphologies of CNS and CCNS

The pristine CNS has a density of 0.400 g/cm^3 and a thickness of 0.25 mm. The top surface of CNS shows that it mainly consists of well-dispersed carbon nanofibers with larger length and smaller diameter. The bottom surface of CNS contains shorter, smaller nanofibers and catalyst particles due to the deposit during filtration process, as shown in Fig. 1. Compared to the nanotube and nanofiber, the clay has much lower thermal conductivity and nanometer size in one dimension, which makes it barrier to the mass transmission. In this study, 0.05 wt% and 0.20 wt% Cloisite Na$^+$ clay were added to CCNS5 and CCNS20, respectively. The CCNS5 has a thickness of 0.27 mm and a density of 0.411 g/cm^3; the CCNS20 has a thickness of 0.28 mm and a density of 0.502 g/cm^3. The addi-

tion of Cloisite Na$^+$ clay increases the density of the nanofiber sheet. Figs. 2 and 3 show the top and bottom surfaces of CCNS5 and CCNS20, respectively. The cross section of CCNS20 indicates the close packing between the nanofibers and the clay particles in the sheet, as shown in Fig. 3c.

3.2. Thermal stability of CNS and CCNS

The thermal stability of the nanofiber sheet is related to the fire performance of polymer composites. The Cloisite Na$^+$ clay, CNS, CCNS5, and CCNS20 were analyzed with TGA, as shown in Fig. 4. The Cloisite Na$^+$ clay has much higher thermal stability with a decomposition peak in the temperature range of 700–800 °C. It has only 6.5% weight loss at 1000 °C. The CNS has a poor thermal stability with two decomposition peaks at ~220 °C and 400 °C, respectively. The weight loss is ~45% at 1000 °C. Therefore, the
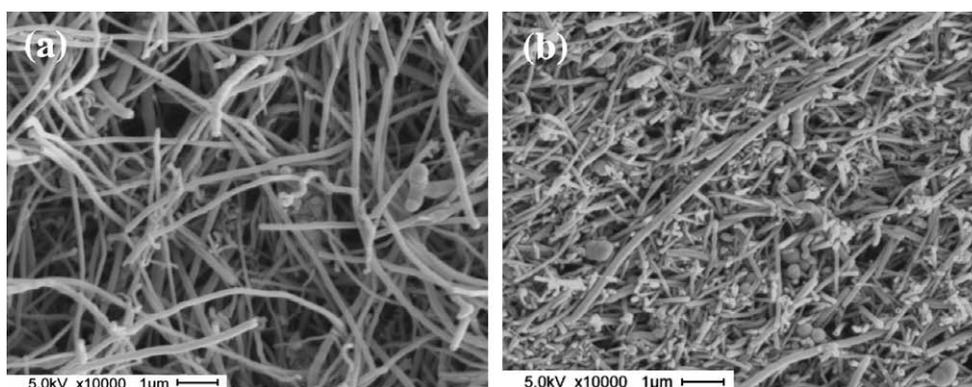

Fig. 2. SEM images of CCNS5: (a) top surface and (b) bottom surface.
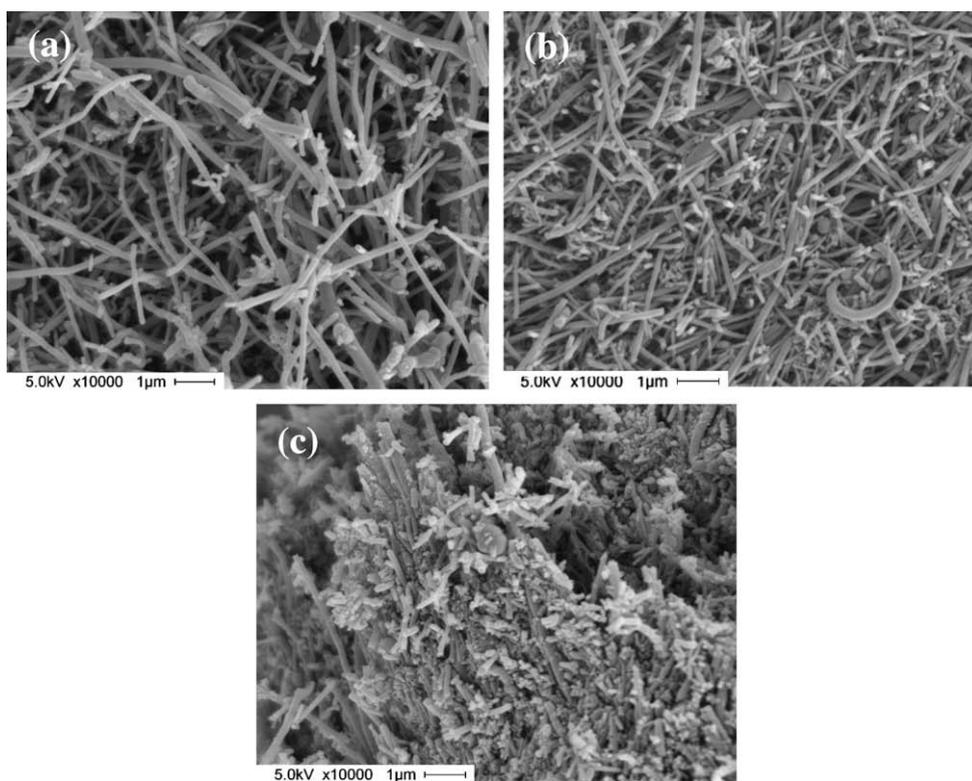

Fig. 3. SEM images of CCNS20: (a) top surface, (b) bottom surface, and (c) cross-section.

thermal stability of CNS needs to be improved for fire retardant application. The TGA results of CCNS5 and CCNS20 indicate that the addition of clay significantly improves the thermal stability of CNS. Although only 0.05 wt% clay is added, CCNS5 has no decomposition peak at ~220 °C and the weight loss decreased to ~33.1% at 1000 °C. With 0.20 wt% loading level of clay, CCNS20 has all decomposition peak significantly decreased and the weight loss is lowered down to ~14.4% at 1000 °C. Therefore, it can be seen that the thermal stability of the nanofiber sheet is significantly improved due to the incorporation of clay.

3.3. Cone calorimeter tests

The CNS, CCNS5, and CCNS20 were integrated onto the surface of laminated composites, designated as GE-CNS-1, GE-CCNS5, and GE-CCNS20, respectively. Cone calorimeter tests were conducted under an external radiant heat flux of 50 kW/m^2. Fig. 5 shows the fire damage of CCNS20, CCNS5, and CNS before and after cone calorimeter tests. The CCNS20 and CCNS5 are not burned off and still remain on the sample surface without any cracks or gaps. However, the residual layer is very fragile, especially in GE-CCNS5

due to the fire damage to carbon nanofibers. The top surface of the residue has a color like the clay and the bottom surface is black, indicating that more clay particles remain on the top surface. In other words, more nanofibers are burned on the top surface. After fire damage, CCNS5 and CCNS20 have their thicknesses decreased from 0.27 mm to 0.09 mm and from 0.28 mm to 0.15 mm, respectively. There are more carbon nanofibers remaining in CCNS20 due to the protection of clay particles. Different from CCNS5 and CCNS20, CNS only has the red metal catalyst particles on the surface. Therefore, the existence of Cloisite Na$^+$ clay plays a crucial role in the residues of CCNS5 and CCNS20.

The heat release rate (HRR) is an important parameter to evaluate the fire performance of polymer composites. Fig. 6 shows the HRR curves of all test samples. Compared to GE-CNS-0, GE-CCNS20 has a significant lower HRR and GE-CNS-1 has a slightly increased HRR. There is a 60.5% reduction in the HRR peak for GE-CCNS20 and a 17.0% increase for GE-CNS-1. The GE-CCNS5 has a similar HRR peak with GE-CCNS20. Obviously, the existence of clay reduces the HRRs of GE-CCNS5 and GE-CCNS20. Meanwhile, an increase in HRR peak of GE-CNS-1 indicates that the CNS does not improve the fire performance of composites. Compared to GE-
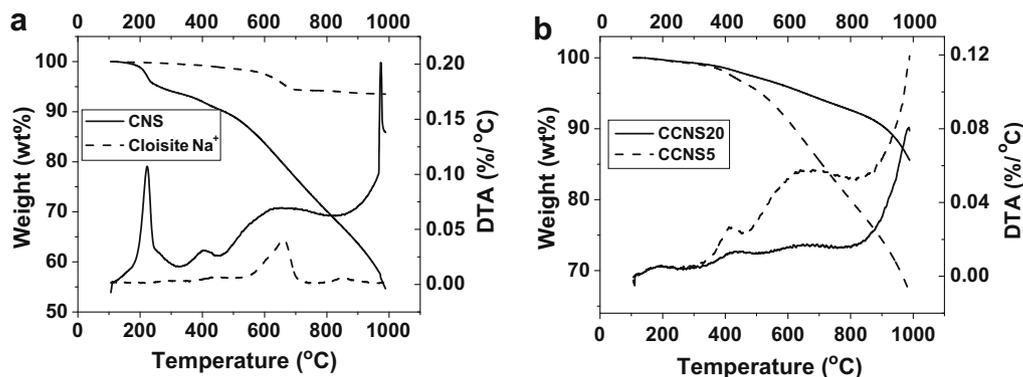

Fig. 4. TGA results of: (a) CNS and Cloisite Na$^+$ clay and (b) CCNS5 and CCNS20.
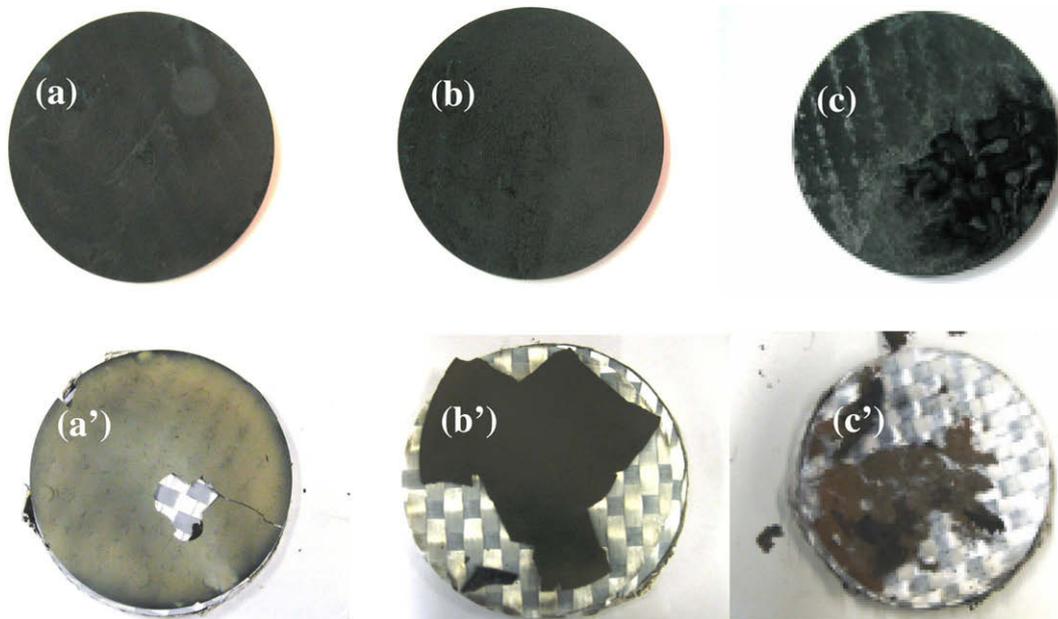

Fig. 5. Sample surfaces before and after cone calorimeter tests: (a, a′) GE-CCNS20 and its residue, (b, b′) GE-CCNS5 and its residue, and (c, c′) GE-CNS-1 and its residue.
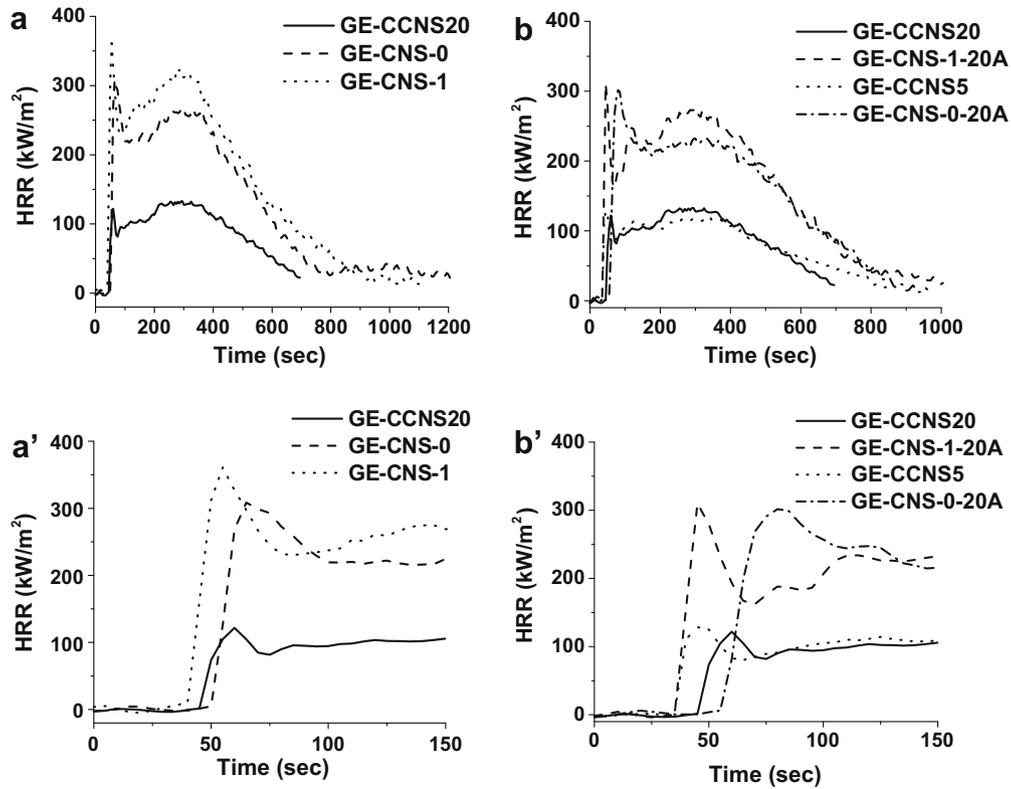
Fig. 6. Heat release rate curves of: (a, a′) GE-CCNS20, GE-CNS-0, and GE-CNS-1 and (b, b′) GE-CCNS20, GE-CCNS5, GE-CNS-0-20A, and GE-CNS-1-20A.

CNS-0 and GE-CNS-1, both GE-CNS-0-20A and GE-CNS-1-20A have their HRR curves slightly decreased. However, their HRRs are still much higher than those of GE-CCNS20 and GE-CCNS5, even though they have 0.20 wt% and 0.05 wt% of Cloisite 20A clay compounded with the polymer resin, respectively. Therefore, it can be seen that the method of directly compounding clay with the resin has lower
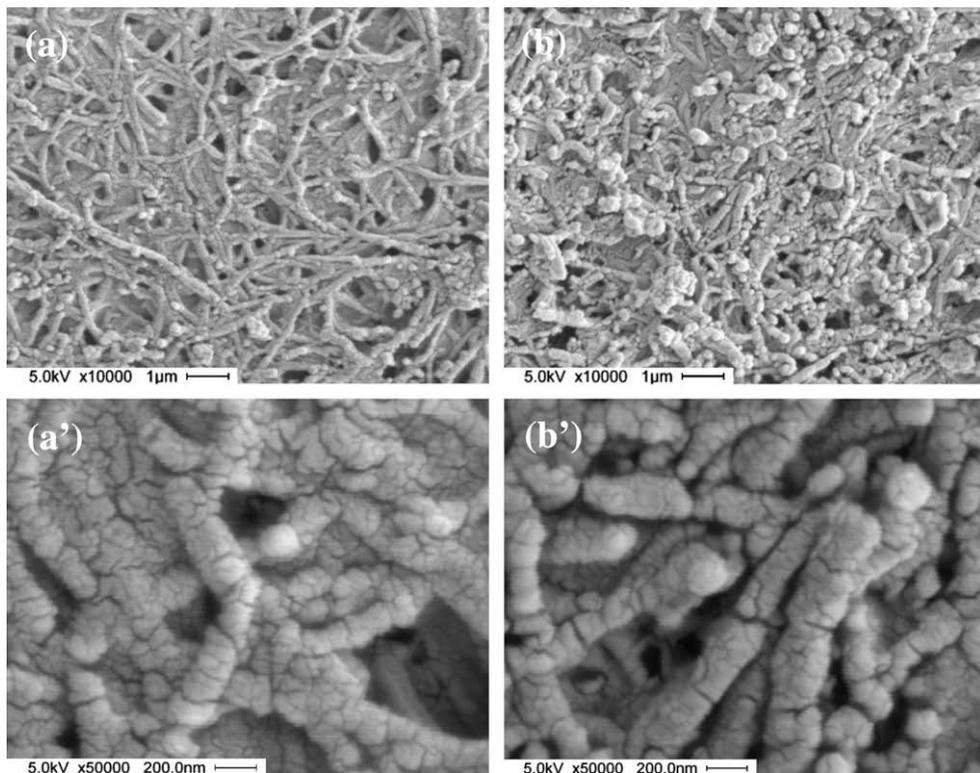

Fig. 7. Morphologies of CCNS20 residue: (a, a′) top surface and (b, b′) bottom surface.

efficiency to improve the fire performance of composites compared to the use of clay/carbon nanofiber hybrid sheet.

Although GE-CCNS20 and GE-CCNS5 have similar HRR curves, GE-CCNS20 has much longer ignition time than GE-CCNS5. The shorter ignition time of GE-CCNS5 is partly due to the complete penetration of CCNS5 by the polyester resin. As shown in Fig. 5, the polyester resin penetrated CCNS5 and formed a very thin layer of resin on the surface of GE-CCNS5. However, there is no obvious resin layer on the surface of GE-CCNS20 due to the lower permeability the nanofiber sheet with 20 wt% of Cloisite Na$^+$ clay. Compared to carbon nanofiber, the polyester resin has lower decomposition and ignition temperature. The excess resin on the sample surface decreases the ignition time of GE-CCNS5. Hence, the loading level of clay should be high enough to delay the ignition, which is important to prevent composites from quickly catching fire. A similar situation takes place in GE-CNS-1 and GE-CNS-1-20A. Their ignition times are obviously shorter than those of GE-CNS-0 and GE-CNS-0-20A.

3.4. Analysis of residues after fire damage

Although CNS could be burned off on the combustion surface of composite samples, the protective layer remaining on the surfaces of GE-CCNS20 and GE-CCNS5 reduces the HRRs. Compared to the morphology of original CCNS20, the residue of CCNS20 has been changed, as shown in Fig. 7. The morphology change can be seen from the appearance of the protective clay layer after fire damage. The clay particles and the nanofiber networks penetrate into each other in the residue of CCNS20. The Cloisite Na$^+$ clay particles not only fill the pores of carbon nanofiber network but also form a protective layer surrounding the nanofibers. Compared to the nanofiber network, the clay protective layer has lower thermal transmission and smaller cracks at the nanometer scale, which could effectively limit the transmission of heat flux and the supply of combustible fuels. Different from CCNS20, CCNS5 has its morphology change on the combustion surfaces of samples during cone calorimeter tests, as shown in Fig. 8. The nanofiber networks on both surfaces are almost burned off. It seems that only clay particles remain on the top surface. On the bottom surface, there are some remaining carbon nanofibers to weakly bond to the clay particles. This can explain why the layer of CCNS5 residue is more fragile than the layer of CCNS20 residue. Although the layers of CCNS5 and CCNS20 residues mostly consist of clay particles, the Cloisite Na$^+$ clay still impart good fire retardancy to CCNS5 and efficiently lower the HRR of GE-CCNS5. However, the clay content needs to be high enough to protect the nanofiber network.

The residues of CCNS5 and CCNS20 were collected for TGA analysis, as shown in Fig. 9a. There is one broad decomposition peak for CCNS5 and CCNS20 residues at 750–950 °C. The polyester resin is completely decomposed below 450 °C, as shown in Fig. 9b. The Cloisite Na$^+$ clay only has one decomposition peak in the temperature range of 700–800 °C. The decomposition peaks of CCNS5 and CCNS20 residues are due to the decomposition of partially damaged carbon nanofiber. The TGA results indicate that there are more materials decomposed above 750 °C in CCNS20. Therefore, there are more carbon nanofibers remaining in the sheet after fire damage.

4. Conclusions

Clay/carbon nanofiber hybrid sheet were developed and integrated onto the composite surface to improve the fire performance of fiber reinforced polymer matrix composites. The heat release rate of the composites with the hybrid sheet was reduced ~60.5%. The hybrid sheet acted as a protective layer in improving the fire retardancy of GE-CCNS5 and GE-CCNS20, in
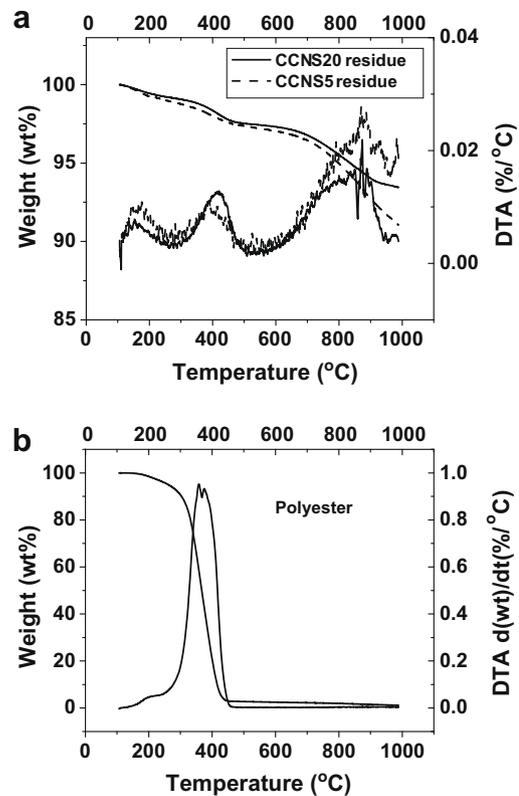
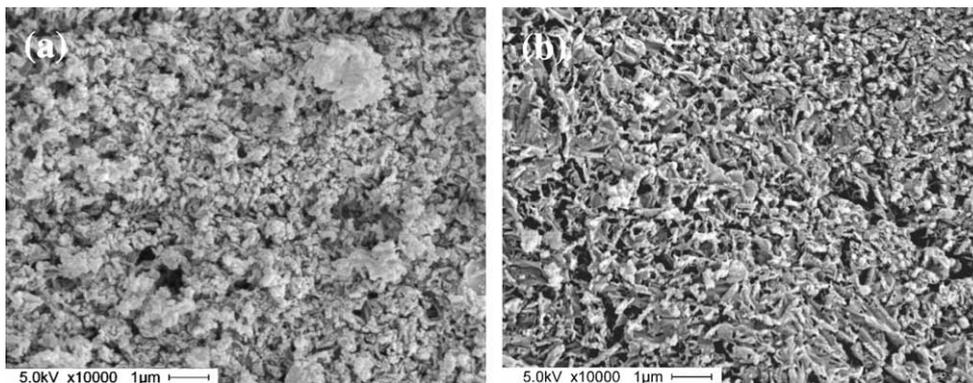**Fig. 9.** TGA results of: (a) CCNS5 and CCNS20 residues and (b) polyester resin.

Fig. 8. Morphologies of CCNS5 residue: (a) top surface and (b) bottom surface.

which the Cloisite Na$^+$ clay plays a determined role due to its high thermal stability and structural characteristics. In the pre-formed sheet, the Cloisite Na$^+$ clay can protect carbon nanofibers from being severely burned. On the other hand, the existence of carbon nanofiber could make the pre-formed Cloisite Na$^+$ clay layer exempt from the damage of the melt flow and the bubbling of the products degraded from the polyester resin. There-fore, the Cloisite Na$^+$ clay layer is strengthened by the nanofiber network, which will be kept as a perfectly continuous barrier to O$_2$ supply and pyrolyzed fuel to the combustion surface of composites.

Acknowledgements

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