Increasing the through-thickness thermal conductivity of carbon fiber polymer–matrix composite by curing pressure increase and filler incorporation

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ABSTRACT

The low through-thickness thermal conductivity limits heat dissipation from continuous carbon fiber polymer–matrix composites. This conductivity is increased by up to 60% by raising the curing pressure from 0.1 to 2.0 MPa and up to 33% by incorporation of a filler (≤1.5 vol.%) at the interlaminar interface. The 7-μm-diameter 7-W/m K-thermal-conductivity continuous fiber volume fraction is increased by the curing pressure increase, but is essentially unaffected by filler incorporation. The thermal resistivity is dominated by the lamina resistivity (which is contributed substantially by the intralaminar fiber–fiber interfacial resistivity), with the interlaminar interface thermal resistivity being unexpectedly negligible. The lamina resistivity and intralaminar fiber–fiber interfacial resistivity are decreased by up to 56% by raising the curing pressure and up to 36% by filler incorporation. The curing pressure increase does not affect the effectiveness of 1-mm-long 10-μm-diameter 900–1000-W/m K-thermal-conductivity K-1100 carbon fiber or single-walled carbon nanotube (SWCNT) as fillers for enhancing the conductivity, but hinders the effectiveness of carbon black (CB, low-cost), which is less effective than K-1100 or SWCNT at the higher curing pressure, but is almost as effective as K-1100 and SWCNT at the lower curing pressure. The effectiveness for enhancing the flexural modulus/strength/ductility decreases in the order: SWCNT, CB, K-1100.

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1. Introduction

Polymer–matrix composites with continuous carbon fiber are important lightweight structural materials for aircraft radiators, directed energy mirror structures, satellites, missiles and other aerospace structures. In addition, due to the thermal conductivity of carbon fiber, such composites are attractive for use as heat sinks for the cooling of aircraft microelectronics, which need to be lightweight. Because of the temperature gradient that is commonly encountered by such aerospace and microelectronic structures, a high thermal conductivity is needed for the purpose of heat dissipation from these structural composites.

The thermal load of aircraft is increasing, due to the limited aircraft idling time, the heating of the fuel by electronics, increased engine performance and increased flight speed. Carbon fiber composites have high in-plane thermal conductivity, but low through-thickness conductivity, which is essentially equal for crossply and quasi-isotropic fiber lay-up configurations [1]. Although the through-thickness thermal conductivity can be significantly increased by three-dimensional weaving [2,3], such that the increase is much more than what can be attained by filler incorporation, it is desirable in numerous applications to enhance the through-thickness thermal conductivity without the complexity of three-dimensional weaving. Both in-plane heat spreading and through-thickness heat removal are important for heat dissipation.

Heat dissipation from aerospace structures is increasingly important, due to the rapidly increasing thermal load of aircraft and other aerospace structures. The thermal load is expected to reach 10,000 kW [4]. The increased thermal load is a consequence of the limited aircraft idling time, the heating of the fuel by electronics, increased engine performance, increased flight speed, and the heat generated by high energy lasers. Heat dissipation from microelectronics is critical to the reliability, power and further miniaturization of microelectronics.

Carbon fiber composites are highly anisotropic due to their lamellar structure, with the continuous fibers in the plane of the lamellae. Within a lamina, the fibers are typically all in the same direction. Because a carbon fiber is itself very anisotropic, with the thermal conductivity much higher in the axial direction than the transverse direction, the thermal conductivity of a lamella is much higher in the fiber direction of the lamella than in the transverse direction. However, for the purpose of obtaining acceptable mechanical properties in all in-plane directions of a composite, a structural composite always involves fibers oriented in different directions for different lamellae. Therefore, the thermal conductivity...
of a structural composite is high in all in-plane directions, such that the conductivity is limited by the axial thermal conductivity of the fiber. On the other hand, the through-thickness thermal conductivity is much lower than the in-plane conductivity, due to the absence of fibers in the through-thickness direction and the fact that the interface between lamellae is relatively rich in the matrix polymer, which is a poor conductor. Thus, the main problem in the thermal conductivity of the composite lies in the through-thickness direction. A similar situation occurs for composites with each lamina in the form of a fabric with woven continuous fibers. However, fabrics are usually not used for high-performance structural composites, because of the bending of the fibers in a fabric.

Due to the structure of a carbon fiber polymer–matrix composite laminate, a number of quantities are expected to contribute to the through-thickness thermal conductivity of the laminate. These quantities include the thermal resistivity within a lamina and that of the interlaminar interface. In particular, the thermal resistivity within a lamina consists of that of the fibers in the lamina and that of the fiber–fiber interfaces in the lamina. The relative importance of these quantities in affecting the through-thickness thermal conductivity of a laminate has not been previously studied. An understanding of the relative importance is valuable for developing effective methods to improve the through-thickness thermal conductivity. Thus, this paper is aimed at providing understanding of the science behind the through-thickness thermal conductivity of carbon fiber polymer–matrix composite laminates.

Another objective is to enhance the through-thickness thermal conductivity through composite modification, with the processing parameters including the curing pressure and the incorporation of fillers. The effect of the curing pressure on the thermal conductivity of the composite has not been previously reported. However, it has been previously reported that an increase in the curing pressure decreases the contact electrical resistivity of the interlaminar interface of a carbon fiber epoxy–matrix composite [5]. The electrical resistivity decrease is attributed to the increased degree of fiber–fiber contact between the fibers of adjacent laminae [5].

A second method of modification involves the incorporation of a thermally conductive filler in the continuous fiber composite. One variation of this method involves incorporation of a conductive filler at the interlaminar interface. The incorporation can be achieved by applying the filler on the surface of the continuous fiber prepreg (a sheet of aligned fibers that have been coated with the matrix or the matrix precursor) prior to stacking the prepreg sheets for forming the composite [6]. An effective filler for improving the through-thickness thermal conductivity of carbon fiber composites is carbon black [6], which is both conductive and conformable. The conformability (squishability), which results from the fact that carbon black is in the form of porous agglomerates of nanoparticles, is valuable, because it enables the carbon black to conform to the topography of the carbon fiber lamella surface, thereby enabling the fibers in adjacent lamellae of the composite to be in better thermal contact. The nanoscale nature of the filler is also valuable, because it allows the interlaminar interface thickness to remain small. A large interlaminar interface thickness is not desirable for both the mechanical properties and the through-thickness thermal conductivity. A special type of interlaminar filler is a carbon nanotube array with the height of the array along the through-thickness direction of the composite; the array increases the through-thickness thermal conductivity by about 50% [7].

Another variation of the second method is the deposition of a thermally conductive filler on a woven carbon fiber fabric prior to combining the fabric with the matrix. This approach has not been used for improving the thermal conductivity of the composite, but it (with carbon nanotube as the filler) has been used for increasing the through-thickness electrical conductivity [8] and the interlaminar shear strength [8,9]. As explained above, fabrics are not attractive for high-performance structural composites.

Yet another variation of the second method is the incorporation of a thermally conductive filler in the matrix prior to combining the continuous fibers with the matrix. This approach has not been used for improving the thermal conductivity, but it (with carbon nanotube as the filler) has been used for rendering electrical-resistance-based damage sensing ability to continuous glass fiber composites [10]. However, it suffers from the increase of the viscosity and the consequent difficulty of the resin to flow. Furthermore, the volume fraction of the filler tends to be higher when the filler is throughout the matrix than when it is only located at the interlaminar interface.

A third method is the combined use of filler incorporation and curing pressure increase. This method has not been previously investigated.

In relation to the second method, the choice of thermally conductive filler in prior work has been limited to carbon black [6], carbon nanotube [8–11] and carbon nanofiber [12]. In particular, carbon nanotube [11] or carbon nanofiber [12] has been incorporated in the matrix of a glass fiber polymer–matrix composite in order to enhance the through-thickness thermal conductivity. This work is thus also directed at extending the second method to various conductive fillers, including the K-1100 carbon fiber, which is well-known for its high thermal conductivity of 900–1000 W/m K.

The carbonization of the polymer–matrix of a carbon fiber composite to form a carbon–carbon composite greatly increases the through-thickness thermal conductivity. Carbonization increases the conductivity from 0.81 to 2.61 W/m K [13]. The additional step of graphitization after carbonization further increases the conductivity to values as high as 32 W/m K [13]. However, carbon–carbon composites are more brittle and expensive compared to the corresponding polymer–matrix composites. Therefore, the conversion of the polymer matrix to a carbon matrix is not a practical method of increasing the through-thickness thermal conductivity.

The objectives of this paper are: (i) to understand the quantities that contribute to the thermal conductivity of carbon fiber epoxy–matrix composite laminates, (ii) to increase the through-thickness thermal conductivity of these composites, (iii) to investigate the effect of the curing pressure on the through-thickness thermal conductivity, (iv) to investigate the effects of various conductive fillers on the through-thickness thermal conductivity, (v) to investigate the combined effect of curing pressure increase and conductive filler incorporation on the through-thickness thermal conductivity, and (vi) to investigate the effect of curing pressure and filler incorporation on the mechanical properties, which are important for these structural composites.

2. Experimental methods

2.1. Materials

Because epoxy is the most common polymer used in these composites, this paper uses epoxy as the matrix. Epoxy is poor in thermal conductivity (0.19 W/m K [14]). The carbon fiber epoxy prepreg is from Tencate Advanced Composites USA, Inc. (Morgan Hill, CA), with the Pyrofil TRS05 15 K fiber (PAN-based, diameter 7 µm, tensile modulus 240 GPa, tensile strength 4.9 GPa, axial thermal conductivity 7 W/m K, transverses thermal conductivity being unknown but is assumed in this work to be 7 W/m K since the anisotropy is small, as suggested by the fact that this is neither a high-modulus fiber nor a high-thermal-conductivity fiber) and TC275 epoxy, and with 150 ± 5 g/m² and 34 ± 2% resin content for the prepreg. Crossply composites are fabricated by hand lay-up and compression molding at 177 °C and either 0.1 or 2.0 MPa.
pressure, for 120 min. The curing pressure recommended by the manufacturer is 0.1 MPa. The fillers are carbon black (CB), single-walled carbon nanotube (SWCNT) and chopped K-1100 carbon fiber.

The carbon black is Vulcan XC72R GP-3820 from Cabot Corp., Billerica, MA. It was a powder with particle size 30 nm, a nitrogen specific surface area 254 m²/g, maximum ash content 0.2%, volatile content 1.07%, and density 1.7–1.9 g/cm³. Furthermore, this carbon black is not pelleted; the fluffiness enhances the dispersability.

The K-1100 carbon fiber is from Cytic Industries, Inc., Woodland Park, NJ. It is made from mesophase pitch, with diameter 10 µm, density 2.2 g/cm³ and thermal conductivity 900–1000 W/m·K. It is manually chpped in this work to lengths of around 1 mm. The SWCNT is from NANO-C, with 1.1 mm diameter and 70% nanotubes.

The filler is incorporated by wet application on both surfaces of a prepreg sheet. A filler is suspended in a solvent at a solid content that is low enough for good workability (spreadability) of the suspension. For CB or K-1100, a solid content of 0.8 wt.% is used [6]; for SWCNT, a solid content of 0.4 wt.% is used. The solvent (ethylene glycol monoethyl ether [3]) is such that it evaporates at room temperature within a day after application of the suspension on a prepreg sheet and that it dissolves away a part of the excessive resin on the surface of the prepreg, so that the thickness of the interlaminar interface region is kept close to that of the unmodified composite. After solvent evaporation, the prepreg sheets are stacked and cured. In the unmodified composite, none of the prepreg sheets is modified. In a modified composite, all of the prepreg sheets are modified.

2.2. Composite fabrication

In composite fabrication, the prepreg sheet is first cut into pieces of size 4 × 3 in. (for subsequent cutting of the resulting composite to size 80 × 11 × 2 mm for flexural testing and 15 × 11 × 2 mm for density measurement) and 6 × 3 cm (for subsequent cutting of the resulting composite to size 1 × 1 in for thermal conductivity testing).

Each layer of carbon fiber epoxy prepreg is separately immersed in a bath of the vehicle (optionally containing a filler). The immersion time is 3 s. If the prepreg is immersed in the bath for an excessive amount of time, the degree of alignment of the carbon fiber in the prepreg may be reduced, due to substantial dissolution of the epoxy resin. The prepreg sheet is then removed from the bath and placed on a substrate in the form of a PTFE (Teflon) coated glass fiber fabric sheet. After this, the vehicle in the sheet is allowed to evaporate to completion in air.

Once the prepreg sheets have dried separately, they are stacked to reach the number of laminae desired. Subsequently the stack is cured using a hot hydraulic press (Carver, Inc., Wabash, IN), which provides heat and pressure. The press involves two metal platens that sandwich a mold containing a prepreg stack and the mating piston above the mold. The mold used has inner dimensions of 1 in for thermal conductivity testing.

The carbon–polymer composite sample top surface is in the temperature controller. This copper block is in contact with one of the four holes (T1, T2, T3 and T4 in Fig. 1, each hole of diameter 3.3 mm) one after the other. Two of the four holes are in each of the 1 × 1 in.² copper blocks. The temperature gradient is determined from T1–T2 and T3–T4. These two quantities should be equal at equilibrium, which is attained after holding the temperature of the heater at the desired value for 30 min. Equilibrium is assumed when the temperature variation is within ±0.1 °C in a period of 15 min. At equilibrium, the temperature of the hot block is 100 °C, that of the cold block is in the range 12–25 °C, while that of the carbon–polymer composite sample top surface is in the range 73–95 °C and the bottom surface 21–35 °C. Thus the average temperature of a sample is around 56 °C. The pressure in the direction perpendicular to the plane of the thermal interface is controlled by using a hydraulic press at a pressure of 0.46 MPa. The system is thermally insulated by wrapping laterally all the copper blocks with glass fiber cloth.
In accordance with ASTM Method D5470, the heat flow \( Q \) is given by

\[
Q = \frac{j_A A}{\Delta T}
\]

(1)

where \( \Delta T = T_1 - T_2 = T_3 - T_4 \), \( j \) is the thermal conductivity of copper, \( A \) is the area of the 1 \( \times \) 1 in\(^2\) copper block, and \( d_A \) is the distance between thermocouples \( T_1 \) and \( T_2 \) (i.e., 25 mm).

The temperature at the top surface of the thermal interface material is \( T_A \), which is assumed to be at the mid-point of the composite–copper interface undulation amplitude. This temperature is given by

\[
T_A = T_2 - \frac{d_A}{d_A^2} (T_1 - T_2)
\]

(2)

where \( d_A \) is the distance between thermocouple \( T_2 \) and the top surface of the specimen (i.e., 5 mm).

The temperature at the bottom surface of the specimen is \( T_D \), which is again assumed to be at the mid-point of the composite–copper interface undulation amplitude. This temperature is given by

\[
T_D = T_3 + \frac{d_A}{d_A^2} (T_3 - T_4)
\]

(3)

where \( d_A \) is the distance between thermocouple \( T_3 \) and the bottom surface of the specimen (i.e., 5 mm) and \( d_A \) is the distance between thermocouples \( T_3 \) and \( T_4 \) (i.e., 25 mm).

The two-dimensional thermal resistivity \( \theta \) is given by

\[
\theta = \frac{(T_A - T_D)A}{Q}
\]

(4)

Note that insertion of Eq. (1) into Eq. (4) causes cancellation of the term \( A \), so that \( \theta \) is independent of \( A \). Each sample is tested at least twice.

Each composite is tested at three or four different thicknesses. In case of three thicknesses, the thicknesses correspond to 2, 3 and 4 laminae. In case of four thicknesses, the thicknesses correspond to 1, 2, 3 and 4 laminae. Testing at multiple thicknesses allows the thermal resistance of the specimen-copper interface to be decoupled from that of the specimen.

2.4. Mechanical testing

Static mechanical testing is performed on 15-lamina crossply composite specimens under flexure (three-point bending) up to failure, using a hydraulic mechanical testing system (MTS Systems Corp., Eden Prairie, MN). The specimen size is 80 \( \times \) 11 \( \times \) 2 mm. The span is 58 mm. The flexural strength is the highest stress prior to failure. The flexural modulus is obtained from the slope of the straight-line portion of the stress–strain curve. This portion constitutes most of each curve. The flexural ductility is the strain at failure, which is taken as the last abrupt drop in stress in the stress–strain curve. For the unmodified crossply composites made at a curing pressure of 0.1 MPa and 2.0 MPa and the modified crossply composites with SWCNT made at a curing pressure of 2.0 MPa, two abrupt drops in stress occur in the route to failure. For the modified crossply composites with K-1100 carbon fiber made at 2.0 MPa curing pressures, only one abrupt drop in stress occurs and coincides with failure. For all the other composites except for the composites mentioned above, one or two abrupt drops in stress occur in the route to failure. At least four specimens of each composition were tested.

2.5. Density measurement

The density of each composite is measured by measuring the mass and dimensions of 15-lamina composite specimens of size 15 \( \times \) 11 \( \times \) 2.0 mm. Three specimens of each type are measured. The composite density is used to obtain the fiber volume fraction, based on the Rule of Mixtures. The densities of the carbon fiber and epoxy matrix are 1.82 and 1.15 g/cm\(^3\) respectively; these values are needed for the calculation of the fiber volume fraction.

2.6. Carbon black squishability testing

The squishability of carbon black in the absence of any binder is studied by SEM examination of the morphology before and after compression at 0.1 and 2.0 MPa, which are the curing pressures used in composite fabrication in this work. The compression is conducted by using a steel cylindrical mold with inside diameter 31.75 mm and a matching piston and containing 270 mg of carbon black. The thickness of the compressed carbon black is 1.9 mm for the pressure of 0.1 MPa and 0.9 mm for the pressure of 2 MPa.

3. Results and discussion

3.1. Through-thickness thermal conductivity

The thermal resistivity \((\text{m}^2 \text{K/W})\) is independent of the area; the thermal resistance \((\text{K/W})\) depends on the area. If there are \( N \) laminae, there are \( N - 1 \) interlaminar interfaces and the thermal resistivity \( R \) of the composite is given by

\[
R = N R_f + (N - 1) R_i,
\]

(5)

where \( R_i \) is the thermal resistivity of a lamina and \( R_f \) is that of an interlaminar interface. The \( R_i \) and \( R_f \) may be determined by measuring \( R \) for different values of \( N \).

Fig. 2 shows the plot of thermal resistivity vs. thickness for the composite containing CB, fabricated at 0.1 MPa. That the plot is a straight line means that \( R = NR_f \), and \( R_i \) is essentially 0. The slope of this line is the inverse of the thermal conductivity. The intercept with the vertical axis at zero thickness is the thermal resistivity of the two specimen-copper interfaces. The resistivity of a specimen-copper interface ranges from \( 6 \times 10^{-5} \) to \( 1 \times 10^{-4} \text{m}^2 \text{K/W} \) (small range in the vertical scale of Fig. 2). For each specimen composition, the specimen-copper interfacial thermal resistivity is increased upon increase of the curing pressure from 0.1 to 2.0 MPa, presumably due to the decrease in the specimen surface roughness by the curing pressure increase. The fractional increase in this resistivity due to the curing pressure increase is 4%, 12%, 19% and

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**Fig. 2.** Plot of thermal resistivity vs. thickness for the composite containing CB, fabricated at a curing pressure of 0.1 MPa.
75% for the cases of no filler, CB, K-1100 and SWCNT respectively. For each curing pressure, this resistivity is increased by the filler incorporation, presumably due to the presence of the filler on the outer surface of the composite specimen. The fractional increase for a curing pressure of 0.1 MPa is 57%, 57% and 5% for CB, K-1100 and SWCNT respectively, and the fractional increase for a curing pressure of 2.0 MPa is 17%, 79% and 77% for CB, K-1100 and SWCNT respectively. The lamina resistivity $R_l$ is obtained by dividing the composite resistivity (with the specimen-copper resistivity excluded) by $N$.

This finding applies to either curing pressure, with and without filler. Thus, the curing pressure and filler essentially do not affect $R_l$, which remains negligible, but they affect $R_c$. Hence, the thermal resistivity is dominated by $R_c$. A decrease in $R_c$ means that the thermal resistivity associated with the interface (in the form of contact points) between continuous fibers in the same lamina is decreased.

The thermal resistivity of a lamina is given by

$$ R_l = R_m + R_s $$

where $R_m$ is the thermal resistivity of all of the M (26, from microscopy) fibers stacked along the thickness of the lamina and is related to the transverse thermal conductivity $k_t$ (7 W/m K) of a single fiber of diameter $d$ (7 μm) by

$$ R_m = \frac{M d}{k_t} = 2.6 \times 10^{-5} \text{ m}^2 \text{ K/W} $$

and $R_s$ is the thermal resistivity of all the interfaces between the stacked fibers in the lamina (i.e., the intralaminar fiber–fiber interfacial thermal resistivity). As shown in Table 1, $R_s$ is dominated by $R_a$. Even if the value of $k_f$ is lower than the assumed value of 7 W/m K (due to the fiber anisotropy), $R_s$ amounts to a substantial fraction of $R_l$. The $R_m$ is not expected to change with the curing pressure or the filler, since the structure within a fiber is not affected by the curing pressure or the filler. However, $R_s$ changes (Table 1), since the degree of fiber–fiber contact within a lamina is affected by the curing pressure and can be affected by the filler as well. For example, the filler may affect the degree of waviness of the continuous fibers, which are not perfectly straight anyway.

The thermal conductivity is increased and $R_s$ and $R_a$ are decreased upon increasing the curing pressure, whether a filler is present or not (Table 1). This effect is because the increase in curing pressure increases the continuous fiber volume fraction and the density (Table 2), thus decreasing $R_s$. The fractional increase in conductivity and the fractional decreases in $R_s$ and $R_a$ due to the curing pressure increase are lowered by CB and slightly affected by K-1100 or SWCNT.

At 0.1 MPa curing pressure, K-1100 and SWCNT are slightly more effective than CB for enhancing the thermal conductivity and decreasing $R_s$ and $R_a$ at 2.0 MPa curing pressure, K-1100 and SWCNT are much more effective than CB (Table 3). Due to its low cost, CB is competitive.

The thermal conductivity is increased and $R_s$ and $R_a$ are decreased by any of the fillers, which have negligible effect on the continuous fiber volume fraction. The filler effect is smaller than the curing pressure effect. The effect of the filler on $R_s$ is probably due to slight increase of the fiber waviness and the consequent increase in the number of contact points between fibers in a lamina.

### Table 1

<table>
<thead>
<tr>
<th>Filler</th>
<th>Conductivity (W/m K)</th>
<th>$R_s$ (10⁻⁴m²K/W)</th>
<th>$R_a$ (10⁻⁴m²K/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 MPa</td>
<td>2.0 MPa</td>
<td>0.1 MPa</td>
</tr>
<tr>
<td>None</td>
<td>0.729</td>
<td>1.091</td>
<td>2.062</td>
</tr>
<tr>
<td>CB</td>
<td>0.891</td>
<td>1.212</td>
<td>1.497</td>
</tr>
<tr>
<td>K-1100</td>
<td>0.903</td>
<td>1.444</td>
<td>1.426</td>
</tr>
<tr>
<td>SWCNT</td>
<td>0.910</td>
<td>1.453</td>
<td>1.457</td>
</tr>
</tbody>
</table>

This phenomenon reduces the effect of the curing pressure, because the additional conductive paths between the continuous fibers make the fiber volume fraction and curing pressure less influential.

The fractional increase in conductivity due to K-1100 or SWCNT is greater for the higher curing pressure, whereas the fractional increase due to CB is greater for the lower pressure. The fractional increase in conductivity and the fractional decreases in $R_s$ and $R_a$ due to a filler are greater for K-1100 or SWCNT than CB, such that the difference between CB and K-1100 or SWCNT is greater at the higher pressure. Based on $R_a$, the effect of K-1100 or SWCNT on the lamina microstructure is not affected by increasing the pressure, whereas that of CB on the lamina microstructure is reduced by increasing the pressure. Its porous agglomerate structure causes CB to be squishable, so that an increase in pressure compacts CB, making it harder for CB to affect the lamina microstructure. The K-1100 and SWCNT are not squishable.

The K-1100 and SWCNT are comparably effective for decreasing $R_s$ and $R_a$ (Table 3), and are comparable in the effect of curing pressure (Table 2), in spite of the much smaller size of the latter. This suggests that the ability of a filler to affect the lamina microstructure is not governed by the filler size and supports the absence of filler penetration of the lamina.

For enhancing the through-thickness thermal conductivity, increase in the curing pressure is recommended. Filler incorporation helps, but by a lesser degree.

The highest value of the through-thickness thermal conductivity obtained in this work is 1.5 W/m K. This is lower than the highest value of 3.3 W/m K previously reported for carbon fiber polymer–matrix composites containing carbon black as an intralaminar filler [6]. The difference from prior work [6] that involves the same type of carbon black is attributed to the difference in the type of prepreg. That the type of prepreg makes a significant difference is shown by comparison of the unmodified composites made from different types of prepregs (from different sources) in

### Table 2

<table>
<thead>
<tr>
<th>Filler</th>
<th>Conductivity (%)</th>
<th>$R_s$ (%)</th>
<th>$R_a$ (%)</th>
<th>Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 MPa</td>
<td>2.0 MPa</td>
<td>0.1 MPa</td>
<td>2.0 MPa</td>
</tr>
<tr>
<td>CB</td>
<td>22</td>
<td>11</td>
<td>27</td>
<td>11</td>
</tr>
<tr>
<td>K-1100</td>
<td>24</td>
<td>32</td>
<td>31</td>
<td>27</td>
</tr>
<tr>
<td>SWCNT</td>
<td>25</td>
<td>33</td>
<td>29</td>
<td>24</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Filler</th>
<th>Conductivity (%)</th>
<th>$R_s$ (%)</th>
<th>$R_a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 MPa</td>
<td>2.0 MPa</td>
<td>0.1 MPa</td>
</tr>
<tr>
<td>CB</td>
<td>50</td>
<td>49</td>
<td>56</td>
</tr>
<tr>
<td>K-1100</td>
<td>36</td>
<td>37</td>
<td>45</td>
</tr>
<tr>
<td>SWCNT</td>
<td>60</td>
<td>46</td>
<td>56</td>
</tr>
</tbody>
</table>

$R_f$ and $R_c$ are the thermal resistivity of all the interfaces between the stacked fibers in the lamina (i.e., the intralaminar fiber–fiber interfacial thermal resistivity). As shown in Table 1, $R_s$ is dominated by $R_a$. Even if the value of $k_f$ is lower than the assumed value of 7 W/m K (due to the fiber anisotropy), $R_s$ amounts to a substantial fraction of $R_l$. The $R_m$ is not expected to change with the curing pressure or the filler, since the structure within a fiber is not affected by the curing pressure or the filler. However, $R_s$ changes (Table 1), since the degree of fiber–fiber contact within a lamina is affected by the curing pressure and can be affected by the filler as well. For example, the filler may affect the degree of waviness of the continuous fibers, which are not perfectly straight anyway.

The fractional change in thermal resistivity due to K-1100 or SWCNT is greater for the higher curing pressure, whereas the fractional increase due to CB is greater for the lower pressure. The fractional increase in conductivity and the fractional decreases in $R_s$ and $R_a$ due to a filler are greater for K-1100 or SWCNT than CB, such that the difference between CB and K-1100 or SWCNT is greater at the higher pressure. Based on $R_a$, the effect of K-1100 or SWCNT on the lamina microstructure is not affected by increasing the pressure, whereas that of CB on the lamina microstructure is reduced by increasing the pressure. Its porous agglomerate structure causes CB to be squishable, so that an increase in pressure compacts CB, making it harder for CB to affect the lamina microstructure. The K-1100 and SWCNT are not squishable.

The K-1100 and SWCNT are comparably effective for decreasing $R_s$ and $R_a$ (Table 3), and are comparable in the effect of curing pressure (Table 2), in spite of the much smaller size of the latter. This suggests that the ability of a filler to affect the lamina microstructure is not governed by the filler size and supports the absence of filler penetration of the lamina.
this work, though the results of the comparative study is not included in this report. However, the highest thermal conductivity obtained in this work is higher than the highest value of 1.2 W/mK previously reported for carbon fiber polymer–matrix

Table 4
Composite density and the volume fractions of the fiber, matrix and filler for crossply carbon fiber epoxy–matrix composites made at a curing pressure of 0.1 MPa and 2 MPa with and without the filler.

<table>
<thead>
<tr>
<th>Filler contenta</th>
<th>Density of composite (g/cm³)</th>
<th>Volume fraction Fiberb</th>
<th>Matrixb</th>
<th>Fillerc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 MPa curing pressure</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>1.538 ± 0.011</td>
<td>0.579 ± 0.016</td>
<td>0.421 ± 0.016</td>
<td>0</td>
</tr>
<tr>
<td>0.8% CB</td>
<td>1.543 ± 0.017</td>
<td>0.582 ± 0.025</td>
<td>0.407 ± 0.025</td>
<td>0.012 ± 0.001</td>
</tr>
<tr>
<td>0.8% K-1100</td>
<td>1.545 ± 0.014</td>
<td>0.581 ± 0.021</td>
<td>0.410 ± 0.021</td>
<td>0.010 ± 0.001</td>
</tr>
<tr>
<td>0.4% SWCNT</td>
<td>1.539 ± 0.017</td>
<td>0.581 ± 0.024</td>
<td>0.405 ± 0.025</td>
<td>0.014 ± 0.001</td>
</tr>
<tr>
<td>2 MPa curing pressure</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>1.583 ± 0.016</td>
<td>0.646 ± 0.024</td>
<td>0.354 ± 0.024</td>
<td>0</td>
</tr>
<tr>
<td>0.8% CB</td>
<td>1.590 ± 0.013</td>
<td>0.649 ± 0.020</td>
<td>0.338 ± 0.019</td>
<td>0.014 ± 0.001</td>
</tr>
<tr>
<td>0.8% K-1100</td>
<td>1.594 ± 0.025</td>
<td>0.650 ± 0.036</td>
<td>0.339 ± 0.036</td>
<td>0.011 ± 0.001</td>
</tr>
<tr>
<td>0.4% SWCNT</td>
<td>1.584 ± 0.003</td>
<td>0.647 ± 0.004</td>
<td>0.338 ± 0.005</td>
<td>0.015 ± 0.001</td>
</tr>
</tbody>
</table>

a Fraction of mass of dispersion.
b Calculated from the measured density, based on the Rule of Mixtures.
c Obtained by dividing the volume of the filler by the volume of the composite, with the volume of the filler obtained by dividing the mass of the filler by the density of the filler. The mass of the filler is obtained by subtracting the mass of the prepreg that has been treated by the solvent in the absence of the filler from the mass of the prepreg that has been treated by the solvent that contains the filler.

Table 5
Interlaminar interface thickness, lamina thickness, composite thickness, and interlaminar interface volume fraction of crossply carbon fiber epoxy–matrix composites fabricated at curing pressures of 0.1 and 2.0 MPa.

<table>
<thead>
<tr>
<th>Filler contenta</th>
<th>Interlaminar interface thickness (μm)</th>
<th>Lamina thickness (μm)</th>
<th>Composite thickness (μm)</th>
<th>Interlaminar interface volume fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 MPa 2.0 MPa</td>
<td>0.1 MPa 2.0 MPa</td>
<td>0.1 MPa 2.0 MPa</td>
<td>0.1 MPa 2.0 MPa</td>
</tr>
<tr>
<td>0%</td>
<td>6.4 ± 2.7</td>
<td>3.4 ± 1.2</td>
<td>125.5 ± 9.1</td>
<td>10.6 ± 8.2</td>
</tr>
<tr>
<td>0.8% CB</td>
<td>6.1 ± 2.2</td>
<td>3.2 ± 1.0</td>
<td>125.1 ± 6.1</td>
<td>109.2 ± 7.7</td>
</tr>
<tr>
<td>0.8% K-1100</td>
<td>6.2 ± 3.3</td>
<td>3.3 ± 1.3</td>
<td>124.5 ± 7.1</td>
<td>109.3 ± 8.0</td>
</tr>
<tr>
<td>0.4% SWCNT</td>
<td>6.0 ± 2.9</td>
<td>3.1 ± 1.1</td>
<td>125.7 ± 6.9</td>
<td>110.3 ± 6.6</td>
</tr>
</tbody>
</table>

a Fraction of mass of dispersion.

Fig. 3. Cross-sectional optical microscope photographs of composites fabricated at a curing pressure of 0.1 MPa. (a) Without filler. (b) With CB. (c) With K-1100. (d) With SWCNT.
composites without filler incorporation [12]. On the other hand, it is lower than the value of 2.6 W/m K previously reported for carbon–carbon composite that has not been graphitized [12] and is much lower than the values for carbon–carbon composites that have been graphitized [12].

3.2. Composite architecture

The composite density is increased by increasing the curing pressure from 0.1 to 2.0 MPa (Table 4). However, the fillers have negligible effect on the density, because of the removal of the excessive resin on the prepreg surface prior to filler application. As a consequence, the continuous fiber volume fraction is increased and the matrix volume fraction is decreased upon increasing the curing pressure, but both volume fractions are negligibly affected by the fillers. The filler volume fraction is comparably low for all the fillers, but it is slightly higher for CB and SWCNT than K-1100. The filler volume fraction is increased slightly by increasing the curing pressure.

As shown by optical microscopy of mechanically polished edges of the composites, the interlaminar interface thickness and the lamina thickness are negligibly affected by the fillers, though they are decreased by the increase in the curing pressure (Table 5). The fillers could not be observed at the interlaminar interface; the interlaminar interface morphology is not affected by the filler (Fig. 3).

3.3. Flexural mechanical properties

The effects of curing pressure and filler incorporation on the flexural strength, modulus and ductility are shown in Table 6. Flexural stress–strain curves are shown in Fig. 4 for the composites made at a curing pressure of 0.1 MPa.

The measured modulus of any of the modified composites is slightly higher than that of the corresponding unmodified composite, whether the curing pressure is 0.1 or 2.0 MPa, and whether or not the modulus of the unmodified composite has been scaled to the value for the higher fiber volume (Table 4) of the modified composite. Among the three types of filler, SWCNT is most effective for enhancing the modulus.

For the curing pressure of 0.1 MPa, the measured strength is slightly lowered by CB or K-1100 but is essentially not affected by SWCNT, whether or not the strength of the unmodified composite is decreased by the increase in the curing pressure (Table 5). The fillers could not be observed at the interlaminar interface; the interlaminar interface morphology is not affected by the filler (Fig. 3).

![Fig. 4. Curves of flexural stress vs. flexural strain during static flexure up to failure for composites fabricated at a curing pressure of 0.1 MPa. (a) Without filler. (b) With CB. (c) With K-1100. (d) With SWCNT.](image)
and high ductility. CB is the second best, whereas K-1100 is the worst. The relatively low effectiveness of K-1100 is due to the large size of K-1100 compared to the size of CB or SWCNT.

For any of the composites, whether a filler is present or not, the modulus is higher at 2.0 MPa curing pressure than that at 0.1 MPa curing pressure. For the curing pressure of 2.0 MPa, the measured modulus of the composite containing any of the fillers is similar to the corresponding value calculated by scaling the measured value for the curing pressure of 0.1 MPa to the value for the higher fiber volume fraction of the corresponding composite fabricated at 2 MPa. This means that the increase in modulus upon increasing the curing pressure is due to the increase in fiber volume fraction.

For any of the composites, whether a filler is present or not, the strength is higher at 2.0 MPa curing pressure than that at 0.1 MPa curing pressure. For CB or K-1100, the increase in strength is beyond that due to the increase in fiber volume fraction, as shown by comparing the measured and calculated strength values. For the unmodified composite and for the composite with SWCNT, the measured and calculated values of the strength are comparable, indicating that the strength increase upon curing pressure increase is due to the increase in curing pressure.

The ductility is essentially unaffected by the curing pressure increase, except for the composite with SWCNT, the ductility of which is increased upon increasing the curing pressure from 0.1 to 2.0 MPa.

3.4. Carbon black squishability

As shown in Fig. 5, carbon black is in the form of porous agglomerates before compression and is highly squishable, such that compression at 0.1 MPa causes the formation of a sheet with a rough surface and compression at 2.0 MPa causes the formation of a sheet with a smoother surface. This supports the notion that the high curing pressure of 2.0 MPa causes less effect of the carbon black on the microstructure within a lamina compared to the low curing pressure of 0.1 MPa.

4. Conclusion

This work increases the through-thickness thermal conductivity (measured around 56 °C by using the Guarded Hot Plate Method) of continuous 7-µm-diameter 7-W/m·K-thermal conductivity PAN-based carbon fiber epoxy–matrix composite by up to 60% by raising the curing pressure from 0.1 to 2.0 MPa and up to 33% by incorporation of a filler (≤15 vol.%), which is applied at the interlaminar interface through prepreg surface modification. The interlaminar interface thickness and the lamina thickness are not affected by the filler incorporation, but are decreased by raising the curing pressure. The continuous fiber volume fraction is increased by the curing pressure increase, but is essentially unaffected by filler incorporation.

The thermal resistivity is dominated by the lamina resistivity (which is contributed substantially by the intralaminar fiber–fiber interfacial resistivity). The interlaminar interface thermal resistivity is unexpectedly negligible, regardless of the curing pressure or the presence of a filler. The lamina resistivity and intralaminar fiber–fiber interfacial resistivity are decreased by up to 56% by increasing the curing pressure (due to the accompanying decreases in the lamina thickness and the interlaminar interface thickness) and by up to 36% by filler incorporation (due to the effect of the filler on the lamina resistivity, presumably associated with the effect of the filler on the lamina microstructure, such as the degree of continuous fiber alignment). Thus, curing pressure increase is more effective than filler incorporation.

The curing pressure increase does not affect the effectiveness of 1-mm-long 10-µm-diameter 900–1000-W/m·K-thermal conductivity K-1100 carbon fiber or SWCNT as fillers for enhancing...
the conductivity, but hinders the effectiveness of CB, which is less effective than K-1100 or SWCNT at the higher curing pressure, but is almost as effective as K-1100 and SWCNT at the lower curing pressure. The increases in the flexural modulus, strength and ductility due to the fillers are small, with the effectiveness for enhancing these flexural properties decreasing in the order: SWCNT, CB, K-1100.

References


