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Enhancing the thermal conductivity and compressive modulus of carbon fiber polymer–matrix composites in the through-thickness direction by nanostructuring the interlaminar interface with carbon black

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ABSTRACT

Heat dissipation from aircraft is important. Carbon fiber polymer–matrix structural composites have high in-plane thermal conductivity, but low through-thickness conductivity. A nanostructuring method involving carbon black at the interlaminar interface was developed to improve the through-thickness conductivity. Ethylene glycol monoethyl ether (EGME) was used for dispersing the carbon black and to partially dissolution of the epoxy resin on the fiber-epoxy prepreg surface. EGME evaporated from the prepreg surface prior to composite fabrication. The optimum carbon black content in EGME for attaining high through-thickness conductivity was 0.8 wt.% for both unidirectional and crossply configurations. Applying EGME without carbon black improved the conductivity by up to 36%, but in the case with carbon black, the improvement was up to 210%. For the same interlaminar interface modification (except for EGME with 1.2 wt.% carbon black), the conductivity and its fractional increase were higher for the crossply configuration than the corresponding unidirectional configuration. The through-thickness compressive modulus and the flexural modulus were increased by up to 14% and 11%, respectively by using EGME with carbon black. The average thickness of the interlaminar interface increased with increasing carbon black content, but it was decreased by the use of EGME alone.

1. Introduction

Heat dissipation from aircraft systems is increasingly important, due to the rapid increase in thermal load, which is expected to reach 10,000 kW [1]. 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. Furthermore, low temperatures are required for the reliability of electron field emitters (cold cathodes).

Polymer–matrix composites with continuous and aligned carbon fiber reinforcement are widely used for lightweight structures, due to their high strength-to-weight ratio, good fatigue resistance and corrosion resistance. They are increasingly used in both commercial and military aircraft. Although the polymer matrix is not conductive, the carbon fibers in the

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composite render the composite high in the in-plane thermal conductivity. Carbon fibers that are even more conductive thermally than copper are commercially available. The high in-plane thermal conductivity promotes heat spreading. However, a drawback of these composites is the low through-thickness thermal conductivity [2–4], which hinders heat removal in the through-thickness direction (the direction perpendicular to the laminae). Both in-plane heat spreading and through-thickness heat removal are important for effective heat dissipation.

Prior methods for increasing the through-thickness thermal conductivity of carbon fiber polymer–matrix composites include the use of continuous fiber with carbon nanofiber grown on its surface [5]. The nanofiber allows heat conduction in all directions, though the continuous fiber is aligned. However, the presence of nanofiber results in a low fiber volume fraction in the composite, thus limiting the reinforcing ability. In addition, this type of fiber makes composite fabrication difficult and costly.

In contrast to prior work, this paper uses interlaminar interface nanostructuring to increase the thermal conductivity of a carbon fiber polymer–matrix composite in the through-thickness direction. As this interface is the polymer-rich region between adjacent laminae, it contributes significantly to the thermal resistance of the composite in the through-thickness direction. Improving the thermal contact across the interlaminar interface is the main objective of this work.

Although polymer–matrix composites with continuous carbon fiber exhibit excellent tensile properties in the fiber direction (in the plane of the laminae in case of a multidirectional composite), the weak link at the interlaminar interface causes the through-thickness compressive properties to be poor. The poor through-thickness compressive properties are of concern to the quality and durability of composite joints made by fastening, which involves the application of a through-thickness compressive stress. This concern is relevant to aircraft safety, as indicated by the 2001 Airbus accident in New York. The accident involved detachment of the tail section from the body of the aircraft (Investigation of the Crash of American Airlines Flight 587. <http://www.airsafe.com/events/aa587.htm>). Increasing the through-thickness compressive modulus is the secondary objective of this work.

A composite panel commonly encounters flexural loading. The weak link at the interlaminar interface is a disadvantage to the flexural properties. Increasing the flexural modulus is the third objective of this work.

The nanostructuring approach used in this work for reaching the three objectives mentioned above involves the application of conductive nanoparticles between the laminae during the fabrication of the composite, such that the nanoparticles fit between the fibers of the adjacent laminae without causing the fibers of the adjacent laminae to become farther apart from one another. Carbon nanoparticles in the form of carbon black are inexpensive, so they are used in this work. In addition, this work investigates the use of a vehicle for dispersing the carbon black and for removing a part of the resin on the surface of the carbon fiber epoxy prepreg. Both the partial resin removal and the carbon black addition are expected to improve the thermal contact across the interlaminar interface.

There are other possible benefits of the interlaminar interface nanostructuring, although they are not addressed in this paper. One benefit relates to increases in the delamination resistance, due to the carbon atomic layers in the nanostructured carbon used for the interlayer being in various directions that include the through-thickness direction, in contrast to the in-plane alignment of the continuous fibers. Another benefit relates to enhanced damping, due to the large area of the interface between the nanostructured carbon and the matrix and the interfacial mechanism of damping. Such benefits have been shown for the case in which carbon nanofiber (0.1 μm diameter) is used to nanostructure the interlaminar interface [6,7]. The viscoelastic interlayer, which is conventionally used for damping improvement, results in a decrease in the storage modulus under flexure from 130 to 37 GPa, whereas the decrease due to the carbon nanofiber interlayer is small, from 130 to 115 GPa only [8].

The effect of the interlaminar interface nanostructuring is expected to depend on the relative orientation of the fibers on the two sides of the interlaminar interface. When the fibers of the two laminae are not parallel, the fibers of one lamina tend to press against those of the adjacent lamina, thus resulting in substantial fiber–fiber contacts across the interlaminar interface (as indicated by a relatively low value of the electrical contact resistivity of the interface [9]). On the other hand, when the fibers of the two laminae are parallel, the fibers of one lamina tend to sink into the adjacent laminae to a certain degree, thus resulting in relatively few fiber–fiber contacts across the interlaminar interface (as indicated by a relatively high value of the contact resistivity of the interface [9]). In practice, structural composites are not unidirectional, but involve fibers of different orientations in the various laminae of the same composite. This work includes investigation of the unidirectional and crossply configurations. The crossply configuration represents the general situation in which the fibers of the two adjacent laminae are not parallel.

In order to reach the three objectives mentioned above, this work was conducted to (i) nanostructure the interlaminar interface of carbon fiber polymer–matrix composite by using carbon black as the nanoscale component, (ii) develop the formulation of nanostructured carbon fiber polymer–matrix composite, (iii) develop an effective method for fabricating nanostructured carbon fiber polymer–matrix composite, (iv) enhance the through-thickness thermal conductivity, through-thickness compressive modulus and flexural modulus of carbon fiber polymer–matrix composite by nanostructuring, and (v) to compare the effect of the nanostructuring for unidirectional and crossply composites.

2. Nanostructuring method

The nanoscale component is the conductive filler for the interlaminar interface. Types of nanostructured carbons include carbon black (CB), carbon nanofiber and carbon nanotube. Of these, only carbon black is squishable [10]; carbon nanofiber and carbon nanotube essentially maintain their shapes during compression, unless the pressure is high. Squishability allows comformability to the topography of the fiber surface at the interlaminar interface. It also allows spreadability, as the nanoscale component forms a thin layer at the interface. Carbon black has greater squishability than the other two types of nanostructured carbons [10]. In addition, carbon black is less textured than carbon nanofiber or carbon nanotube, and hence it has no need for alignment. Besides, it is inexpensive compared to the nanofiber or nanotube.

The carbon black chosen was Vulcan XC72R GP-3820 from Cabot Corp., Billerica, MA. It was a powder with particle size 30 nm (Fig. 1), a nitrogen specific surface area 254 m^2/g, maximum ash content 0.2%, volatile content 1.07%, and density 1.7–1.9 g/cm^3. Furthermore, this carbon black is not pelleted; the fluffiness enhances the dispersibility.

Dry and wet methods are available to apply a nanoscale component to a surface. In the dry method, the component is directly applied to the interface in the dry state. The advantage of this method is that a liquid is not involved and the issue of subsequent liquid removal is not of concern. However, the distribution of the component may not be uniform, due to the difficulty of controlling it. In the wet method, the component is mixed with a vehicle (a liquid) and the dispersion is then applied to the surface. Subsequently, the vehicle is allowed to evaporate. This method is advantageous in the superior degree of component dispersion, but it is more expensive than the dry method.

In this work, the nanoscale component was mixed with a vehicle by ultrasonic vibration, which was conducted for a time ranging from 30 min to an hour. The goal of the nanostructuring is to remove a part of the insulating polymer resin at the interlaminar interface and filling the interlaminar space between the carbon fibers of adjacent laminae with a conductive nanoscale component (Fig. 2). The vehicle serves to dissolve the resin for the purpose of resin removal. Once the nanoscale component is dispersed on the prepreg surface, it is necessary to allow the vehicle to evaporate in order to avoid air void formation during subsequent curing.

In applying carbon black in the form of dispersion to the interlaminar interface (i.e., using the wet method), an appropriate vehicle is needed. Criteria for the choice of a vehicle include the following.

(i) It disperses carbon black well.
(ii) It evaporates at room temperature in a reasonable time frame.

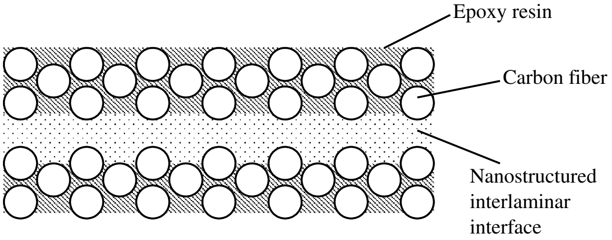


Fig. 2 – Schematic of a nanostructured composite.

(iii) It dissolves (but not excessively) epoxy resin in order for the carbon black to contact the carbon fiber directly (Fig. 2).
(iv) It should not hinder the reaction between epoxy and curing agent. For example, ketones such as acetone are known to hinder the reaction, and also acid reacts with amine and produces amidoamine [11].

The first criterion is the most basic and was used to screen the vehicle choices. Chloroform is known to disperse carbon black well, due to its polar character [12,13]. This led us to the choice of polar solvents. Related to this criterion is that the vehicle must keep the carbon black suspended. The second criterion needs to be satisfied, so that no voids are created during the subsequent curing of the prepreg. However, evaporation that is too fast is not suitable, since it is in practice difficult to apply the dispersion in a very short time frame. After a vehicle has been found to meet criteria (i) and (ii), it is considered in relation to criterion (iii).

Investigation in relation to criterion (i) was conducted by visually observing the extent of agglomeration of the carbon black in the vehicle. Investigation in relation to criterion (ii) was conducted by comparing the previously reported vapor pressures of the various vehicles, as listed in Table 1. Investigation in relation to criterion (iii) was conducted by weighing the prepreg (1 cm × 6 cm) before and after immersion in the vehicle (20 ml) in a screw-capped glass bottle for a week and weighing the dissolved epoxy in the bottle after complete evaporation of the vehicle.

The vehicles tested are listed in Table 1. They are ethylene glycol monoethyl ether (abbreviated EGME), di(ethylene glycol) butyl ether, 2-propanol, chloroform, tetrahydrofuran, and acetone. All of these, except acetone, were found to have

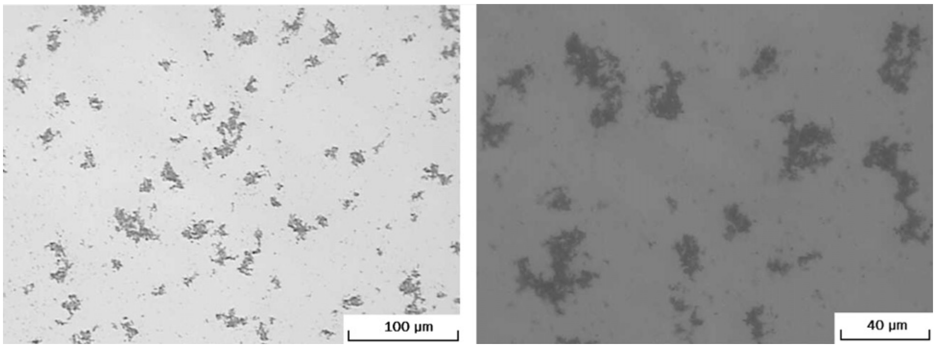
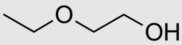
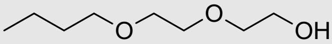
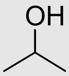
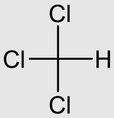
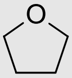
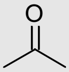


Fig. 1 – Scanning electron microscope photographs of carbon black, showing aggregates. From [14].

Table 1 – Summary of vehicles tested

Vehicle	Vapor pressure (mmHg)[a]	Epoxy dissolvability
Ethylene glycol monoethyl ether (EGME) $CH_3CH_2OCH_2CH_2OH$ 	3.8 (20 °C)	High
Di(ethylene glycol) butyl ether $CH_3(CH_2)_3O(CH_2)_2O(CH_2)_2OH$ 	30 (130 °C)	High
2-Propanol $(CH_3)_2CHOH$ 	33 (20 °C)	Low
Chloroform $CHCl_3$ 	160 (20 °C)	Very high
Tetrahydrofuran C_4H_8O 	143 (20 °C)	Very high
Acetone CH_3COCH_3 	184 (20 °C)	High

[a] <http://www.sigmaaldrich.com/>, as on December 8, 2007.

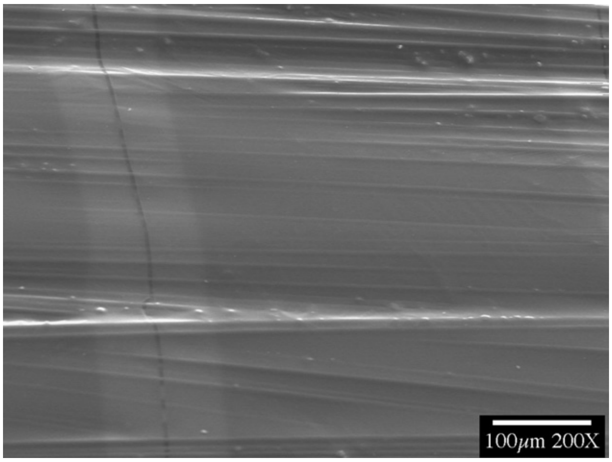


Fig. 3 – SEM photograph of the prepreg surface without modification.

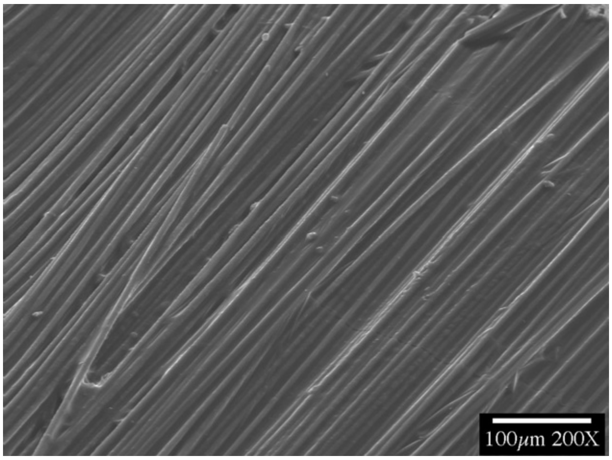


Fig. 4 – SEM photograph of the prepreg surface after application of a dispersion of carbon black in ethylene glycol monoethyl ether (EGME), $CH_3CH_2OCH_2CH_2OH$.

the desired carbon black dispersion ability. Among the five vehicles that dispersed carbon black well, chloroform met criterion 2 the best, but it dissolved epoxy excessively (criterion 3). Although di(ethylene glycol) butyl ether dissolved the

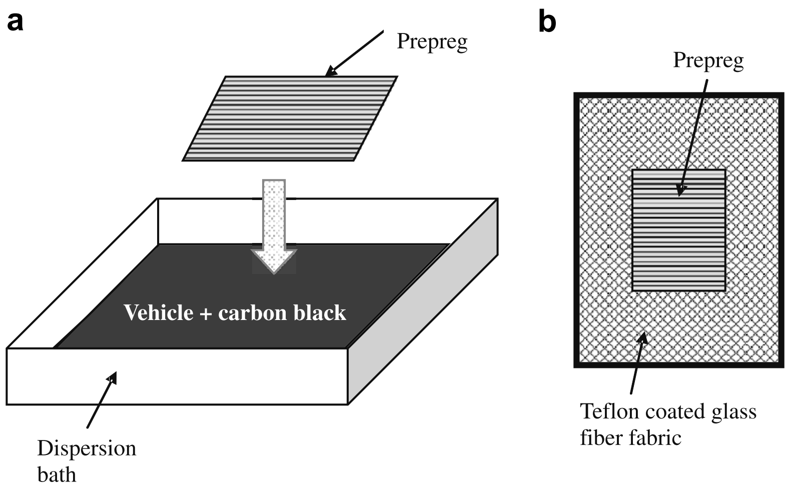


Fig. 5 – Apparatus for interlaminar interface nanostructuring. (a) Prepreg about to be immersed in a dispersion bath containing the vehicle, optionally with carbon black. (b) Prepreg on a fabric support after removal from the bath.

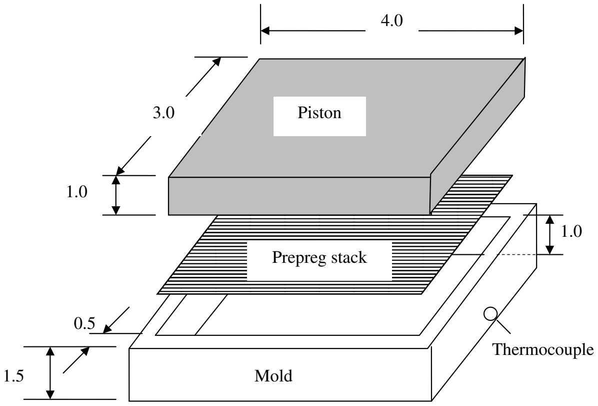


Fig. 6 – Apparatus for composite fabrication by hot pressing.

Table 2 – Technical data of SIGRAFIL CE 1222-255-37 carbon fiber epoxy prepreg (according to SGL Carbon Group, Meitingen, Germany)

Resin system	Epoxy 201
Fiber	12 K Carbon
Weight of fiber per surface area	255 g/m^2
Weight of prepreg per surface area	405 g/m^2
Resin content	37 ± 3%
Thickness of prepreg before compression into laminated sheet (60 vol.% fiber)	0.24 mm
Density	1.60 g/cm^3
Shear strength	70–80 MPa
Young's modulus	215 GPa
Tensile strength	1.45 GPa
T_g	140 °C

epoxy resin sufficiently, it did not vaporize quickly at room temperature. On the other hand, EGME satisfied all four criteria and was therefore chosen to be the vehicle for this work.

Figs. 3 and 4 show SEM images of the unmodified and modified prepreg surfaces, with the modification involving carbon black dispersed in EGME. Without modification, the epoxy resin coated the carbon fibers well (Fig. 3). For the case of EGME, exposed carbon fiber along with well-dispersed carbon black particles were observed (Fig. 4).

The nanoscale component content, or concentration, affects the thermal conductivity of the through-thickness direction. If the nanoparticle content is excessive, the fibers in the adjacent laminae are farther apart and poor conduction results. On the other hand, if the nanoparticle content is too low, a conductive path is unable to form through the interlaminar interface. Therefore, the carbon black content in the vehicle (EGME) was systematically varied in this work for the purpose of determining the optimum content. The contents used were 0%, 0.40%, 0.60%, 0.80%, 1.0% and 1.2% by weight of the total vehicle, which comprised EGME and carbon black, if any. These weight fractions correspond to 0%, 0.21%, 0.31%, 0.41%, 0.52% and 0.62% by volume of the total vehicle.

In composite fabrication, each layer of carbon fiber epoxy prepreg was separately immersed in a bath of the vehicle (optionally containing carbon black in order to investigate the effect of carbon black) for 3 s (Fig. 5a). 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 was then removed from the bath and placed on a substrate in the form of a PTFE (Teflon) coated glass–fiber fabric sheet (Fig. 5b). After this, the vehicle in the sheet was allowed to evaporate to completion in air.

Once the prepreg sheets had dried separately, they were stacked to reach the number of laminae desired. Subsequently the stack was cured using a hot hydraulic press (Carver, Inc., Wabash, IN), which provided heat and pressure. The press involved two metal platens for sandwiching a mold containing a prepreg stack and the mating piston above the mold (Fig. 6). The mold used for this project had inner dimensions of 4×3 in^2 and wall thickness 0.5 in. The piston was a tight-fit to the mold, with dimensions $4 \times 3 \times 1$ in^2. Both the mold and piston were made of steel. The small hole on the bottom side at the center of the mold allowed a thermocouple (Type K) to

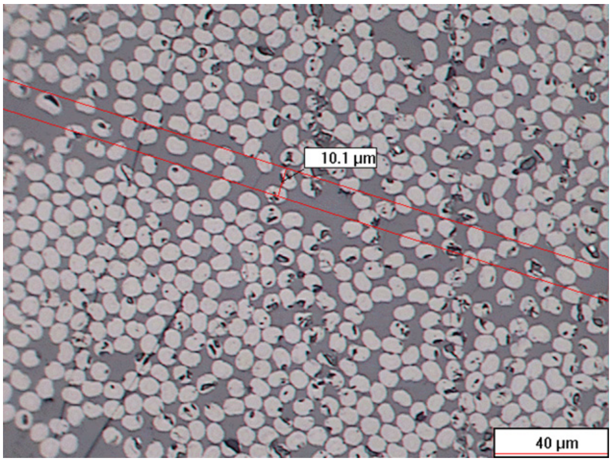


Fig. 7 – Optical microscope photograph of the cross section of a unidirectional composite without modification to the interlaminar interface.

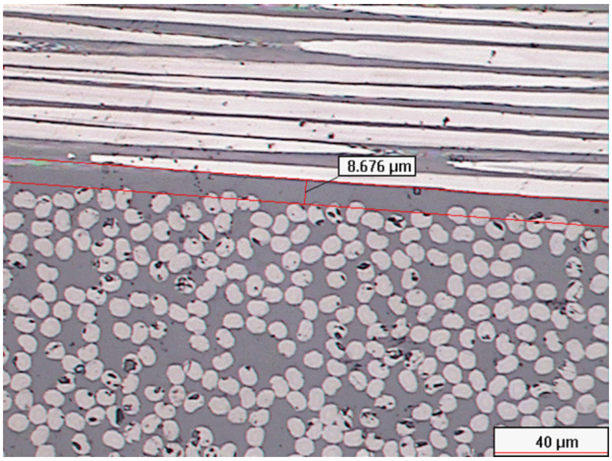


Fig. 8 – Optical microscope photograph of the cross section of a crossply composite without interlaminar interface modification.

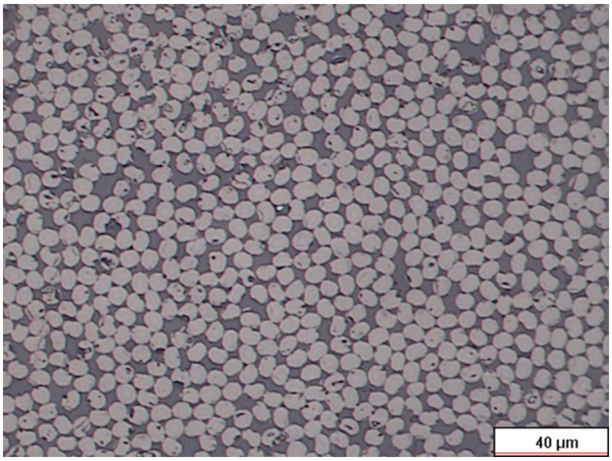


Fig. 9 – Optical microscope photograph of the cross section of a unidirectional composite, with the vehicle EGME (without carbon black) applied to the interlaminar interface.

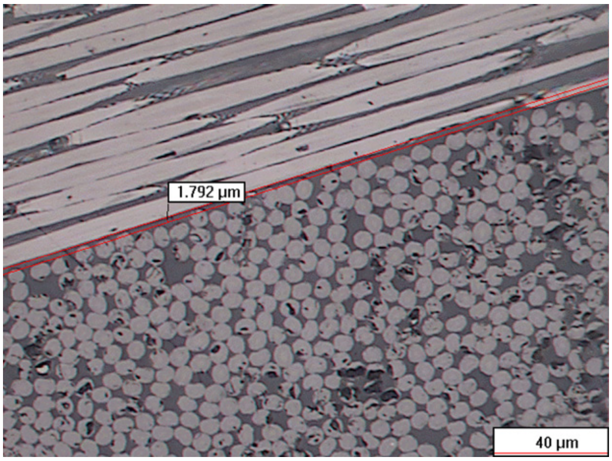


Fig. 10 – Optical microscope photograph of the cross section of a crossply composite with the vehicle EGME (without carbon black) applied to the interlaminar interface.

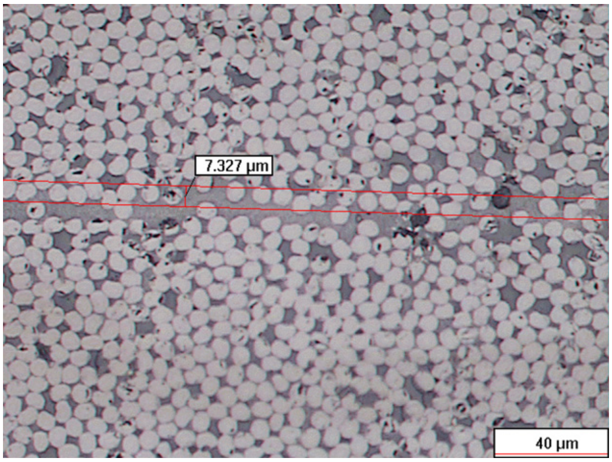


Fig. 11 – Optical microscope photograph of the cross section of a unidirectional composite, with vehicle (EGME) containing 0.8 wt.% carbon black applied to the interlaminar interface.

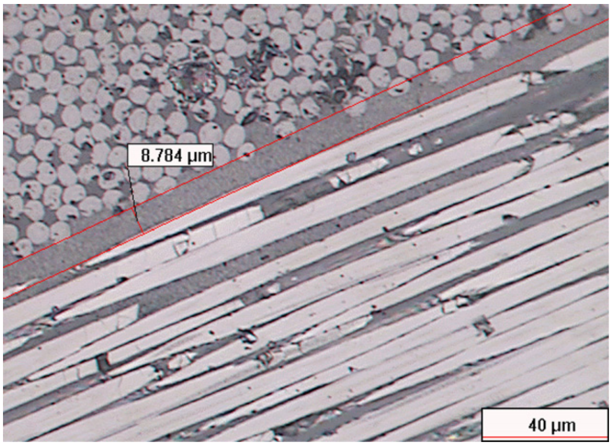


Fig. 12 – Optical microscope photograph of the cross section of a crossply composite with the vehicle (EGME) containing 0.8 wt.% carbon black applied to the interlaminar interface.

Table 3 – Interlaminar interface thickness (μm) of fabricated carbon fiber epoxy–matrix composites, based on optical microscopy of the cross section

Interlaminar interface type	Unidirectional	Crossply
Without carbon black, without vehicle	10 ± 4	9 ± 5
With vehicle, without carbon black	[a]	2 ± 2
With vehicle + carbon black (0.4 wt.%)	4 ± 2	3 ± 2
With vehicle + carbon black (0.6 wt.%)	6 ± 2	4 ± 2
With vehicle + carbon black (0.8 wt.%)	8 ± 3	8 ± 4
With vehicle + carbon black (1.0 wt.%)	8 ± 4	11 ± 7
With vehicle + carbon black (1.2 wt.%)	14 ± 7	15 ± 7

The vehicle is EGME.
[a] The interlaminar interface could not be distinctly observed.

measure the temperature. The thermocouple was fed to a temperature controller (Watlow Electric Manufacturing Company, St. Louis, MO, Series 981C-10CA-ARRR), which controlled the curing process temperature (heating, holding at the maximum temperature and then cooling).

The carbon fiber epoxy-matrix prepreg was ®SIGRAFIL prepregs CE 1222-255-37 (with the properties shown in Table 2). The curing of the prepregs was conducted using the apparatus illustrated in Fig. 6. The curing temperature was 130 °C, with a heating rate of 3.67 °C/min from room temperature (20 °C) to 130 °C and holding at 130 °C for 1.5 h. The pressure was 0.8 MPa during curing.

3. Interlaminar interface microstructural examination

The interlaminar interface was observed by optical microscopy of the cross section (plane containing the through-thickness direction) of composites with and without various interlaminar interface modifications (Figs. 7–12). The interface was associated with a thickness, which varied considerably within the same interlaminar interface, due to the small thickness (compared to the thickness of the composite) and the curvature of the interlaminar interface. In spite of the variation, the average thickness of the interlaminar interface increased with increasing carbon black content, as shown in Table 3.

Relative to the unmodified interlaminar interface, the interface thickness decreased upon use of the vehicle in the absence of carbon black, as observed for the crossply configuration. In the unidirectional case, the interlaminar interface could not be distinctly observed when the composite involved use of the vehicle in the absence of carbon black.

The effect of the interlaminar interface modification on the interlaminar interlayer structure can be observed from the optical microscope photographs for the crossply configuration (Figs. 8, 10 and 12). Comparing the composite with the vehicle (EGME) alone applied to the interface (Fig. 10) to that with the unmodified interface (Fig. 8), the fibers in adjacent laminae on the two sides of the interface were in greater proximity for the former. This is consistent with the observation that the fibers on the surface of the prepreg were partially exposed by the treatment using EGME (Section 2). In the case with both carbon black and EGME applied to the interlaminar interface (Fig. 12), the carbon black conformed to the surface of the lamina and filled the space between the adjacent laminae. The conformability is consistent with the fact that carbon black is squishable.

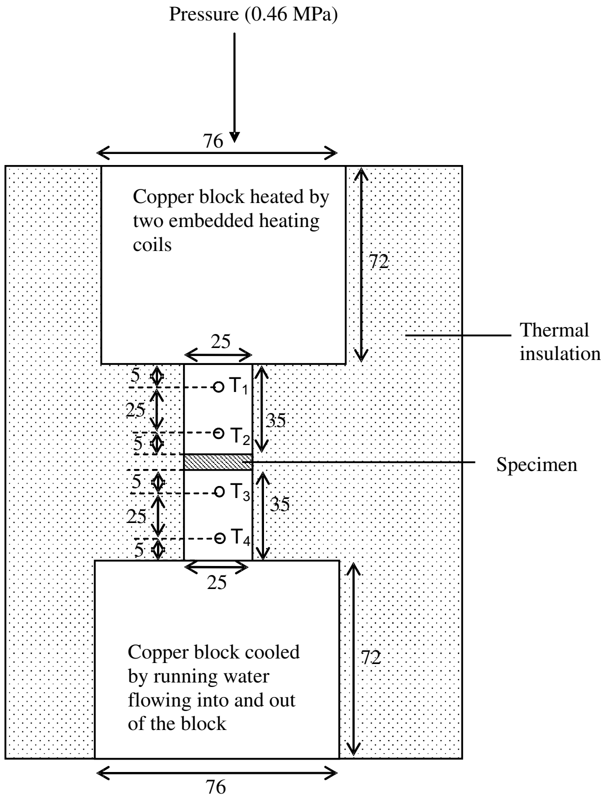


Fig. 13 – Set-up for thermal conductivity measurement using the guarded hot plate method. The heat flux is in the direction from the top copper block to the bottom copper block. All dimensions are in mm.

4. Thermal conductivity evaluation

4.1. *Thermal conductivity evaluation method*

The thermal contact conductance between two 1 × 1 in.^{2} (25 × 25 mm^2) copper blocks with a composite specimen between them is measured using the guarded hot plate method, which is a steady-state method of heat flux measurement (ASTM Method D5470). The heat is provided by a 3 × 3 in.^{2} (76 × 76 mm^2) copper block that has two embedded heating coils (top block in Fig. 13). During the period of temperature rise, the heating rate is controlled at 3.2 °C/min by using a temperature controller. This copper block is in contact with one of the 1 × 1 in.^{2} copper blocks that sandwich the composite sample. The 1 × 1 in.^{2} copper blocks have a surface roughness of

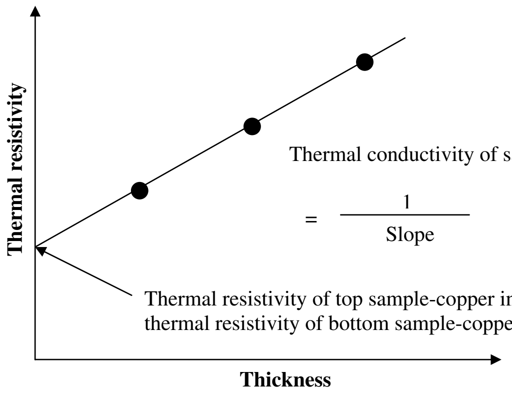


Fig. 14 – Schematic illustration of the linear dependence of the thermal resistivity on the specimen thickness. The thermal conductivity is equal to the reciprocal of the slope of the plot.

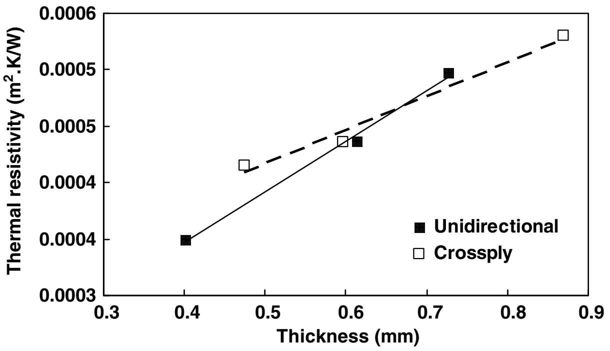


Fig. 15 – Variation of the thermal resistivity with the composite thickness for composites with vehicle (EGME) containing 0.8 wt.% carbon black applied to the interlaminar interface. For each type of composite (unidirectional or crossply), data points are provided for three thicknesses, which correspond to composites with 2, 3 and 4 laminae.

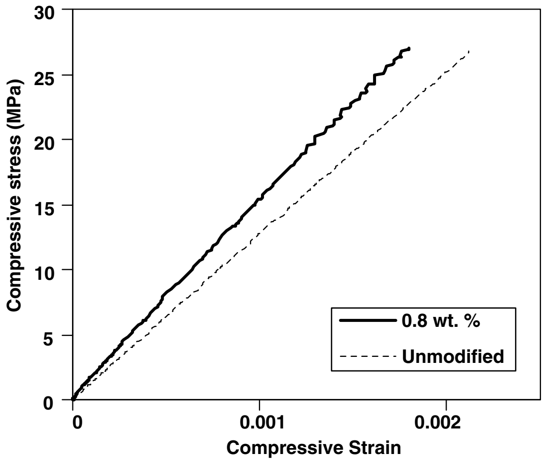


Fig. 16 – Compressive stress–strain curves in the elastic regime during loading and subsequent unloading for the unmodified crossply composite and for the crossply composite with interlaminar interface modification using the vehicle (EGME) containing 0.8 wt.% carbon black.

15 μm, which translates to a copper-specimen interface undulation amplitude of 15 μm. The cooling in this test is provided by a second 3 × 3 in.^{2} copper block, which is cooled by running water that flows in and out of the block (bottom block in Fig. 13). This block is in contact with the other 1 × 1 in.^{2} copper block that is in contact with the composite sample. An RTD (resistance thermometer) probe (connected to Digi-Sense ThermoLogR RTD Thermometer from Fisher Scientific Co., with accuracy ±0.03 °C) is inserted in four holes (T_1, T_2, T_3 and T_4 in Fig. 16, 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 $T_1 - T_2$ and $T_3 - T_4$. 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. 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

$$Q = \frac{\lambda A}{d_A}\Delta T \tag{1}$$

where $\Delta T = T_1 - T_2 = T_3 - T_4$, λ is the thermal conductivity of copper, A is the area of the 1 × 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

$$T_A = T_2 - \frac{d_B}{d_A}(T_1 - T_2) \tag{2}$$

where d_B is the distance between thermocouple T_2 and the top surface of the thermal interface material (i.e., 5 mm).

The temperature at the bottom surface of the thermal interface material 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

$$T_D = T_3 + \frac{d_D}{d_C}(T_3 - T_4) \tag{3}$$

where d_D is the distance between thermocouple T_3 and the bottom surface of the thermal interface material (i.e., 5 mm) and d_C is the distance between thermocouples T_3 and T_4 (i.e., 25 mm).

The two-dimensional thermal resistivity θ is given by

$$\theta = (T_A - T_D)\frac{A}{Q} \tag{4}$$

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

Table 4 – Thermal conductivity (W/m K) of unidirectional and crossply carbon fiber polymer–matrix composites with and without various interlaminar interface modifications

Interlaminar interface type	Unidirectional	Crossply
Without carbon black, without vehicle	1.0400 ± 0.0001	1.0700 ± 0.0001
With vehicle, without carbon black	1.372 ± 0.003	1.457 ± 0.002
With vehicle + carbon black (0.4 wt.%)	1.761 ± 0.009	2.273 ± 0.006
With vehicle + carbon black (0.6 wt.%)	1.955 ± 0.007	2.400 ± 0.023
With vehicle + carbon black (0.8 wt.%)	2.234 ± 0.002	3.338 ± 0.025
With vehicle + carbon black (1.0 wt.%)	1.869 ± 0.005	2.149 ± 0.033
With vehicle + carbon black (1.2 wt.%)	1.602 ± 0.005	1.540 ± 0.027

The vehicle is EGME.

Each composite was tested at three different thicknesses. For example, the three thicknesses correspond to 2, 3 and 4 laminae. A two-lamina composite has one interlaminar interface. A three-lamina composite has two interlaminar interfaces. A four-lamina composite has three interlaminar interfaces. The thermal conductivity (W/m K) of the composite is the inverse of the slope of the curve of the thermal resistivity vs. thickness (Fig. 14). The measured thermal resistance is the sum of the two interfacial thermal resistances (each of the two sample–copper interfaces) and the thermal resistance of the sample.

4.2. *Thermal conductivity evaluation results*

As shown in Table 4, the thermal conductivity was enhanced by the use of the vehicle (EGME) without carbon black for interlaminar interface modification and was further increased by the use of EGME with carbon black. The optimum carbon black content for attaining the highest thermal conductivity was 0.8 wt.% (with respect to the vehicle). The trend was the same for unidirectional and crossply configurations, but the thermal conductivity was higher for the crossply configuration than the unidirectional configuration for every case except for the highest carbon black content of 1.2 wt.%. At the optimum carbon black content of 0.8 wt.%, the thermal conductivity increase (relative to the case of no interlaminar interface modification) was 115% and 212% for unidirectional and crossply configurations, respectively. Fig. 15 shows the experimental results corresponding to the schematic of Fig. 14 for the case of 0.8 wt.% carbon black.

Although both EGME and the carbon black were useful for improving the through-thickness thermal conductivity, the effect of carbon black was greater than that of EGME, as shown by the much larger fractional increase in thermal conductivity relative to the unmodified composite when both carbon black and EGME were used than when EGME was used alone, whether the configuration was unidirectional or crossply.

That the thermal conductivity was increased by the use of EGME without carbon black is consistent with the fact that the vehicle dissolved away a part of the resin at the interface, thereby allowing greater proximity between the fibers of the adjacent laminae. That the thermal conductivity was further increased by the use of EGME with carbon black is consistent with the fact that the carbon black was a conformable and conductive filler that improved the thermal contact across the interlaminar interface. That an excessive content of carbon black decreased the thermal conductivity relative to the value at the optimum carbon black content was due to the separation of the fibers of the adjacent laminae when the carbon black content was excessive. That the thermal conductivity was higher for the crossply configuration than the unidirectional configuration was due to the larger number of fiber–fiber contacts across the interlaminar interface for the crossply configuration.

5. Through-thickness compressive modulus evaluation

5.1. *Through-thickness compressive modulus evaluation method*

Through-thickness compressive modulus measurement was conducted on specimens that consisted of 84 laminae, each of which was a square of dimensions 12.7 × 12.7 mm. The thickness of the composite (after curing) was 12.0 mm. The compressive stress applied in the through-thickness direction during testing was within the elastic regime. Due to the small values of the through-thickness strain involved in the measurement, parallelism of the two opposite surfaces perpendicular to the through-thickness direction was important. Through careful mechanical polishing, deviation from the parallelism was within 10 μm. In order to measure the through-thickness strain during compressive testing, a strain gage was attached to the center of each of two 12.7 × 12.0 mm opposite surfaces that contained the through-thickness direction. The average of the values indicated by the two strain gages was taken as the strain. The deviation between two strain gages on the same specimen ranges from 10% to 50%, due to variation in the degree of parallelism. By taking the average of the strain values given by the two strain gages, we obtained stress–strain curves that were essentially linear.

Compressive testing involved compressing the specimen between two steel plates. The testing machine was SINTECH 2/D (MTS Systems Corp., Marblehead, MA) equipped with a 2000-lb load cell. The maximum load, maximum stress and displacement rate were 1000 lb, 28 MPa, and 0.5 mm/min, respectively. Two specimens for each combination of fiber lay-up configuration and interlaminar interface condition were tested. The compressive modulus was obtained from the average slope of the stress–strain curve up to 28 MPa. This stress range is in the low-stress portion of the elastic regime.

Table 5 – Through-thickness compressive modulus (GPa) of unidirectional and crossply carbon fiber polymer–matrix composites with and without various interlaminar interface modifications

	Unidirectional		Crossply	
	During loading	During unloading	During loading	During unloading
Without carbon black, without vehicle	12.3 ± 0.4	13.0 ± 0.3	12.7 ± 0.1	12.7 ± 0.1
With vehicle, without carbon black	9.2 ± 0.4	9.3 ± 0.4	10.5 ± 0.2	10.5 ± 0.2
With vehicle + carbon black (0.4 wt.%)	10.5 ± 0.3	10.6 ± 0.2	12.3 ± 1.0	12.4 ± 0.9
With vehicle + carbon black (0.6 wt.%)	11.4 ± 0.2	11.3 ± 0.3	12.9 ± 0.4	12.9 ± 0.4
With vehicle + carbon black (0.8 wt.%)	14.0 ± 0.9	14.0 ± 1.0	14.5 ± 0.4	14.3 ± 0.4
With vehicle + carbon black (1.0 wt.%)	11.6 ± 0.3	11.6 ± 0.2	11.0 ± 0.2	11.2 ± 0.2
With vehicle + carbon black (1.2 wt.%)	10.0 ± 0.5	10.3 ± 0.2	11.2 ± 1.0	11.3 ± 1.0

The vehicle is EGME.

5.2. *Through-thickness compressive modulus evaluation results*

Fig. 16 shows through-thickness compressive stress–strain curves in the elastic regime during loading and subsequent unloading for the unmodified crossply composite and for the crossply composite with interlaminar interface modification using the vehicle (EGME) containing 0.8 wt.% carbon black. The curves are reversible upon unloading. They are essentially linear, although they are slightly nonlinear for a minority of the specimens tested, due to insufficient parallelism between the opposite surfaces of the same specimen. Table 5 shows the values of the through-thickness compressive modulus. The modulus is decreased by the use of the vehicle (EGME) in the absence of carbon black, such that the decrease is more for the unidirectional composite than the crossply composite. This difference between unidirectional and crossply composites is attributed to the negligible thickness of the interlaminar interface for the unidirectional composite and the observable thickness of the interface for the crossply composite (Table 3). However, the combined use of the vehicle (EGME) and carbon black causes the modulus to increase from the value for modification with the vehicle alone. The optimum carbon black content in the vehicle (EGME) for reaching the highest value of the modulus is 0.8 wt.%, whether the composite is unidirectional or crossply. Beyond the optimum value, the modulus decreases, due to the excessive thickness of the interlaminar interface (Table 3). When the vehicle (EGME) contains the optimum amount of carbon black, the modulus exceeds that of the unmodified composite by up to 14% and exceeds that of the composite modified with the vehicle (EGME) alone by up to 52%. The fractional increase of the modulus relative to the corresponding unmodified composite is similar for the unidirectional and crossply composites.

6. Flexural modulus evaluation

6.1. *Flexural modulus evaluation method*

Flexural testing was conducted under three-point bending with a span of 50 mm. The specimen was of length 76.2 mm in the direction of the span. The width and thickness were size 10 and 2.2 mm, respectively. The composite comprised 12 laminae. The testing machine was SINTECH 2/D (MTS Systems Corp., Marblehead, MA). The maximum load, maximum stress and midspan deflection rate were 50 lb, 340 MPa and 0.5 mm/min, respectively. Two specimens for each combination of fiber lay-up configuration and interlaminar interface condition were tested. The flexural modulus was calculated according to ISO 14125 [15], using the equation

$$E_f = \frac{L^3 m}{4bd^3}, \tag{5}$$

where L is the span, m is the slope of the tangent to the part of the load deflection curve in the low-stress regime (below 68 MPa), b is the width of test beam, and d is the thickness of test beam.

6.2. *Flexural modulus evaluation results*

Fig. 17 shows the curves of flexural stress vs. midspan deflection in the elastic regime during loading and subsequent unloading for the unmodified crossply composite and for the crossply composite with interlaminar interface modification using the vehicle (EGME) containing 0.6 wt.% carbon black. The curves are slightly concave, probably because of the increasing stress needed for further deflection as fibers on the two sides of an interlaminar interface become closer to one another. The curves are reversible upon unloading. Table 6 shows the values of the flexural modulus. For each specimen

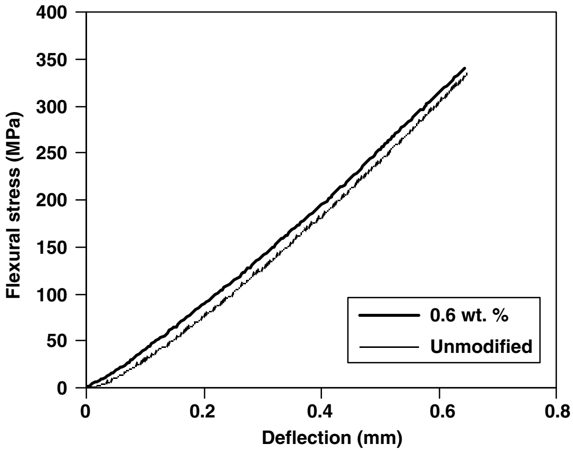


Fig. 17 – Flexural stress vs. midspan deflection curves in the elastic regime during loading and subsequent unloading for the unmodified crossply composite and for the crossply composite with interlaminar interface modification using the vehicle (EGME) containing 0.6 wt.% carbon black.

Table 6 – Flexural modulus (GPa) of unidirectional and crossply carbon fiber polymer–matrix composites with and without various interlaminar interface modifications

	Unidirectional		Crossply	
	During loading	During unloading	During loading	During unloading
Without carbon black, without vehicle	125.2 ± 1.0	122.8 ± 1.0	84.8 ± 1.0	85.7 ± 1.0
With vehicle, without carbon black	122.7 ± 2.6	123.1 ± 1.2	87.4 ± 5.0	91.3 ± 1.0
With vehicle + carbon black (0.4 wt.%)	126.3 ± 2.8	126.4 ± 3.3	93.4 ± 3.6	93.8 ± 4.1
With vehicle + carbon black (0.6 wt.%)	133.2 ± 3.8	128.5 ± 6.4	94.4 ± 1.0	95.3 ± 2.1
With vehicle + carbon black (0.8 wt.%)	124.4 ± 1.0	126.6 ± 1.0	88.8 ± 2.3	89.1 ± 1.0
With vehicle + carbon black (1.0 wt.%)	122.7 ± 1.5	124 ± 1.0	87.6 ± 1.0	87.9 ± 1.7
With vehicle + carbon black (1.2 wt.%)	122.6 ± 1.0	123.5 ± 1.3	79.6 ± 1.0	80.8 ± 1.1

The vehicle is EGME.

condition, the modulus is higher for the unidirectional composite than the crossply composite. This is because of the 90° fiber of the crossply composite not contributing to the flexural stiffness. The modulus is essentially not affected by the use of the vehicle (EGME) in the absence of carbon black. However, the combined use of the vehicle (EGME) and carbon black causes the modulus to increase from the value for modification with the vehicle alone. The optimum carbon black content in the vehicle (EGME) for reaching the highest value of the modulus is 0.6 wt.%, whether the composite is unidirectional or crossply. Beyond the optimum value, the modulus decreases, due to the excessive thickness of the interlaminar interface (Table 3). When the vehicle (EGME) contains the optimum amount of carbon black, the modulus exceeds that of the unmodified corresponding composite by up to 6% and 11% for unidirectional and crossply composites, respectively, and exceeds that of the corresponding composite modified with the vehicle alone by up to 9% and 8% for unidirectional and crossply composites, respectively. The fractional increase of the modulus, whether it is relative to the corresponding unmodified composite or relative to the composite modified by using the vehicle (EGME) alone, is comparable for the crossply and unidirectional composites. This occurs in spite of the fact that the 90° fiber of the crossply composite does not contribute to the flexural stiffness and the interlaminar interface is between 0° and 90° laminae. It is probably partly due to the tendency for the 0° and 90° fibers in the crossply composite to press on to one another during flexure, thus increasing the importance of the interlaminar interface.

The effect of the interlaminar interface modification on the flexural modulus is less than that on the through-thickness compressive modulus, particularly when the composite is unidirectional. For example, for the unidirectional configuration, the fractional increase in through-thickness compressive modulus relative to the unmodified composite is up to 14%, whereas the fractional increase in flexural modulus relative to the unmodified composite is up to 6%. Although the improvement of the flexural modulus is small, it is important that the optimum interlaminar interface modification does not degrade the flexural modulus.

7. Conclusion

A nanostructuring method was developed to improve the through-thickness thermal conductivity of continuous carbon fiber polymer–matrix composites, which are known for their high in-plane thermal conductivity. The method involved applying carbon black to the interlaminar interface, so that the interface thickness was up to 20 μm. Ethylene glycol monoethyl ether (EGME) was used as the vehicle for dispersing the carbon black and for partial dissolution of the epoxy resin on the fiber-epoxy prepreg surface after the dispersion had been applied to the prepreg surface. EGME was allowed to evaporate from the prepreg surface prior to the fabrication of composites. The carbon black concentration in the dispersion was up to 0.62 vol.% (1.2 wt.%).

The average thickness of the interlaminar interface increased with increasing carbon black content. For high through-thickness thermal conductivity and high through-thickness compressive modulus, the optimum carbon black content in EGME was 0.41 vol.% (0.80 wt.%) for both unidirectional and crossply configurations. For high flexural modulus, the optimum carbon black content in EGME was 0.31 vol.% (0.60 wt.%) for both unidirectional and crossply configurations.

For the same modification of the interlaminar interface (except for the case of 1.2 wt.% carbon black plus EGME), the thermal conductivity and its fractional increase were higher for the crossply configuration than the corresponding unidirectional configuration. EGME applied without carbon black improved the through-thickness thermal conductivity by up to 36%, though it decreased the through-thickness compressive modulus. In case of EGME with carbon black (0.41 vol.% or 0.80 wt.%), the improvement in thermal conductivity was up to 210% and the increase in through-thickness compressive modulus was up to 14%, relative to the unmodified composite. The carbon black had greater impact than EGME, though combined use of both was most effective.

Both the through-thickness compressive modulus and the flexural modulus were improved by using an optimum carbon black content, though the effect is more for the former than the latter. Unidirectional and crossply composites are similarly improved.

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