Lightweight carbon nanotube surface thermal shielding for carbon fiber/bismaleimide composites

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1. Introduction

Advanced carbon fiber reinforced polymers (CFRP) are being increasingly used in aerospace applications due to their desired mechanical and lightweight properties. However, the service life of CFRPs is limited by the thermal stability of their polymer matrix materials. CFRPs with epoxy and bismaleimide (BMI) matrix offer limited service in temperatures up to 177 °C and 232 °C, respectively. At elevated temperatures, the resin matrices will suffer performance degradation or even complete decomposition. Therefore, an important strategy to reduce or eliminate overheating damage is to shield CFRP materials from excessive heat using thermal protection (TP) materials.

The commonly used TP materials are ceramic coatings [1,2], carbon/carbon (C/C) composites [2], and polymeric TP materials [3]. Ceramic coatings provide exceptionally high-temperature resistance, but the thermal mismatch between different materials yields a significant challenge. C/C composites combine the mechanical properties of carbon fibers with the high thermal resistance of a carbon matrix. However, the cost and complicated fabrication process limit its applications [4]. Also, TP materials used in aerospace must be as lightweight as possible to increase payload and reduce fuel consumption. Due to these limitations, ablative composites with a polymeric matrix, such as phenolic Hexion SC-1008 [5], are often used in the TP systems [6]. Phenolic resin is one of the widely used polymeric matrices because of its high thermal stability, ablative properties, dimension stability, and chemical resistance [7]. Recent studies to improve thermal resistance involved doping and incorporating fillers, such as boron, phosphorus [8], zirconium [9], titanium or silicon compounds [10–12], carbon nanotubes (CNT) [13,14], graphene [15], ceramic particles [9,16,17], and nano-clay [18], into phenolic resins [11,16,19–22]. CNTs may potentially be an ideal functional material for composites that will improve electrical, thermal, and mechanical properties [23–33].
Using CNT sheets or buckypaper, which are networks of entangled CNTs, is offering promising results for effectively transferring the properties of CNTs into structures to improve thermal conduction performance for TP materials [34,35].

These CNT sheets have been shown to enhance the fire retardancy of polymer composites [36–39]. The main fire-retardant mechanism involves the CNT networks separating the under layer of the composites from oxygen to minimize damage from the combustion process [36]. However, research involving the high concentration of CNTs in phenolic composites is in terms of thermo-mechanical and ablation performance is limited, especially regarding the integrated thinner thermal protectors on CFRP composites [40].

This paper reports a new, simple, and reliable systematic design of a sacrificial thermal protection layer (TPL) with heat shield functionality while maintaining the mechanical strength of traditional CFRP composites. By taking advantage of high thermal stability offered by phenolic resin and high in-plane thermal conductivity offered by buckypaper, this flexible skin TPL can provide protection and retain the mechanical integrity of the composites system against thermal degradation when undergoing a low-to-moderate heat flux situation. Compared to conventional ablative materials, this study provided a new integrated design of thermal protection system with composites structures. In addition, post-flame mechanical performance of CFRP has been reported for the first time, proving the effectiveness of TPLs. A two-step curing process was developed to fabricate hybrid composites with a buckypaper/phenolic TPL that is lightweight, affordable, conformable, and durable. A bonding layer of ultra-thin (40 gsm) unidirectional carbon fiber was introduced to the design system to provide better adhesion between the TPL and CFRP substrates. Using this method, the buckypaper/phenolic TPLs were successfully bonded onto the CFRP composites, ensuring a strong interface between the two polymer matrices of the hybrid composites. The new systematic design demonstrated excellent mechanical properties using a thinner thermal shield, which minimized additional weight. This study also evaluated the thermal resistance performance of the thin buckypaper/phenolic TPLs by exposing the hybrid composite to the low heating environments (<20 W/cm² heat flux) for short periods. Results showed that the hybrid composites exhibited excellent mechanical performance, lower thermal conductivity, lower coefficient of thermal expansion (CTE), and higher ablative resistance by the new systematic design. With these integrated advantages, this systematic design could lead to scalable manufacturing of CFRPs with enhanced performance characteristics at elevated temperatures for aerospace applications.

2. Experimental

2.1. Materials

CNT sheets, supplied by Nanocomp Technologies (Merrimack, USA), were used as received without any pre-treatment. The plain-weave carbon fiber BMI prepreg was supplied by Aldila Composite Materials. Two types of unidirectional (UD) carbon fiber tapes (CFs) of 40 and 80 gsm aerial density were used. SC-1008 resol-type phenolic resin manufactured by Hexion was dissolved into isopropyl alcohol (IPA) at a solid content between 60 and 64%.

2.2. Fabrication of hybrid composites

The buckypaper/phenolic TPLs were produced using an infiltration and hot-plate curing process. Phenolic resin solutions containing 1, 3, 5, 10, and 20 wt% concentrations were prepared. The 5 wt% resin solution was selected to fabricate TPLs based on the results shown in Fig. S3. Fig. 1 shows the manufacturing process.

The CNT sheets or buckypapers were immersed in the phenolic resin solutions for 24 h, then removed from the resin solutions and allowed to dry for 24 h. Stacks of three or six layers of saturated CNT sheets were made to form the TPLs of varying thicknesses. One-layer of UD CF prepreg or one-layer dry buckypaper (BP) was selected as the bonding layer to be applied on the top of the stacked TPLs. The phenolic resin solution was added into the UD CF bonding layer at a 50% resin volume fraction, which was designed to partially impregnate the UD CF preform. The dry CNT sheet bonding layers were used as-received without further treatment. The samples were cured using hot-plates with vacuum bag under 100 psi of pressure, as shown in Fig. 1.

Table 1 shows the designs and compositions of the sample lay-ups. The bonding layer was designed to improve the bonding strength between TPLs and CFRP substrates and to reduce the discrepancies between their CTEs [41]. Designs without the bonding layer were also manufactured to act as the control sample. To prepare the hybrid composites, cured buckypaper/phenolic TPLs and CFRP prepregs were laminated on a steel mold. The assembly was vacuum-bagged and cured in an autoclave. By heating and applying pressure to the hybrid composite assembly during the autoclave process, the BMI resin in the CF prepreg was forced into the bonding layer. This methodology yielded a two-resin bonding layer with phenolic and BMI resins, as shown in Fig. 2. The CFRP composite was prepared as an additional control sample using the same curing procedure. The curing behavior and thermal stability of the SC-1008 phenolic resin was provided in Figs. S1 and S2.

Fig. 1. Fabrication of the buckypaper/phenolic TPL nanocomposites.
2.3. Characterization

The morphology of the fracture surface of the composite was examined using a scanning electron microscopy (SEM) (JEOL JSM-7401F USA, Inc.). The samples were coated with gold particles using sputter coating. The density was measured according to Archimedes’ principle. Thermogravimetric analysis (TGA) using a TGA Q50 (TA Instruments) evaluated the resin decomposition temperature and char yields at a heating rate of 10 °C/min up to a maximum temperature of 800 °C in a nitrogen atmosphere. Flexural strength and flexural modulus were tested by three-point bending (3 PB) tests in accordance with ASTM D7264 using a SHIMADZU AGS-J system at a crosshead speed of 1 mm/min. The samples were prepared in dimensions of 50.8 × 12.7 × 1 mm. The thermal diffusivities were determined using a laser-flash diffusivity instrument (LFA 457, NETZSCH). Square specimens (10 mm × 10 mm × 1 mm) were cut using a diamond saw and coated with graphite. Testing was performed over a temperature range of 40–400 °C using a light flash diffusivity system, and the thermal diffusivity was obtained from the transient pulse using Cowen analysis. CTE measurements were performed with a Thermal Mechanical Analyzer (TMA) (TMA Q400, TA Instruments) with an expansion mode heated from 30 to 350 °C at a heating rate of 5 °C/min. The preload force and applied force were set to 0.01 N and 0.1 N, respectively.

In accordance with ASTM D4541 standards, pull-off tests were conducted to determine the bonding strength of different adhesion methods. The pull-off tests were performed by securing a 20 mm diameter aluminum dolly perpendicular to the surface of TPLs with glue (Loctite E-30CL epoxy adhesive). The joints were held under pressure until the glue cured. The TPLs were cut with a saw around the dolly. The pull-off tests were carried out by applying a uniform tensile force at 0.2 MPa/s to the dolly using a DeFelsko PosiTest AT-A Automatic Adhesion Tester.

Fig. 3(a) shows the basic setup for the flame tests used to simulate high temperatures and high heat flux scenarios. A propane torch served as the heat source for the burning test (Worthington Cylinder Corp, 14.1 oz. propane hand torch cylinder). The propane

<table>
<thead>
<tr>
<th>Materials composition with volume fraction (%)</th>
<th># of saturated BP layers</th>
<th># of the Bonding layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFRP control</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CFRP-BP (6.7%)</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>CFRP-BP (9.0%)</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>CFRP-UD CF (3.5%)–BP (6.3%)</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>CFRP-UD CF (3.5%)–BP (11.6%)</td>
<td>6</td>
<td>1 (40 gsm)</td>
</tr>
<tr>
<td>CFRP-UD CF (8.1%)–BP (6.9%)</td>
<td>3</td>
<td>1 (80 gsm)</td>
</tr>
</tbody>
</table>

Fig. 2. Fabrication of hybrid composites.

Fig. 3. (a) Flame test set-up and (b) the details of the sample holder and sample dimensions (c) temperature-time curve of calibration.
torches provide a flame temperature of about 1982°C to the front surface of buckypaper/phenolic TPLs.

The flame was set perpendicular to the hybrid CFRP composites. A thermocouple (K type) was applied to the back of composites and connected to a Keithley digital multimeter. The edges of the composite samples were protected by a stainless-steel mold (Fig. 3(b)) to ensure only buckypaper/phenolic TPLs were exposed to the flame. The torch and the sample were secured in relative position to one another during testing. Fig. 3 (c) shows the calibrated temperature-burning time curve of the stainless steel. The heat flux penetrating the composite was calculated by the equations provided in the Supporting Information.

3. Results and discussion

3.1. Morphology and physical properties of hybrid composites

Fig. 4 shows the cross-sectional hybrid composites protected by buckypaper/phenolic TPLs with different volume fractions with and without UD CF bonding layers. No obvious voids were seen in SEM images of the hybrid composites, except for Fig. 4(b). Fig. 4(a) shows two components: the CFRP and the buckypaper/phenolic TPLs. The measured thickness for buckypaper/phenolic TPLs in Fig. 4(a) was 88 μm. Fig. 4(b), (c), and (d) display the cross-sections of hybrid composites with the UD CF bonding layer between the CFRP and the buckypaper/phenolic TPLs. The thicknesses of the UD CF bonding layer were about 40 μm in Fig. 4(c) and (d) and 80 μm in Fig. 4(b). The UD CF bonding layers were infiltrated with polymeric matrix and densely packed.

However, in the case of UD CF of 80 μm, Fig. 4(b) shows a significant number of voids in the thicker UD CF, indicating poor interfacial bonding between the CFRP and the buckypaper/phenolic TPLs. These voids would likely reduce the mechanical properties. Therefore, the hybrid composite design with an 80 μm UD CF bonding layer was not selected for further study. Fig. 4(e) and (f) show the hybrid composites with the dry CNT sheet bonding layer. Table 2 shows the density of hybrid composites and the volume fractions of each component. The density of hybrid composites provides a comparison of the weight saving of hybrid composites.

3.2. Bonding strength of TPLs

Pull-off tests were conducted to evaluate the bonding strength of TPLs with the CFRP substrate. An aluminum dolly was glued to the hybrid composite on the TPLs surface, as shown in Fig. 5. Three failure modes were observed where debonding occurred at the bonding layer (case A), buckypaper layer (case B), or the epoxy adhesive layer (case C) (Fig. 5(a)). In the case of A, failure occurred at the bonding layer, indicating a weak bonding interface between the TPLs and underneath the CFRP substrate. For case B, the failure initiated at the buckypaper layer, denoting excellent bonding strength between the TPLs and CFRP substrate interface. For case C, failure occurred in the glue layer, indicating a weak adhesive bonding. The sample without a bonding layer failed with buckypaper delamination (Fig. 5(b)), and samples with one-layer dry buckypaper bonding layer broke at the bonding layer (case A) leading to CFRP exposure (Fig. 5(c)).

The loss of the attached TPL resulted in complete loss of thermal protection over a large area, which if introduced to a heated environment would likely result in structural failure. For the hybrid composites with UD CF bonding layers, only a thin layer of the CNT sheet was pulled-off the TPLs, and the bonding layer was exposed, which indicates that the bonding strength between TPLs and CFRP was stronger than the buckypaper delamination strength, showing the bonding layers enhanced the bonding failure, as shown in Fig. 5(d) and (e).

3.3. Thermal stability of TPLs

The thermal stability of buckypaper/phenolic TPLs was investigated by TGA and compared to the neat phenolic resin and the neat BMI resin (Fig. 6). The thermal degradation of the neat BMI resin occurred at 400°C, and the char yield was approximately 33 wt% at 800°C. The neat phenolic resin decomposed at 400°C with the final char yield of about 63 wt% at 800°C. When compared to the two neat resins, the buckypaper/phenolic TPLs exhibited the same onset decomposition temperature but a higher residual, which included char of phenolic and CNTs at 800°C. The weight loss of buckypaper...
phenolic TPLs from 400 to 600 °C was lower than the neat phenolic resin, which indicates the BMI resin did infiltrate into the voids of buckypaper/phenolic TPLs during the second curing process of hybrid composites.

The two resins in the bonding layer potentially resulted in better adhesion between TPLs and the CFRP substrate because of BMI infiltrated into microporous TP layer preformed to form the mechanical locking. For the temperatures above 650 °C, degradation occurred, and char gradually formed. The higher residual weight with an increased thickness of TPLs was beneficial to char retention on the surface of hybrid composites.

### 3.4. Influence of TPLs on the coefficient of thermal expansion (CTE)

The CTE is a critical thermophysical property in the selection of materials for engineering applications. The through-thickness CTE of each produced hybrid composite was measured and calculated, as shown in Fig. 7(a). The CTE values of the hybrid composite samples were found to be lower than the CTE of CFRP control samples. The CTE value decreased as the volume fractions of CFRP in

### Table 2

<table>
<thead>
<tr>
<th>Hybrid composites</th>
<th>Density (g/cm³)</th>
<th>TPL thickness (μm)</th>
<th>TPL* vol%</th>
<th>UD CF thickness (μm)</th>
<th>UD CF* vol%</th>
<th>Hybrid CFRP thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFRP control</td>
<td>1.58</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1010 ± 4</td>
</tr>
<tr>
<td>CFRP-BP (6.7%)</td>
<td>1.57</td>
<td>73.2 ± 2.6</td>
<td>6.7</td>
<td>0</td>
<td>0</td>
<td>1092 ± 5</td>
</tr>
<tr>
<td>CFRP-BP (9.0%)</td>
<td>1.57</td>
<td>101.9 ± 5.2</td>
<td>9.0</td>
<td>0</td>
<td>0</td>
<td>1130 ± 4</td>
</tr>
<tr>
<td>CFRP-UD CF (3.5%)-BP (6.3%)</td>
<td>1.55</td>
<td>112.9 ± 6.4</td>
<td>6.3</td>
<td>40</td>
<td>3.5</td>
<td>1157 ± 3</td>
</tr>
<tr>
<td>CFRP-UD CF (3.5%)-BP (1.6%)</td>
<td>1.56</td>
<td>174.4 ± 4.4</td>
<td>11.6</td>
<td>40</td>
<td>3.5</td>
<td>1160 ± 4</td>
</tr>
<tr>
<td>CFRP-UD CF (8.1%)-BP (6.9%)</td>
<td>1.54</td>
<td>148.0 ± 5.0</td>
<td>6.9</td>
<td>80</td>
<td>3.5</td>
<td>982 ± 5</td>
</tr>
</tbody>
</table>

*Unidirectional carbon fiber (UD CF) or thermal protection layer (TPL) volume fraction is defined as the thickness of UD CF or TPL divided by the entire hybrid composite thickness.

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**Fig. 6.** (a) Thermogravimetric analysis of BMI resin, phenolic resin, and BP/phenolic TPLs (b) char yield at 800 °C.
the hybrid composites increased. The hybrid composites with 6.7% (v/v) TPLs was measured at 14 ppm/°C at room temperature (RT), which was 45% of the CFRP control. With the addition of 9.0% (v/v) TPLs to the hybrid composites, the CTE value decreased to 25% of the CFRP control. The through-thickness CTE of the composites also showed considerable variations with increasing temperatures. This could be explained by the shrinkage of the matrix resin without the restraint from the reinforcement in through-thickness direction. The $T_g$ of the CFRP control and hybrid composites were about 225 °C. As expected, the CTE for the CFRP control composites at temperatures above $T_g$ was also much higher than the CTE value of the hybrid composites.

Fig. 7(b) shows the influence of TPLs in the hybrid composites on the CTE of in-plane direction. The results maintained the same trend as the CTE in the through-thickness direction. The TPLs did appear to effectively decrease the CTE in the in-plane direction perhaps because of the high level of interaction between the TPLs and the CFRP composites. Some studies have reported that CNTs mixed in a resin matrix can be beneficial in reducing the CTE of polymer matrix composites [43–45], which may be due to the CNTs interaction with polymer matrix causing restriction of polymer chain movement [46]. For the hybrid composites, the buckypaper/phenolic TPLs had interfacial bonding between the random CNTs network and the surface of the CFRP control [43]. Hence, the TPLs achieved greater CTE reduction than the CFRP control in both through-thickness and in-plane directions.

The lower CTE indicates lower thermomechanical stresses when the material was subjected to thermal variations. A major advantage of the buckypaper/phenolic TPLs is its dimension stability, especially when the hybrid composite is subjected to a high-temperature situation. A lower CTE is often desirable to achieve good dimensional stability. One engineering consideration is that the lower CTE of composites should match the CTE of the surrounding materials in applications to avoid thermal stresses. For this study, the buckypaper/phenolic TPLs readily adhered to the CFRP substrate and overcame any CTE mismatch to avoid delamination. The CTE of CNTs has been estimated to be negative in both longitudinal and transverse directions [47,48]. In composites, a low CTE in the direction perpendicular to the fibers can be achieved either by incorporating a low CTE filler materials in the matrix or strengthening the interfacial of fiber/matrix through fiber sizing [45]. Therefore, CNT sheets incorporated into CFRP composites could potentially reduce the CTE of hybrid composites.

3.5. Thermal conductivities of the hybrid composites

Fig. 8 shows the plot of out-of-plane thermal conductivity with different volume fractions of buckypaper/phenolic TPLs from RT to 400 °C using Eq. (S4). The thermal conductivity of CFRP control was approximately 1.106 W m$^{-1}$ K$^{-1}$ at RT. By increasing the loading of TPLs to 9.0% (v/v), the thermal conductivity decreased from 1.106 to 0.922 W m$^{-1}$ K$^{-1}$ or 17%, comparatively. The buckypaper/phenolic TPLs lowered the through-thickness thermal conductivity of the hybrid CFRP possibly due to the nanoscale pores introduced into the TPLs. The heat transfer across the pores was affected by the pore volume fraction, as well as the size, shape, orientation, and emissivity [49]. The decrease of thermal conductivity of materials with random porous structures is known to be proportional to the increase of the pore fraction [49]. Besides buckypapers acting as an excellent heat conductor, its in-plane thermal conductivity property (20–30 W m$^{-1}$ K$^{-1}$ at RT [50]) was significantly higher than the phenolic resin (0.28 W m$^{-1}$ K$^{-1}$ [51]). Thus, the buckypaper/phenolic composite demonstrated good in-plane thermal conductivity properties with the CNT networks allowing dispersion of heat in-plane rather than through the composite thickness. This lower through-thickness thermal conductivity was beneficial to protecting the under layers of CFRP structures when exposed to a high-temperature environment.

3.6. Flame test

Fig. 9(a) shows the back-surface temperatures of the flame test plotted against time. The temperature curves provide an insight into how well the hybrid composites performed with the TPLs. For a 30 s burning time, the back-surface temperature of CFRP increased to 325 °C, whereas the hybrid composites peaked at a back-surface temperature of about 220 °C in the CFRP-BP (6.7%). With the increasing CNT volume fractions in hybrid composites, the
maximum back-surface temperature decreased to 200 °C. The experimental results of the burning tests indicate that the TPLs reduced heat penetration into the CFRP substrate. Masses of all samples were measured before and after the burning tests to measure the percentage of mass loss. The mass burning rates of the hybrid composites were obtained using the equation: 
\[ R_m = \frac{(m_0 - m_1)}{t} \]
where \( R_m \) is the mass burning rate; \( m_0, m_1 \) is the sample mass before and after burning, respectively, and \( t \) is the burning time. The mass loss rate of CFRP control was calculated as 3.9 mg/s. As a comparison, hybrid composites showed lower mass loss rates. The hybrid composites with highest TPLs volume fraction had the lowest mass loss rate at about 1.9 mg/s, which was a 51% reduction (Fig. 9(b)).

3.7. Mechanical properties and residual strength after burning

To determine the mechanical properties of the hybrid CFRP and the thermal protection capability, three-point bending tests were calculated on the pristine and burned hybrid composites (Eqs. S1 and S3). Fig. 10(a) shows the mechanical properties of hybrid composites prepared with the different volume fractions of TPLs. The CFRP control had a flexural strength and modulus of 1034 MPa and 43 GPa, respectively. When protected with TPLs, the flexural strength and modulus slightly decreased. The hybrid composite with a UD CF volume fraction of 3.5% maintained 94% of the strength and modulus compared to the CFRP value, indicating that the UD CF bonding layer had a positive influence on the mechanical properties. However, if the volume fraction of the UD CF bonding layer increased to 8.1%, the flexural strength decreased to 67% compared to the CFRP control, which may be because the thicker UD CF bonding layer induced a high quantity of voids, thereby decreasing the mechanical properties. The mechanical performance of final hybrid composites were greatly affected if taking the thickness of TPL into account when calculating the flexural strength and modulus (see Eqs. S1 and S3 in supplemental information). However, TPLs were not intended to influence on the mechanical properties of final hybrid composites. Thus to eliminate the thickness effect, the load applied to the 3 PB test is also presented in Table S2.

After the flame test, all samples underwent three-point bending tests to determine the residual strength and modulus, as shown in Fig. 10 (b). After a 30 s burn, the CFRP control had a strength and modulus of 115 MPa and 9 GPa, respectively. The measured residual strength and modulus properties were 11% and 21%, respectively, compared to the properties of the CFRP control prior to burning. With an increase of TPLs volume fraction, the residual mechanical properties improved. The CFRP-UD CF (3.5%)-BP (11.6%) possessed the highest residual mechanical properties with a strength of 369 MPa and modulus of 30 GPa. Comparatively, these approximately coincided with a 39% residual strength and 70% residual modulus.

These results indicate that the enhanced flame resistance is related to the TPL serving as a protective barrier, indicating their importance in improving the thermal protective properties. The TPL formed by CNT networks reduced the heat release rate since the layer acted as a thermal shield from energy feedback from the flame. Also, the CNT network emitted the most incident radiation back into the gas phase from its hot surface, which limited the
transmitted heat flux beneath the CFRP composites, reducing the BMI pyrolysis rate in CFRP composites [52]. Meanwhile, the char yield pyrolyzed by phenolic resin can protect the CNTs from the oxidation during the burning process to minimize the oxidation of CNTs [53]. Table 3 shows the mechanical properties of hybrid composites before and after the flame test.

### 3.8. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) measurements were performed on the CFRP reference and hybrid composite samples, as shown in Fig. 11(a). The storage modulus, which can be determined by the stiffness of the matrix and the interface adhesion between the matrix and fibers, is important for using composites in structural applications. The initial storage modulus of CFRP composites was recorded as 50 GPa. The DMA results did not indicate an obvious trend of the buckypaper/phenolic TPLs’ influence on storage modulus, which indicates the good interfacial adhesion between the TPL and the CFRP substrate. Furthermore, the initial storage modulus was highly dependent on the completed polymerization of the BMI matrix, which directly influenced load transfer between the carbon fiber and BMI resin in the composite materials. These results indicate that the fabrication process of hybrid composites does not affect the mechanical properties of the hybrid composite systems. Fig. 11(b) shows the damping parameters (tan\(\delta\)) of the composites in relation to temperature. The peak of tan\(\delta\) designates the \(T_g\) of CFRP composites, which was about 270 °C, as shown in Fig. 11(b). \(T_g\) depends on the crosslinking degree and the motion of the molecular segments of resins. Fig. 11(b) shows that the \(T_g\) of all the hybrid composites was approximately 270 °C, which was the same as the \(T_g\) of the CFRP reference.

After the flame test, the storage modulus of CFRP significantly decreased to 12 GPa, suggesting less stress transfer occurred between the BMI resin and carbon fibers due to the BMI resin decomposition during the flame test (Fig. 11(c)). However, the hybrid composite with 11.6% volume fractions of TPL resulted in the highest initial storage modulus of approximately 27 GPa, as shown in Fig. 11(c), and maintained the greatest storage modulus at the higher temperature.

The damping parameter is closely related to the properties of vibration dissipation and impact resistance. After burning, the damping peak tended to become broader, as shown in Fig. 11(d). The first damping peak appeared at 210 °C and the second peak appeared at 270 °C. The broader shape of tan\(\delta\) may be used to

| Table 3 | Mechanical properties of hybrid composites before and after the flame test. |
|------------------|------------------|------------------|------------------|------------------|
|                  | Before burning   | After burning    | Residual strength (%) | Residual modulus (%) |
|                  | Flexural strength (MPa) | Modulus (GPa) | Flexural strength (MPa) | Modulus (GPa) | Flexural strength (MPa) | Modulus (GPa) |
| CFRP control     | 1034 ± 60        | 43 ± 5           | 9 ± 1              | 11.12            | 20.93                |
| CFRP-BP(6.7%)    | 894 ± 42         | 40 ± 3           | 219 ± 16          | 17 ± 2            | 24.50                | 42.50          |
| CFRP-BP(9.0%)    | 951 ± 50         | 39 ± 2           | 206 ± 9           | 19 ± 5            | 21.66                | 48.72          |
| CFRP-UD CF (3.5%)-BP(6.3%) | 968 ± 114  | 39 ± 5           | 266 ± 12          | 20 ± 3            | 27.48                | 51.28          |
| CFRP-UD CF (3.5%)-BP(11.6%) | 950 ± 73   | 43 ± 1           | 369 ± 32          | 30 ± 2            | 38.84                | 69.77          |
| CFRP-UD CF (8.1%)-BP(6.9%) | 690 ± 44   | 45 ± 3           | -                | -                | -                    | -              |

*Residual strength/modulus is defined as the strength/modulus after burning divided by the strength/modulus before burning.

Fig. 11. DMA results of hybrid composites (a) storage modulus (b) damping factor (tan\(\delta\)), and after flame test (c) storage modulus (d) damping factor (tan\(\delta\)).
evaluate the complexity of the molecular phases within the composites. Broadening tan δ peak suggests an increasing possibility of the existence of more than one network structure. The first damping peak at 210 °C was attributed to the Tg of the small molecular chains, which were possibly generated from the BMI thermal decomposition process, while the second peak at 270 °C was the same as BMI resin.

3.9. SEM analysis after flame tests

Fig. 12 shows the morphologies of the char surface of the samples after the flame tests. In the experimental tests, the front surface CFRP control sample was damaged, as seen in Fig. 12(a) and (b). The carbon fibers experienced a high degree of fracture, and most of the resin decomposed. The morphologies of the hybrid composites with zones underneath the TPL were also investigated, as shown in Fig. 12(d) and (e). The comparison of the CFRP control and the hybrid composites indicate the insulation behavior of TPLs effectively prevented the BMI resin decomposition. The covering TPL of char appeared to serve as a heat shield to decelerate the diffusion of heat and oxygen into inner CFRP layers, and the remaining CNT networks also maintained the char strength. Many large cracks and bubble formations occurred on the burned TPLs, indicating the escaping of gas from the TPLs, as Fig. 12(c) shows. These bubbles are believed to be generated by gaseous products from the matrix degradation and released entrapped moisture from cured phenolic resin within the TPL during flame treatment. When the internal pressure became sufficiently higher, the gases diffused through the TPL to the bubble structures distributed on the TPL surface. The closed bubbles burst when the trapped gases reached a critical pressure, which is prevalent in many charring ablators [40,54]. At a higher magnification on the TPL surface, the SEM images evidenced an entangled CNTs network with a series of bright spots that possibly show the residual of burned phenolic resin after exposure to the flame produced char particles, as shown in Fig. 12(f).

4. Conclusion

The hybrid composites were successfully manufactured using CNT sheets or buckypaper/phenolic TPLs and a bonding layer of UD CF. The thermal conductivity, CTE, thermal stability, burning behavior, and mechanical properties were evaluated. The results indicate that the through-thickness thermal conductivity of hybrid composites is lower than CFRP control due to CNT networks allowing dispersion of heat in-plane rather than through-thickness directions of the composite. The CTE of the hybrid composites decreased in both the in-plane and through-thickness directions because of the CNTs interaction with polymer matrix causing restrictions in polymer chain movement. The flame test results show that the TPLs reduce heat transfer into the inner structure of the CFRP. The mass loss rate and post-burning SEM images of the hybrid composites indicate that the sacrificial buckypaper/phenolic TPLs decreased the amount of resin decomposition in the CFRP. Also, the strength and modulus of the CFRP protected with TPLs was similar to the CFRP control, indicating the fabrication process did not decrease the mechanical properties of composites. The strength and modulus of hybrid composites retained 40% of initial mechanical performance, whereas the control sample only sustained 8% after burning. The results indicate that the TPLs can provided effective thermal protection capabilities that could reduce thermal damage of internal CFRP materials. The developed approach involves a simple manufacturing process and lightweight TPLs, which can be used in future integrated TP application for structural composites.

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Appendix A. Supplementary data

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References


