



## Thermal Conductivity Behaviour of Silicon Carbide Fiber/Phenolic Resin Composites by the Introduction of Graphene Nanoplatelets†

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Silicon carbide (SiC) represents many unique properties, such as high strength, corrosion resistance, high thermal conductivity and high temperature stability. In recent years, the SiC fibers have been widely studied for use as a fillers in polymer-matrix composite materials due to these characteristics. In order to improve the properties of such polymer-matrix composite materials dramatically, the use of graphene as an additive has been investigated both academically and industrially, as it can induce synergetic effect in the polymer-matrix composite materials, including thermoplastic and thermoset composite. In this study, we fabricated highly thermally conductive composites using Tyranno<sup>®</sup>-SA3 SiC fibers and a phenolic resin. Graphene nanoplatelets were added to composites to improve their thermal conduction properties. Thermal conductivity measurements indicated that in case of the graphene-free composites, thermal conductivity was the highest (4.1 W/m-K) when the filler was added in an amount of 50 vol %, due to the resulting structure formed by filler and matrix being closed-packed. The thermal conductivity and thermal diffusivity measurements of the graphene-nanoplatelets-containing composites showed that addition of the graphene nanoplatelets increased the thermal conductivity values of the composites. In case of the composite containing 50 vol % filler, the thermal conductivity increased to 5.5 W/m-K. This increase was due to a synergetic effect between the SiC filler and the binder induced by the graphene nanoplatelets.

**Key Words:** Silicon carbide fiber, Tyranno<sup>®</sup>-SA3, Phenolic resin, Graphene nanoplatelets, Composites, Thermal conductivity.

### INTRODUCTION

Nowadays, the market for packaging for light-emitting diodes is growing faster than ever before. Accordingly, the need for faster electronic devices with smaller form factors has led to an increase in the demand for heat-dissipating components. The heat dissipation is an important issue in light-emitting diode packaging. Heat transfer in light-emitting diode packaging primarily depends on the phenomenon of thermal conductivity. Therefore, the higher thermal conductivity of the material that makes up the packaging, the higher the degree of heat transfer. In addition, effective heat dissipation is possible only when the thermal resistance of each material forming an interface with another material in the packaging is low. Thus, the development of high-power light-emitting diode packaging technology applies high thermal conductivity material and designed the effective heat dissipation in the structure of a packaging<sup>1,2</sup>. Nanofillers that have high thermal conductivities have been investigated intensively for use as additives that can increase the thermal conductivities of polymer-matrix

composites. Chen *et al.*<sup>3</sup> studied on thermophysical properties of vapour grown carbon fiber (VGCF)-based epoxy composite. It exhibits an unprecedented high thermal conductivity of 695 W/mK. Lee *et al.*<sup>4</sup> have investigated the aluminum nitride (AlN), wollastonite, SiC whisker and boron nitride (BN) in different sizes and shapes as various inorganic fillers to be used alone or in combination with a thermally conductive polymer. In recent years, graphene, graphene oxide and carbon nanotubes (CNTs)-based composites have also attracted a lot of attention owing to their excellence mechanical, thermal and electrical properties<sup>5,6</sup>. Especially, functionalized graphene/epoxy composites was continuously investigated to improve the thermal conductivity<sup>7</sup>. Because of their unique nano-scale sizes, shapes and material composition, graphene can be used to improve the multifunctional properties. In addition, the various properties graphene-filled composites is very promising candidates for the high thermally interface material for heat dissipation from electronic devices<sup>8</sup>. Kuilla *et al.*<sup>9</sup> reviewed on modification of graphene and the fabrication of various graphene-based polymer composite. We believe that graphene

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TABLE-1  
 PROPERTIES OF SILICON CARBIDE FIBER (TYRANNO<sup>®</sup>-SA3) AT ROOM TEMPERATURE (RT)<sup>11</sup>

SiC fiber	Elemental composition (wt %)	Average diameter (μm)	Density (g/cm <sup>3</sup> )	Axial thermal conductivity (W/mK)	Tensile strength (GPa)	Elastic modulus (GPa)
Tyranno-SA3 <sup>®</sup>	68Si + 32C + 0.6Al	7.5	3.1	65(RT)	2.9(RT)	375(RT)

can help increase the connections between the inorganic filler and the polymer matrix of a filler/polymer composite being used as an light-emitting diode packaging material and thus increase the thermal conductivity of the closely packed composite. In current study, thermal conducting materials was prepared from SiC-fiber (Tyranno<sup>®</sup>-SA3), a phenolic resin and graphene nanoplatelets. A hybrid composite was fabricated by mixing SiC fibers and a phenolic resin. Graphene nanoplatelets were added to this mixture, which was then hot-pressed, resulting in samples of the graphene-nanoplatelets-containing filler/polymer composite. The thermal diffusivities and thermal conductivities of the composite specimens were measured by the laser flash method.

## EXPERIMENTAL

**Fabrication of SiC/phenolic resin composites and the addition of graphene nanoplatelets to these composites:** The composites comprised the thermally conductive SiC filler (Tyranno<sup>®</sup>-SA3), which is fabricated by Ube Industries Ltd. (Japan). The typical properties of Tyranno<sup>®</sup>-SA3 fibers were shown in Table-1. Tyranno<sup>®</sup>-SA3 fibers were removed sizing at 1000 °C in argon. Then, chopped Tyranno<sup>®</sup>-SA3 fibers were used as the filler. A phenolic resin (dissolved in methanol) (TD-2493D) (Kangnam Chemical Co. Ltd., Korea) was used as the binder and matrix phase. Graphene nanoplatelets (grade M) were purchased from XG Sciences, Inc. (USA). According to the manufacture's specification, each particle consists of several sheets of graphene with an overall thickness ranging from an average of approximately 6 to 8 nm and a typical surface area of 120 to 150 m<sup>2</sup>/g.<sup>10</sup> The existence of functional groups at the edges can lead hydrogen or covalent bond with polymer matrix. The concentration of the filler in the composites was controlled by varying its volume fraction from 0 to 90 %. In addition, graphene nanoplatelets, which were added to the composites to increase their thermal conductivity, were added in amounts varying from 1 to 5 wt % fraction for concentrations of the filler ranging from 50 to 60 %. Each mixture was heated to 60 °C after being ultrasonicated for 15 min. Then, the mixtures were placed in a mold having a diameter of 13 mm and were hot-pressed (Carver, USA) at 100 °C for 1 min using a pressure of 196 MPa. This led to the formation of graphene-nanoplatelets-containing disc-shaped fiber/polymer composite specimens having a diameter of 12.5 mm and a thickness of 2 mm. Finally, the hybrid composites were cured at 180 °C for 12 h.

**Analysis of the microstructures and thermal properties of the filler/polymer composites:** The morphologies of the Tyranno<sup>®</sup>-SA3 fibers and the graphene-nanoplatelets-containing fiber/polymer composite specimens were observed using field-emission scanning electron microscopy (FE-SEM) (JSM-6700F, Jeol, Japan), operating at 15 kV and 20 μA. The elements of Tyranno<sup>®</sup>-SA3 fiber was analyzed by energy dispersive X-ray spectroscopy (EDS) (Genesis 2000 XMS,

USA). Transmission electron microscopy (TEM) was performed with a JEM-2000EX (Jeol, Japan) microscope operating at an accelerating voltage of 200 kV. Crystallization phase of graphene nanoplatelets was analyzed by X-ray diffraction (Rigaku Miniflex, Japan) at 3° min<sup>-1</sup> of scan speed in the range of 10 to 60° using a CuK<sub>α</sub> X-ray radiation (=1.5406 Å). To confirm the functional group of graphene nanoplatelets and phenolic resin, fourier transform infrared spectroscopy (FT-IR) was used at attenuated total reflectance (ATR) mode in wavelength of 650-4000 cm<sup>-1</sup> (Jasco-4100, Japan). The thermal properties of the composite specimens, including their thermal diffusivities, given by  $\kappa = \rho \times C_p \times \alpha$ , were measured by laser flash method (Netzch, LFA-427, Germany) at room temperature, here  $\kappa$  is thermal conductivity (W/mK),  $\rho$  is bulk density of samples (g/cm<sup>3</sup>),  $C_p$  is the specific heat (J/g/K) and  $\alpha$  is the thermal diffusivity (mm<sup>2</sup>/s) and the bulk density of each specimen was calculated by Archimedes law.

## RESULTS AND DISCUSSION

**Characterization of the SiC fibers, graphene nanoplatelets and phenolic resin:** Fig. 1(a), (b) present the magnification image of Tyranno<sup>®</sup>-SA3, respectively. The surface of fiber shows the smooth and fine pores [Fig. 1(c), (d)]. The developed near-stoichiometric Tyranno<sup>®</sup>-SA3 of third generation fiber is possible to maintain a thesile strength of 2.5 GPa and in-plane thermal conductivity of 65 W/mK at room temperature<sup>12</sup>. EDS analysis results [Fig. 1(e)] indicated that the SiC fiber elements including silicon 62 atomic %, carbon 38 atomic % and aluminum 0.5 atomic %.

Graphene nanoplatelets (Fig. 2) are unique nanoparticles consisting of short stacks of one or more graphene sheets having a platelet shape. XRD pattern (Fig. 3) was shown that a strong peak at the front (26°) and a weak peaks at the back (44°, 54°). A C(002) of strong peak can see the distance of graphene interlayer space and C(100) is carbon interatom distance in basal plane<sup>13</sup>. The presence of C(004) diffraction peak is also the indicative of high crystallinity of the carbon structure in graphene nanoplatelets. Therefore, it can discuss the properties of graphene interlayer space at sharper diffraction peak. The distance of graphene C(002) layer was calculated as 3.413 Å. The Bragg's equation is  $n\lambda = 2d \sin\theta$ , where  $n$  is the integer,  $\lambda$  is the wavelength of incident wave,  $d$  is the spacing between the planes in the atomic lattice,  $\theta$  is the angle between the incident ray and the scattering planes.

As indicated by Fig. 4, the FT-IR spectra of phenolic resin contained a large peak 3300 cm<sup>-1</sup> that was associated with the O-H stretches. The peaks of C-H stretching vibrations at 2942 and 2832 cm<sup>-1</sup> can be associated with methyl groups and methylene groups. The peaks at 1604 and 1471 cm<sup>-1</sup> represent aromatic C=C stretches and 1233 cm<sup>-1</sup> shows C-OH stretches. Substituted aromatic group and mono and polycyclic compounds are indicated by the peaks between 900-650 cm<sup>-1</sup>. Furthermore, a strong signal of epoxide group are indicated

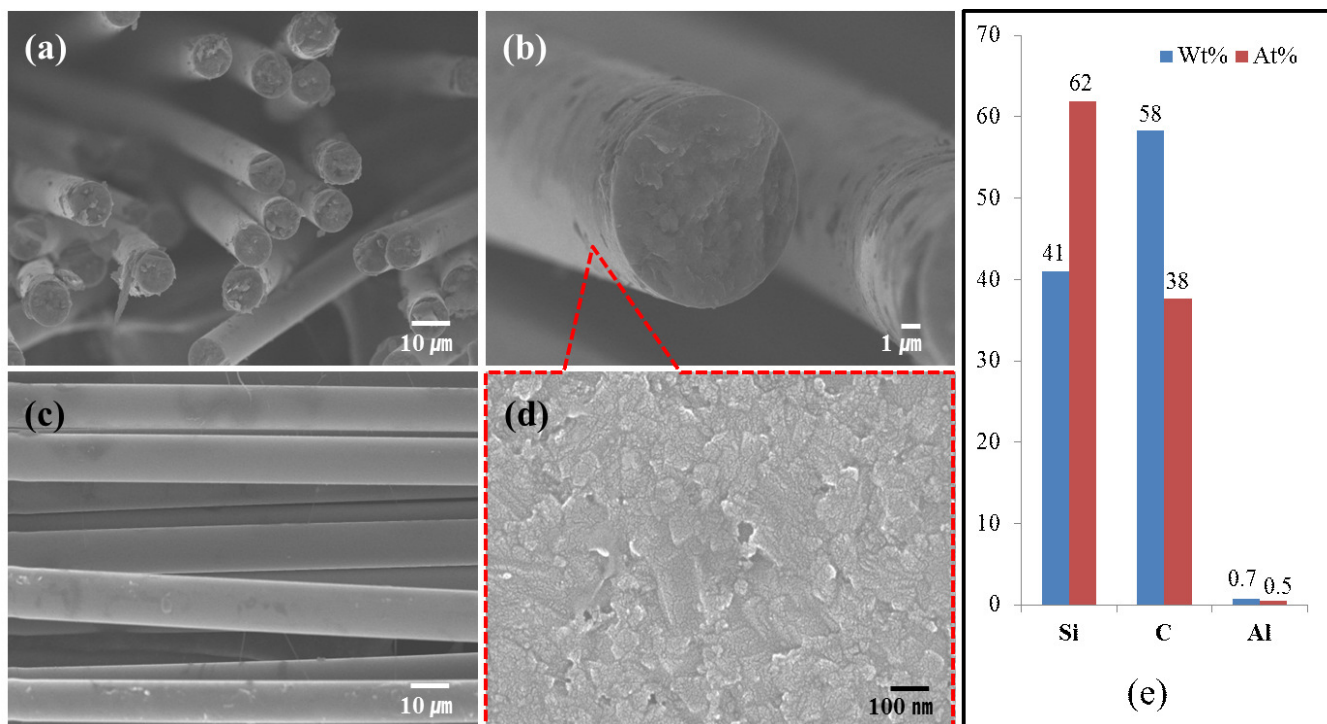


Fig. 1. FE-SEM image of (a) cross-section image of Tyranno<sup>®</sup>-SA3 image (x1000), (b) x5,000, (c) surface image, (d) magnification of surface image (x100,000) and (e) elements analysis graph of Tyranno<sup>®</sup>-SA3 using EDS

by the adsorption peak at 1010 cm<sup>-1</sup>. The FT-IR spectra of graphene nanoplatelets are represented by double bond of carbon at 1540 cm<sup>-1</sup> and hydroxyl group (-OH) at 1244 cm<sup>-1</sup>. In addition, epoxide groups are represented by the adsorption peak at 1010 cm<sup>-1</sup>. There are fewer hydroxyl groups than

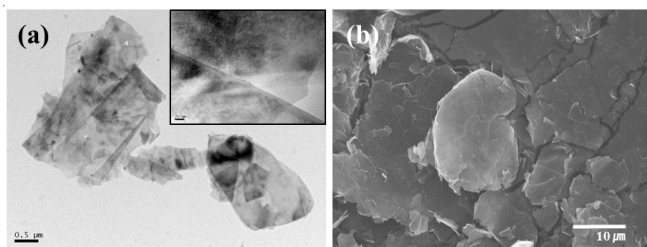


Fig. 2. TEM image of (a) graphene nanoplatelets and FE-SEM images of (b) graphene nanoplatelets

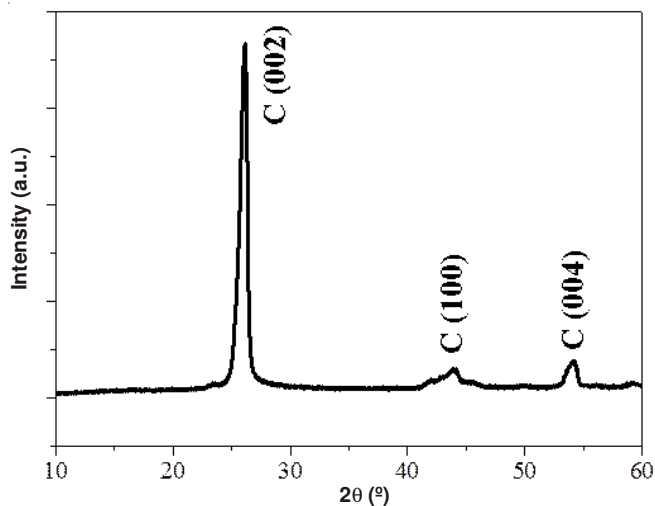


Fig. 3. XRD pattern of graphene nanoplatelets

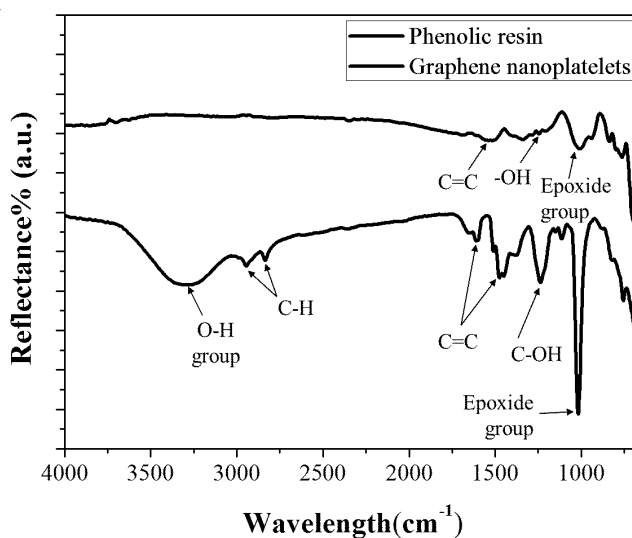


Fig. 4. FT-IR spectra of phenolic resin and graphene nanoplatelets

epoxide groups. This functional groups helps facilitate hydrogen or covalent bonding within a polymer matrix.

**Orientation of the SiC fibers in the polymer matrices of the composite specimens:** The microstructures of the hybrid composites are shown in Fig. 5. As can be seen from the SEM micrographs [Fig. 5. (b)], chopped-SiC fibers diameters in the range of 6-10 μm and length distributions in the range of 10-150 μm; the mean length and diameter of the SiC fibers were 50 μm and 7.5 μm, respectively. It can also be seen that short fibers of the filler were primarily horizontal oriented within the polymer matrix. However, when the amount of filler added was less, it resulted in the agglomeration. Conversely, an increase in the filler concentration to the appropriate level let to them being distributed uniformly within the polymer matrix, resulting in fewer and smaller pores. Also,



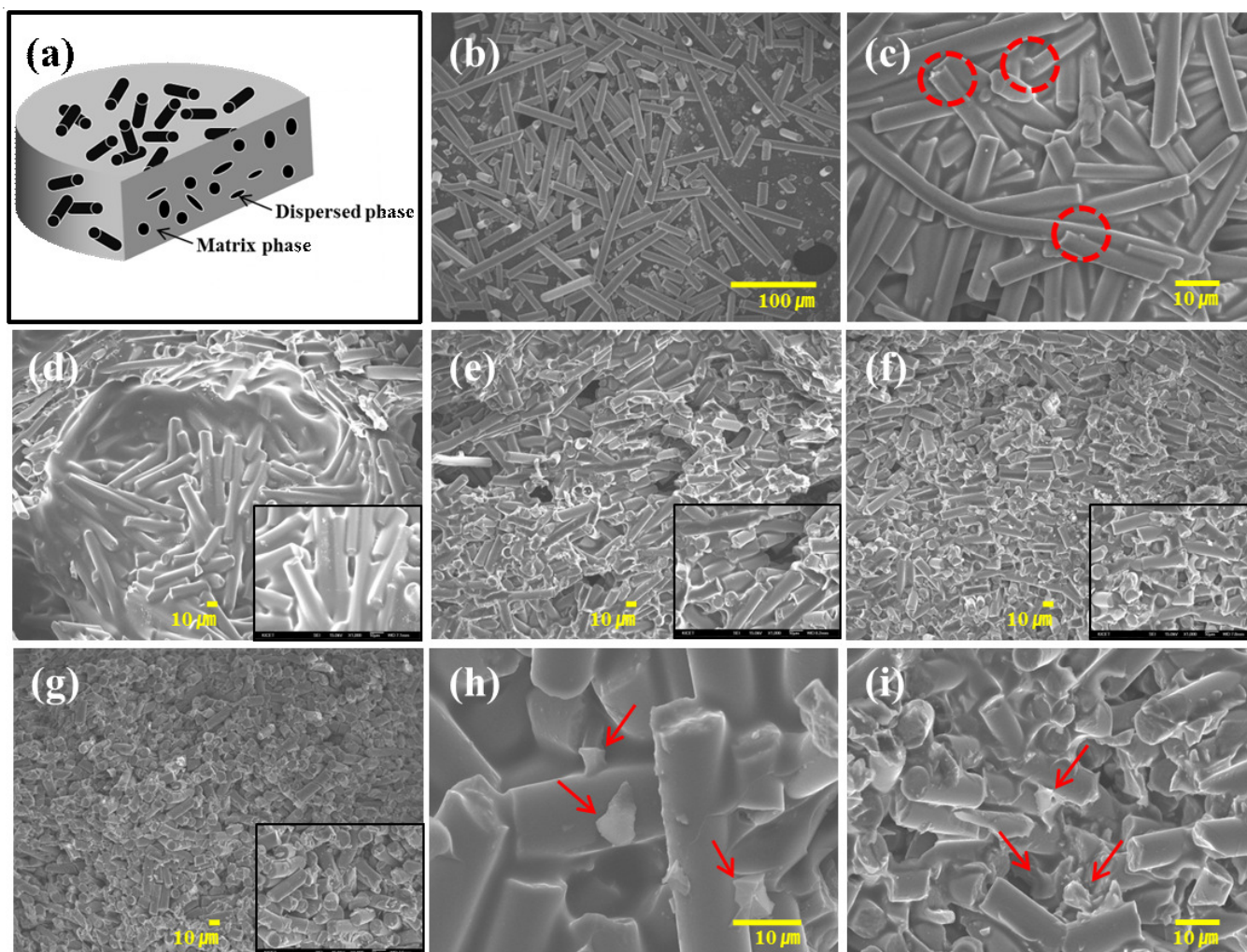


Fig. 5. (a) Schematic diagram of the configuration of the SiC fibers and FE-SEM images of (b) ground-Tyranno<sup>®</sup>-SA3 fibers, (c) a filler/graphene/polymer composite (the graphene bond is depicted by red circle with a cross); cross-sections of the composite specimens containing, (d) 20 vol % filler, (e) 40 vol % filler, (f) 60 vol % filler, (g) 80 vol % filler, (h) 50 vol % filler with the addition of 1 wt % graphene nanoplatelets and (i) 60 vol % filler with the addition of 1 wt % graphene nanoplatelets (a red arrow indicates the location of a graphene nanoplatelets)

the graphene-nanoplatelets-containing composites showed in Fig. 5(h), (i). Graphene nanoplatelets represent that mixed between the polymer matrix and the SiC fiber. It is expected to improve that interfacial connects synergies materials at fiber and polymer matrix substances.

**Calculation of the thermal conduction properties of the composite specimens:** Fig. 6 shows the variations in the thermal diffusivities and thermal conductivities of the composite specimens with respect to the volume fraction of the added filler. Composite density was higher at 50 vol % in hybrid composite at  $2.01 \text{ g/cm}^3$  (Table-2). According to the Fig. 6, the thermal conductivity also has highest values at higher density. The pores can be reduced by uniform distribution between filler and binder and thereby the density grows up. Because, the thermal conductivity and thermal diffusivity values of the composites increase with the volume fraction added of the filler. This is because of the formation of relatively small pores, the degree of connectedness between the filler and the polymer matrix. It can lead to minimized phonon scattering in composite interface at the filler and the binder. A theoretical model based on Horsfield's packing model and the Andrensen equation has been used to determine the highest

density possible in the case of an inorganic filler<sup>14</sup>. In addition, Nielsen's *et al.*<sup>15</sup>, reported that the efficiency of heat transfer could be improved to a greater degree by the use of a large-aspect-ratio filler than by a conventional powder-based filler.

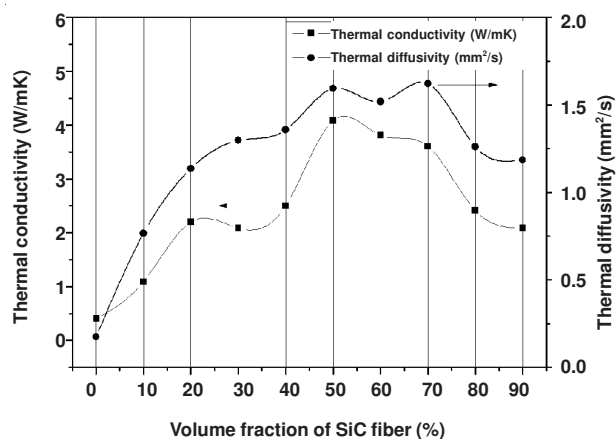


Fig. 6. Thermal diffusivities and thermal conductivities of the fiber/polymer matrix composite specimen containing 0 to 90 vol % filler

**TABLE-2**  
BULK DENSITIES, SPECIFIC HEAT, THERMAL DIFFUSIVITIES AND THERMAL CONDUCTIVITIES OF HYBRID COMPOSITES WITH RESPECT TO THE FRACTION OF FILLER

Vol % of filler	Bulk density (g/cm <sup>3</sup> )	Specific heat (J/g/K)	Thermal diffusivity (mm <sup>2</sup> /s)	Thermal conductivity (W/mK)
0	1.2141	1.9318	0.1750	0.4105
10	0.8979	1.5871	0.7660	1.0917
20	1.1540	1.6802	1.1360	2.2026
30	1.5173	1.0608	1.2970	2.0877
40	1.7074	1.0765	1.3580	2.4961
50	2.0033	1.2793	1.5940	4.0849
60	1.9593	1.2802	1.5190	3.8100
70	1.9006	1.1705	1.6210	3.6062
80	1.8165	1.0544	1.2610	2.4152
90	1.7710	0.9972	1.1850	2.0928

As shown in Fig. 7 and Fig. 8, the graphene nanoplatelets of 1 to 5 wt % was loaded at the maximum thermal conductivity in closed-packed structure composite (50 and 60 vol %). The two plots shows that the thermal conductivity of the composites increased dramatically as the graphene nanoplatelets were added in progressively increasing amounts; the addition of 1 wt % graphene nanoplatelets at 50 vol % filler resulted in an approximately 25.5 % (5.45 W/m·K) increase in the thermal conductivity and composite at 60 vol % filler; the addition of 1 wt % loading of graphene nanoplatelets resulted in an approximately 2.6 % (3.85 W/m·K) increase in thermal conductivity. The closed-packed structure was formed at 1 wt % loading of graphene nanoplatelets, respectively; higher density values *ca.* 1.943 g/cm<sup>3</sup> at 50 vol % filler and 2.058 g/cm<sup>3</sup> at 60 vol % filler (Tables 3 and 4). As the results, good thermal conductivity requires a strong filler/polymer thermal interface. Because of these thermal interface between filler and polymer was connected by covalent bonding in graphene nanoplatelets. The thermal conductivity was increased by introducing enhanced conducting networks at filler/polymer/graphene nanoplatelets composition. Therefore, it could be summarized that this composition resulted in the inducement of synergetic effects and a reduction in the cost of the composite material as compared to composites fabricated using conventional powder-based filler, because of the use of smaller amounts of the fibrous filler.

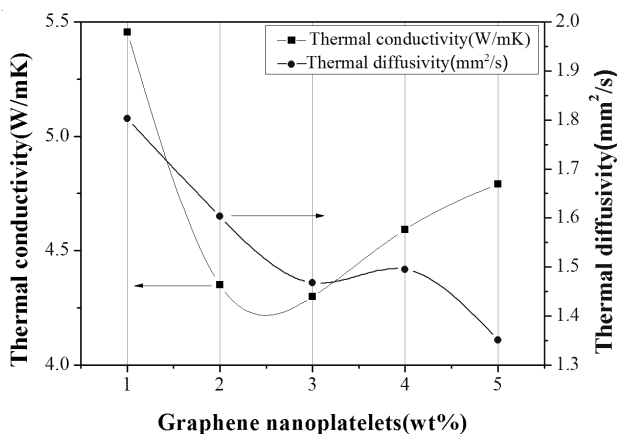


Fig. 7. Thermal diffusivities and thermal conductivities of the addition of graphene nanoplatelets in polymer-matrix composite at 50 vol % filler

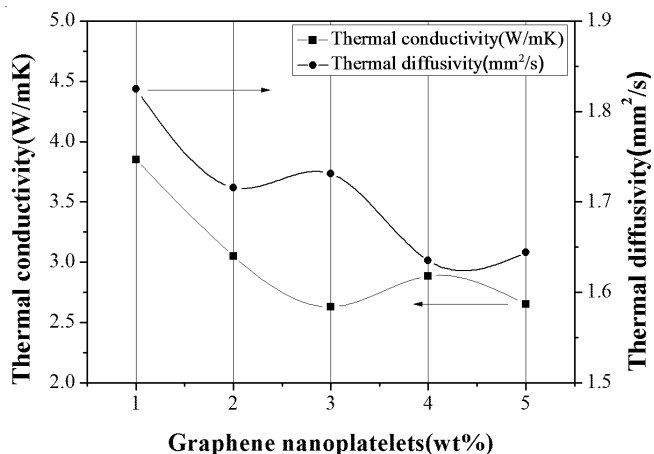


Fig. 8. Thermal diffusivities and thermal conductivities of the addition of graphene nanoplatelets in polymer-matrix composite at 60 vol % filler

**TABLE-3**  
LISTS OF BULK DENSITIES, SPECIFIC HEAT, THERMAL DIFFUSIVITIES AND THERMAL CONDUCTIVITIES OF HYBRID COMPOSITES WITH RESPECT TO THE FRACTION OF FILLER AT 50 vol %

50 vol % of filler in an addition of graphene (wt%)	Bulk density (g/cm <sup>3</sup> )	Specific heat (J/g/K)	Thermal diffusivity (mm <sup>2</sup> /s)	Thermal conductivity (W/mK)
1	1.9434	1.5570	1.8030	5.4557
2	1.8520	1.4650	1.6030	4.3492
3	1.7768	1.6480	1.4680	4.2985
4	1.7154	1.7910	1.4950	4.5931
5	1.7638	2.0110	1.3510	4.7920

**TABLE-4**  
LISTS OF BULK DENSITIES, SPECIFIC HEAT, THERMAL DIFFUSIVITIES AND THERMAL CONDUCTIVITIES OF HYBRID COMPOSITES WITH RESPECT TO THE FRACTION OF FILLER AT 60 vol %

60 vol % of filler in an addition of graphene (wt %)	Bulk density (g/cm <sup>3</sup> )	Specific heat (J/g/K)	Thermal diffusivity (mm <sup>2</sup> /s)	Thermal conductivity (W/mK)
1	2.0580	1.0260	1.8250	3.8535
2	1.8503	0.9610	1.7160	3.0513
3	1.7061	0.8900	1.7310	2.6284
4	1.7552	1.0710	1.6350	2.8855
5	1.7507	0.9210	1.6440	2.6508

**Conclusion**

SiC fiber/phenolic resin composites containing graphene nanoplatelets were fabricated with the filler being added in different volume fraction. The graphene nanoplatelets were added to the filler/polymer composites to increase their thermal conductivity values. The appropriate amount of the polymer and the filler mixed has brought the small pores and the improvement of composite density. The graphene nanoplatelets was combined by the interface between the polymer and fiber. The results of the thermal conductivity measurements showed that owing to the closely packed nature of the composites, the thermal conductivity was highest (4.1 W/m·K) in the case of a filler concentration of 50 vol %. When graphene nanoplatelets were added to the the hybrid mixture, the resulting composites showed an increase in their thermal conductivity

values, with the thermal conductivity increasing by approximately 25.5 % in the case of a filler concentration of 50 vol % (5.45 W/m·K) and approximately 2.6 % in the case of a filler concentration of 60 vol % (3.85 W/m·K).

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