CARBON NANOPAPER ENABLED STRUCTURAL AND MULTIFUNCTIONAL NANOCOMPOSITES

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Introduction

Vapor grown carbon nanofibers (VGCNF) are ideal reinforcing fillers for polymer composites owing to their promising mechanical properties, excellent thermal and electrical properties [1-2]. Although CNF has much higher percolation threshold in enhancing the properties of polymer composites than carbon nanotubes, it is commercially available with much lower cost. Therefore, there is an increasingly interest to explore potential applications of CNFs.

Recently, we have developed a novel method to convert CNFs into CNF paper, which could be further integrated into laminated composites through resin transfer molding (RTM) or vacuum-assisted resin transfer molding (VARTM) process [3-4]. This new process method can overcome some key issues involved into nanocomposites processing such as heavy reagglomeration of nanoparticles and the high viscosity of the solution. In addition, in order to achieve multifunctionalities, CNF paper can simply interacted with other nanoparticles such as nickel nanostrands and nanoclay to improve the electrical conductivity, thermal stability and mechanical properties. In this study, the treated-CNF paper has been integrated into laminated composites for lightning strike protection, fire retardancy and damping augmentation.

Experimental

Materials

Vapor grown carbon nanofibers (Pyrograf III PR-19-PS) and Cloisite Na^+ clay were supplied from Applied Sciences Inc. and Southern Clay Products, Inc., respectively. The EPON 862 epoxy resin (Bisphenol F epoxy) and EPI-CURE W hardner supplied from Miller-Stephenson Chemical Company, Inc. were mixed at a weight ratio of 100:26.5. The unsaturated polyester resin and MEK peroxide hardner supplied from Composites One were mixed at a weight ratio of 100:1.25. The carbon fiber was 12K unidirectional fiber supplied from Carbcom, Inc.

Preparation of CNF Paper and Nanocomposites

CNFs were purified and mildly functionalized with hydrochloric acid (HCl) and rinsed thoroughly with deionized water to remove residual metal catalyst particles. CNFs were further oxidized in the nitric acid and more chemical functional groups were created on the surface of CNFs. The as-treated CNFs were grinded in a mortar with a small amount of de-ionized water. After grinding, they were transferred into container and more de-ionized water was added to prepare the suspension with a concentration of 1 mg/ml. The suspension was subsequently pumped into the sonicator and thereafter to the filtration system to make CNF paper. During CNF papermaking process, other nanoparticles such as nickel nanostrands and nanoclay were added to the CNF suspension and further sonicated. The as-prepared CNF paper was integrated into composite laminates through RTM process for vibrational damping test or VARTM process for cone calorimeter test and lightning strike test.

Electrical Conductivity & Lightning Strike Test

The electrical resistivity of CNF paper was measured with four-point cylindrical probe with SIGNATONE QUADPRO system. The lightning strike test was performed by Lightning Technologies, Inc. (Pittsfield, MA). The panels were tested under various lightning strike parameters such as Amperage and strike time.

Cone Calorimeter Test

The flammability of CNF paper composites was evaluated with cone calorimeter test. The external radiant heat flux of 50 kW/m^2 was applied on the circular samples with a diameter of 75 mm. The CNF papers were characterized with TGA Q500 at 10^oC/min from 100 to 1000^oC in N_2 with a flow rate of 60 cm^3/min.

Vibrational Damping Test

The composite plate without CNF paper and the nanocomposite plate with CNF paper were used as the specimens for vibrational damping tests. For each plate, a PZT (Lead Zirconate Titanate, a type of piezoceramic material) patch (20mm × 20mm) was attached at the center of the plate as an actuator to excite the plate and a smaller PZT patch (10mm × 8mm) was attached at the corner of the plate as a sensor to detect the plate's vibration.

Results and Discussion

Lightning Strike Protection of CNF Paper

Three 16" × 16" composite panels (designated as CE-NCNS-1, CE-NCNS-2, and CE-NCNS-3) were manufactured with three types of CNF papers (designated as NCNS-1, NCNS-2 and NCNS-3, respectively) through VARTM process. Table 1 shows the electrical conductivity, nickel content, and structure of CNF papers. The NCNS had its electrical conductivity slightly increased after being integrated onto the surface of composite panel CE-NCNS. In other words, the surface of composite panel CE-NCNS had higher conductivity than original CNF paper - NCNS. Among three panels, the panel CE-NCNS-1 and the panel CE-NCNS-3 had higher electrical conductivity. Therefore, the higher nickel content in CNF paper resulted in higher electrical conductivity, leading to an improved lightning strike performance. In addition, the thicker CNF paper or CNF paper with latex binder could have better handling strength.

The damaged surface areas of three composite panels were measured after their exposure to lightning strike. It was found that the area of the damaged surface on each panel correlated to the surface conductivity of the panel. The CE-NCNS-2 panel had the largest damaged surface area. There was ~5.9% damaged area on the panel CE-NCNS-2. However, there were only ~1% and ~3.3% damaged surface area on panel CE-NCNS-1 and panel CE-NCNS-3, respectively. Fig. 1 shows the damaged surface area of the panel CE-NCNS-1 after lightning strike test.

Table 1 Electrical conductivity, nickel content and structure of CNF paper.

CNF Paper	Conductivity ($S \cdot m^{-1}$)	Nickel Content	Structure
NCNS-1	3.41E+4	19.55 g	Monolayer No binder
NCNS-2	2.22E+2	< 9.75 g	Monolayer Latex binder
NCNS-3	3.10E+4	19.55 g	Bi-layer Latex binder

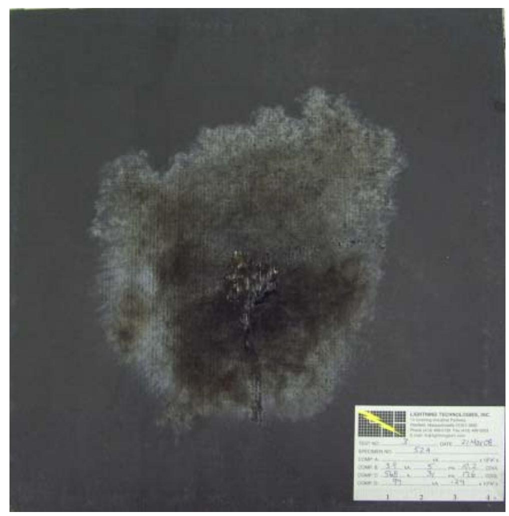

Fig. 1 Surface damage of the panel CE-NCNS-1 after lightning strike test.

Fire Retardancy of CNF Paper

The thermal stability of CNF paper played an important role in improving the fire retardancy of polymer composites. The Na^+ clay, CNF paper (designated as CNS) and CNF paper containing 20wt% of Na^+ clay (designated as CCNS20) were characterized with TGA for their thermal stabilities (Fig. 2). Clearly, the addition of nanoclay significantly improved the thermal stability of CNF paper. The CCNS20 paper had all decomposition peak significantly decreased and the weight loss at 1000^oC was lowered down to ~14.4%.

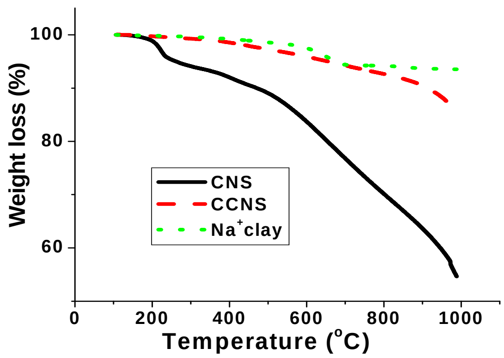

Fig. 2 Thermal stability of nanoclay and CNF paper.

In this study, CNF paper was co-molded with glass fiber mats with polyester resin to manufacture composite structure (designated as GE-CNS-1) to study the fire retardancy. Compared to the composite panel without carbon nanofiber (designated as GE-CNS-0), the CNF paper could be burned out on the surface and its effectiveness on the fire retardant performance was negative. However, the introduction of nanoclay changed the fire retardant effectiveness of the CNF paper due to the nanoclay's high thermal stability and non-combustible components. The CNF paper containing 20wt% of pristine nanoclay was integrated onto the surface of the composite panel (designated as GE-CCNS20). Its heat release rate (HRR) curve clearly demonstrated that the existence of clay in the CNF paper significantly reduced heat release rate (Fig. 3).

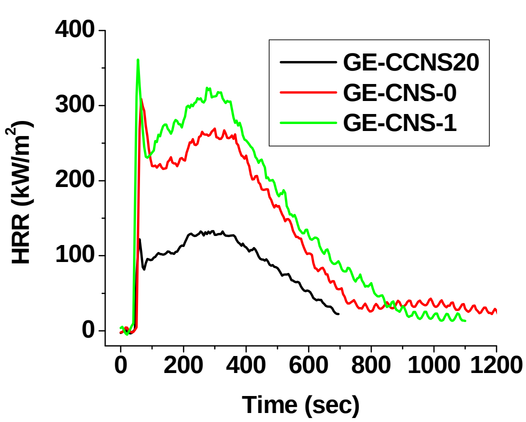

Fig. 3. Heat release rates (HRR) of GE-CCNS20, GE-CNS-0 and GE-CNS-1.

Vibrational Damping

Two different sweep sine signals were used for the damping test. One sweep sine was from 100Hz to 2000Hz to get detailed information about the first mode frequency. The other sweep sine was from 100Hz to 10,000Hz to excite the first few modes. The sweeping period of both sweep sines was set as 20 seconds. The sampling frequency was set as 40k Hz. For the nanocomposite plate with the CNF paper as surface layer, the time responses of both sweep sine excitation (Fig 4 and Fig 5). The peak value in the sweep sine response represents resonance at a certain natural frequency. From the sweep sine responses, it can be clearly seen that the peak of first mode, second mode and third mode are significantly reduced for the nanocomposite plate, which indicates that the nanocomposite plate has improved damping property.

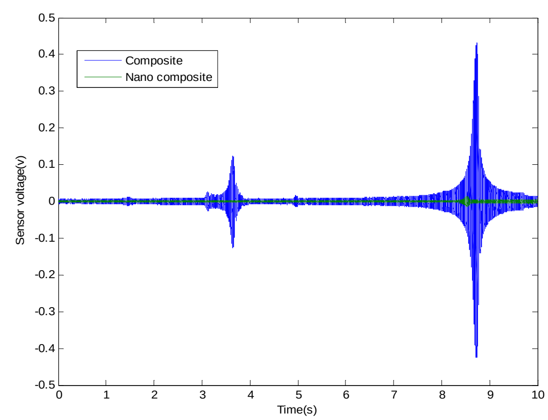

Fig. 4. Sweep sine response (100-2000Hz) of composite plate and nanocomposite plate

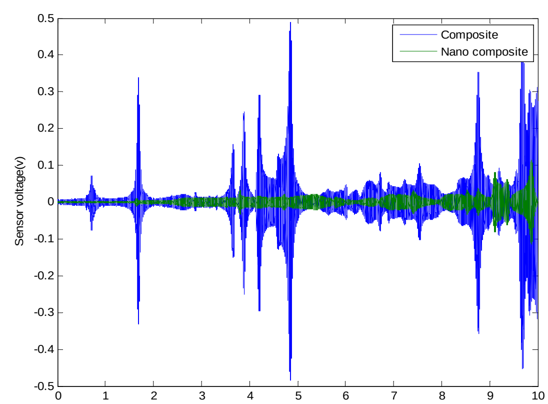

Fig. 5 Sweep sine response (100-10,000Hz) of composite plate and nanocomposite plate.

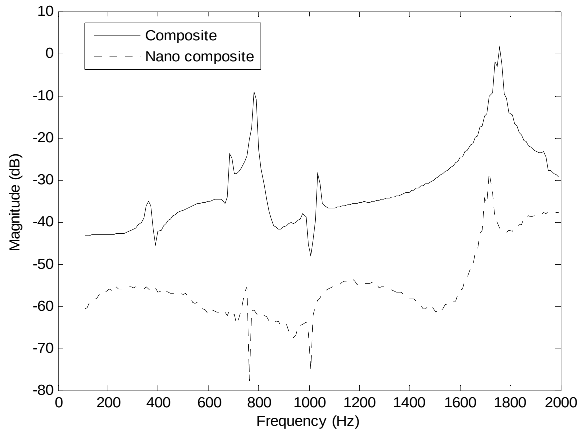

Fig. 6 Frequency responses (100-2000Hz) for composite plate and nanocomposite plate.

To further demonstrate an improved damping for the nanocomposite plate, the frequency responses of the regular composite plate and the nanocomposite plate are compared in Fig. 6 and Fig. 7, which clearly shows that the peak magnitude of the first three modes has dropped dramatically. This means the damping ratio values of the nanocomposite plate at these three natural frequencies are much larger than those of the regular composite plate.

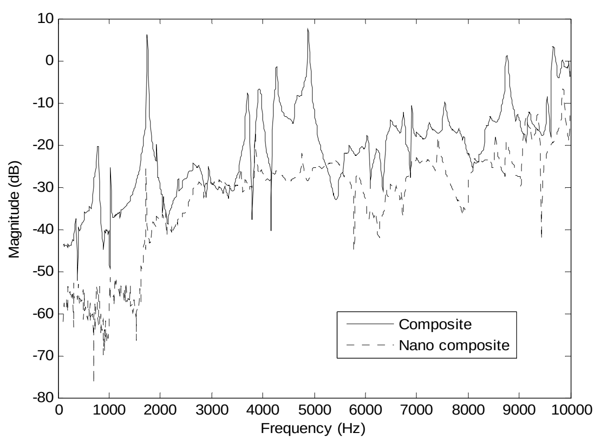

Fig. 7 Frequency responses (100-10,000Hz) for composite plate and nanocomposite plate.

Conclusions

The CNF paper has been multi-functionalized by adding various types of nanoparticles. The electrical conductivity of CNF paper was increased by adding nickel nanostrands. The high conductive pathway of the CNF paper could provide an efficient protection when the composite panels were struck by the lightning. The lightning strike tests showed that lightning strike performance depended on the surface conductivities of the panels, which further correlated to the content of nickel nanostrands. The CNF paper incorporated with nanoclay acted as a protective layer to improve the fire retardancy of polymer composites. In the CNF paper, Na+ clay played a determined role due to its high thermal stability and structural features. On the other hand, the Cloisite Na+ layers strengthened by CNFs would be kept as a perfectly continuous clay barrier to O_2 supply and pyrolyzed fuel on the burning surface. Finally, the vibrational damping tests indicated a significant increase of the damping ratios at higher frequencies and slight change in stiffness of composite laminates due to the incorporation of the CNF paper into laminated composites.

Acknowledgement

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