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Enhancement of thermal conductivity of materials using different forms of natural graphite

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Enhancement of thermal conductivity of materials using different forms of natural graphite

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Abstract. The quest for improvement of thermal conductivity in every area including aerospace structures is gaining momentum as the modern day technology is embedded with electronics which generate considerable amounts of heat energy. In some other applications, the thermal energy must be absorbed or released at a very fast rate. Natural graphite is highly anisotropic and has excellent thermal and electrical conductivity in a-direction hence; it is one of the potential candidates to enhance thermal conductivity. This paper encompasses various preparation routes used to enhance thermal conductivity in materials/composites using graphite flakes in its natural and treated forms along with characterization results of thermal conductivity and/ or electrical resistivity where available. Addition of graphite has shown to improve thermal conductivity in some materials by 30-130 times whereas one method of preparation described here shows composites to have thermal conductivity as high as 750 W/m K.

1. Introduction

In recent years, the number of applications requiring more efficient and light weight thermal management, e.g. advanced aircraft, car navigation systems, high density electronic equipments, etc., has considerably increased. As each new generation of electronics equipment exhibits higher performance and more and more power into ever smaller packages, this has aggravated the problem associated with heat dissipation in the electronic industry and thus produced a need for improved thermal interface materials in modern chip packaging (Aiping Yu. et al, 2007).

Along this line of thinking, there exists increasingly new thermal management materials applications and these are also being considered as potential interface and attachment techniques.

Interfaces between materials have a significant impact on the thermal impedance of electronic systems and in practice they can be the dominant factor in achieving effective thermal transfer. The interface materials and processes in question are the methods used to join an electronic device to the thermal transfer medium (e.g. substrate, heat pipe, heat sink), including coatings and bonding techniques. In this respect they may need to perform the tasks of attachment, stress/strain relief and thermal transfer. Therefore, these industries are focusing attention on alternate materials to replace conventional heat sinks and heat spreaders.

Although miniaturization has built focus of thermally conducting materials, thermal energy storage (TES) for free-cooling applications also face a major challenge due to relatively low heat transfer rates / thermal conductivity of the materials usually used to fabricate these systems commonly known as phase change materials (PCM). Various methods such as metal matrix structures and finned tubes have been widely used (Zalba B. et al, 2003) and methods of using water as heat transfer medium are proposed to enhance the heat transfer in these latent heat thermal storage devices. Cabeza L. F. et al (2002) and Fukai J. et al (2000) and Ply X. et al (2001) proposed the use of graphite-compound material to enhance thermal conductivity by having the PCM embedded inside a graphite matrix.

In recent year, several research studies have been carried out to improve the thermal conductivity of the polymeric composites by using different fillers in the form of fibers and particles. The researchers at Oak Ridge National Laboratory (ORNL) identified the potential of carbon foams for enhancing heat transfer. Although pyrolytic graphite was well known for its high thermal conductivity, the processing cost has always led to have its applications only in niche areas. However, with the use of graphite foams as heat exchangers, natural graphite (NG) has become a popular material in thermal enhancement and thermal management research.

Mariner J. T. et al (1999) invented electrically conductive composites by combining thermally treated graphite flakes with a polymeric binder. The thermal conductivity of these composites was found to be greater than 100 W/m/K.

Prieto R. et al (2008) prepared different composites with different reinforcements for Al-Si and Ag-Si alloys. The fillers used were a combination of different range of proportions of graphite flakes and carbon fibers, graphite flakes and SiC, diamond, graphite particles, carbon fibers and graphite foam. They found that the graphite flake/ metal composites exhibited superior thermal properties (in-plane thermal conductivity ranging from 350 W/m K to 548 W/m K).

GrafTech International Ltd developed natural graphite/epoxy laminate material (eGraf™) for plasma display panels (PDP) and ‘Spreadshield™’ as heat-spreader in notebooks, digital cameras, etc.. The in-plane thermal conductivity of this laminate was reported to be ~370 W/m K, which is 77% higher than aluminum and comparable to that of copper whereas eGraf 1200 is reported to have an in-plane thermal conductivity of 120 W/m K (Technical Bulletin 268M) Following advances in the material development, an in-plane thermal conductivity of approximately 400 W/m K (i.e. approximately equal to that of copper) is achieved in this composite (Norley J., 2003). Spreadshield™ heat spreaders developed by Graftech are known to have thermal conductivity upto 1500 W/m K.

This paper will focus on summarizing natural flake graphite and its forms used in enhancing thermal conductivity. In the end, we will briefly describe method of using graphene to prepare composites.

Natural graphite (NG) being well known as highly anisotropic forms of carbon with low density ($d \approx 1.94$ g/cc) and is abundantly available in nature. The carbon atoms in graphite are hexagonally arranged in a planar condensed ring system with 1.42 Å and the layers are stacked over one another (Mantell C., 1968) with large spacing (3.35 Å). These layers are held together by weak van-der-Waals forces whereas the atoms within the plan are held by covalent bonds.

Single crystal graphite is one of the stiffest materials in nature (elastic modulus of over 1 TPa) with lower density (Zheng W. G. et al, 2002; Chen G. H. et al, 2001).

Natural graphite has good thermal conductivity ($k \approx 2000$ W/m/K in a-direction) and is highly temperature dependent (it can be higher than the quoted value (Kelly B.T., 1981)). The electrical conductivity of natural graphite is 10^4 S/cm at room temperature (Usuki A, Kojima Y., Kawassumi M., Okada A. and Fukushima Y., 1993; Giannelis E.P., 1996 and Lebaron P.C., Wang Z. and Pinnavaia T., 1999). The superior thermal property along two directions makes it one of the potential candidates to combat thermal management problems. Natural graphite has high chemical and thermal stability over a

range of temperatures with a very high melting point, high thermal and electrical conductivity and is resistant to attack by most chemical reagents. Hence, graphite has attracted researchers to enhance thermal conductivity in various applications.

1.1 Possible uses of Graphite in different forms

Flake graphite can be directly used in its natural form in composites or it can be intercalated with different chemical species to form nanolayers which can then be used to form composites. These nanolayers can be obtained by taking advantage of this weak bonding between flakes by inserting various chemical species to form graphite intercalation compounds (GICs) (Guohua Chen G. H. et al, 2003). Such intercalated graphite is referred as expanded graphite/ exfoliated graphite/ worm like graphite/ garland graphite in the literature. However, expanded/ exfoliated graphite is more popular.

Pyrolytic graphite, graphite fibres, reinforced carbon and polymer matrix composites heat-treated to temperatures (~3000 °C), graphite foams, etc. are all forms of graphite that can be categorised as “synthetic graphite” or “artificial graphite”. In spite of meeting the required thermal conductivity, synthetic graphite has found its application only in high performance applications due to its high processing costs.

1.1.1 Expanded graphite (EG) to enhance thermal conductivity

Natural graphite has no reactive ion groups on the surface layers hence; it is difficult to incorporate organic molecules or polymers directly into the interlayer of graphite through an ion exchange reaction to prepare the polymer/graphite composite. However, EG have worm-like appearance and the expansion along the c-direction can be as high as two orders of magnitude when intercalate is heated over a critical temperature. This form of graphite contains multipores ranging from 2 to 10 nm in large numbers, functional acids and OH groups that promote affinity of EG to both organic compounds and polymers. Hence, EG can absorb some monomers, initiators and polymers, and result in the formation of conductive/graphite nanocomposite (Zheng W., Wong S.C. and Sue H.J., 2002; Li J, Kim J. and Sham M., 2005). The layered structure in EG is similar to nanoclays but EG is very cost effective with superior mechanical, electrical and thermal properties as compared to carbon nanotubes (Fukushima H., 2003; Kalaitzidou K., 2006).

Lincoln V. F. and Claude Z. (1983) proposed dispersion of intercalated graphite in polymeric resin by conventional composite processing techniques in 1980s. Aylsworth J. W. (1916) developed and proposed EG as a reinforcement of polymer in 1910s. Research has been conducted on EG-reinforced polymer composites after these studies. More recently, research by the Drzal group (2007, 2009) has shown that exfoliated graphite nanoplatelets have the ability to provide a large enhancement in physical and chemical properties.

1.1.2 EG/Epoxy Composites

Debelak B. and Lafdi K. (2007) dispersed EG flakes in an epoxy resin and studied the thermal and electrical properties of the composites. In this study, natural graphite flakes of an average diameter of 500 µm and EPON Resin 862 was used as a polymer matrix. Exfoliated graphite was prepared by mixing nitric and sulfuric acid and natural graphite. After 24 h of reaction, intercalated graphite compound was obtained. The mixture was then filtered, washed with water and dried in an oven at low temperatures. The intercalated graphite compound was then subjected to sudden heat treatment temperature of 900 °C for rapid expansion. The expansion ratio was as high as 300 times (c-direction). During this study, three kinds of exfoliated graphite filled polymers, having different graphite particle sizes, were prepared. The graphite

flakes were separated using 50, 100, and 150 mesh sieves and were labeled as large, medium, and small flakes respectively. Polymer materials containing different concentrations by weight of exfoliated graphite were prepared (0.1, 0.5, 1, 2, 4, 8, 12, 16, and 20%). Exfoliated graphite flakes were placed in a solvent and sheared in a homogenize rotating at a very high speed (13500 turns/minute). The blade of the homogenizer rotates and breaks the larger graphite flakes into even smaller nanosheets. Ultrasonication was used to assist and improve the dispersion of these graphite nanosheets. After the mixing process completed, the mixture was filled into a silicone rubber mold. The mold with the mixture was loaded in a hydraulic press to cure under a pressure of 10000 lb at 121 °C for 2 h and then at 177 °C for two more hours.

The electrical resistivity of the composites with varying EG concentration was studied for all three sizes of graphite flakes according to Debelak B. and Lafdi K. (2007). It should be noted that epoxy is not an electrically conducting polymer at room temperature (RT) and has a resistivity of $1.5^8 \Omega\text{cm}$ in its dry state. Addition of EG was found to lower the electrical resistivity of the epoxy resin with a sharp transition of a polymer from electrical insulator to an electrical conductor. It was seen that the electrical resistivity of EG/epoxy composites decreased with increasing concentration of EG (Fig. 1). This is attributed to the Nanoscale dispersion of graphite nanosheets within the polymer and the formation of conducting networks. Hence, it is clear that the conductivity depends upon the factors such as the percentage of EG in the composite and its into the matrix. The larger graphite flake filled epoxy showed lowest resistivity for every concentration as compared to the medium and small flake filler. It is well reported that electrical conductivity of carbon composites depends upon the grain and crystallite size and hence, the large flake filler composites show higher conductivity as expected.

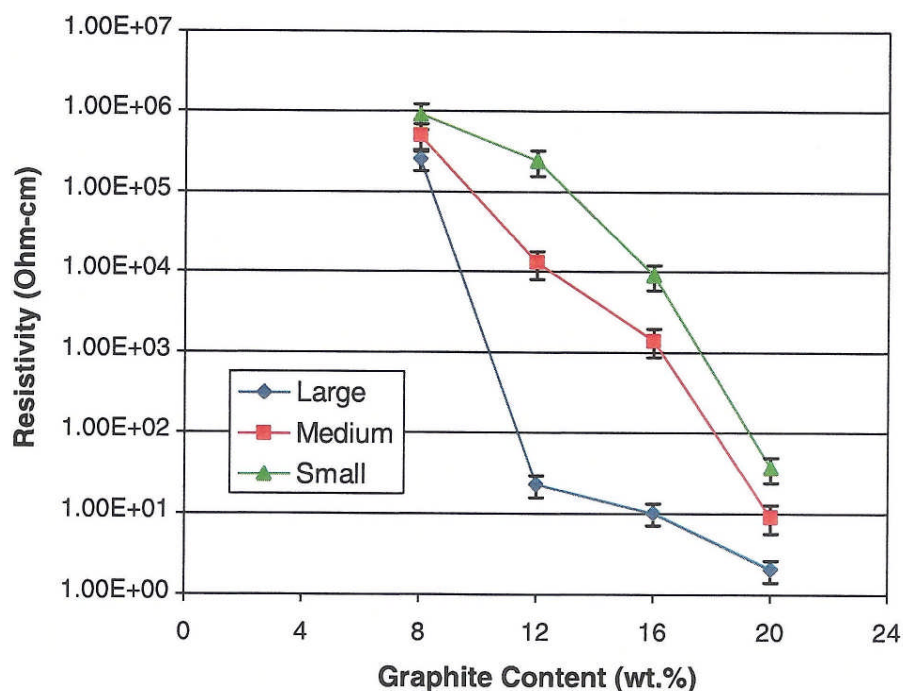


FIGURE 1 Electrical resistivity of exfoliated graphite filled polymer with different graphite sizes as a function of the graphite content (taken from Debelak B. and Lafdi K., 2007).

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Fig. 2 shows thermal conductivity of composites prepared using the three sizes of exfoliated graphite filled epoxy composites with varying concentration of EG content. As seen with electrical resistivity, the thermal conductivity increases with increase in EG concentration. Superior transport properties are seen in composites with larger flake filler as compared to medium and small flake content for a given concentration level which again can be attributed to the larger grain and crystallite size of large flake graphite.

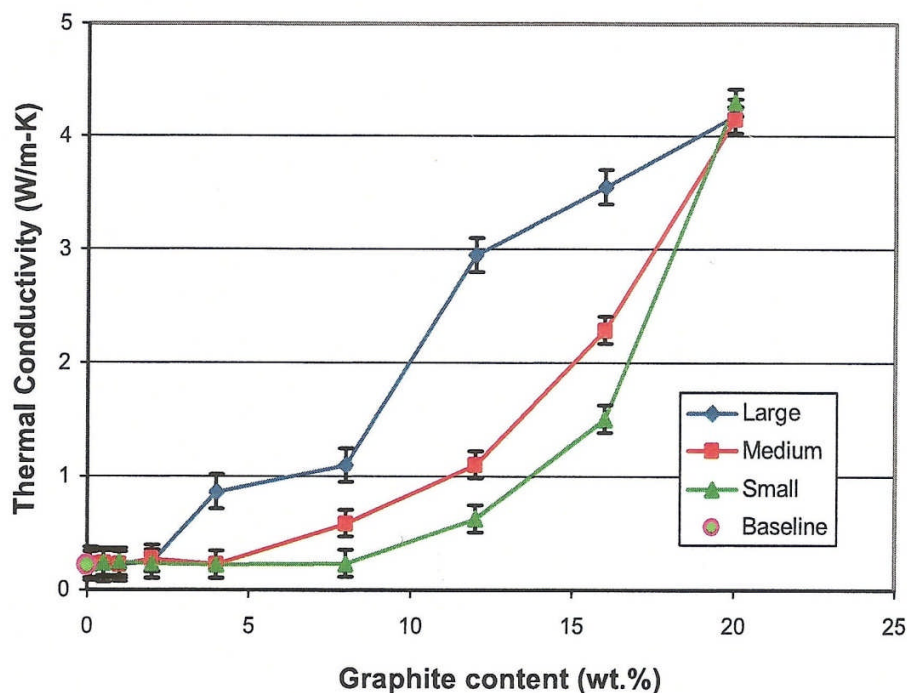


FIGURE 2 Thermal conductivity of exfoliated graphite filled polymers with different graphite flake sizes as a function of the graphite content (taken from Debelak B. and Lafdi K., 2007)

The authors conducted a comparative study of thermal conductivity of 20% large flake EG filled epoxy composite with polymer composites with carbon nanofiber and high heat-treated (HHT) nanofiber. The results showed (Fig. 3) EG filled composites to have superior thermal conductivity as compared to the

nanofiber and HHT nanofibers (Matzek M. D., 2004). The superior property is due to the strong thermal conductive network produced by EG with its higher aspect ratio as compared to typical carbon nanofiber.

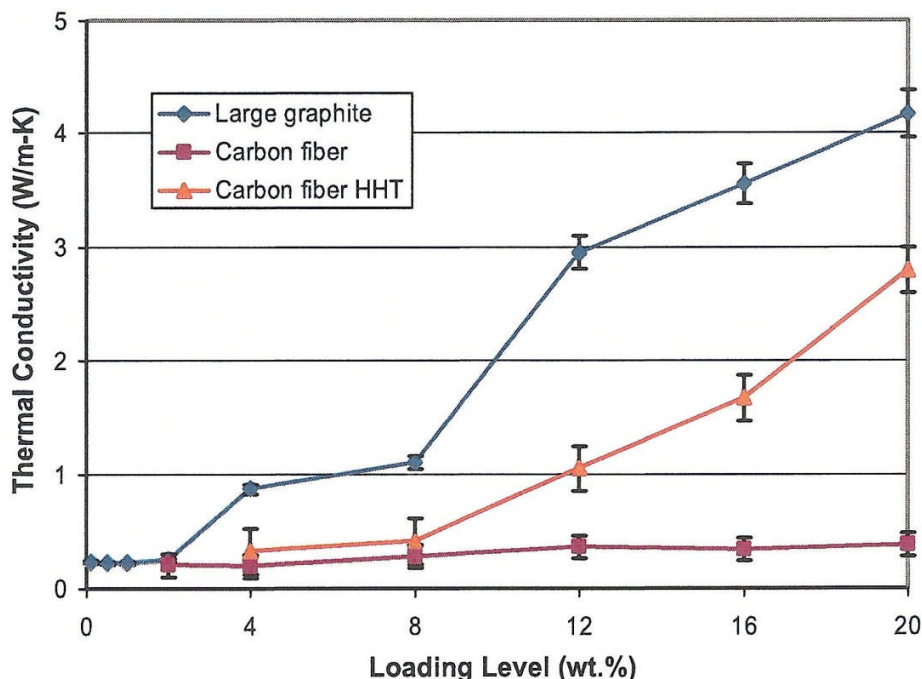


FIGURE 3 Thermal conductivity comparison of graphite flake filled polymers versus carbon nanofiber and HHT carbon nanofiber composites (taken from Debelak B. and Lafdi K., 2007)

Ganguli S. et al (2008) used EG supplied by Graftech International Ltd., Parma OH and prepared composites (EG/epoxy) using Epon 862 (an epoxy bisphenol F resin) and Epicure W (an aromatic amine curing agent). Epicure 537 (consisting of organic salts) was used as an accelerating agent to accelerate the curing reaction which in turn aided in 'locking in' the dispersed morphology. Flacktek Speedmixer was used to disperse the graphite nanoparticles in the epoxy. The high speed mixer (2750 rpm) consisted of a one direction spinning arm with the basket containing the mixture rotating in the opposite direction. This combined force in opposite planes enabled fast mixing. The composites were synthesized with different volume fraction of EG ranging from 2% - 20% (2, 4, 6, 8, 16 and 20%).

Ganguli S. (2008) prepared another set of samples with same volume fractions but with functionalized exfoliated graphite (FN/epoxy). The grafting reaction was carried out in the mixture of water and ethanol in the ratio of 25:75 by volume. 3 g of γ -APS (3-aminopropoxyltriethoxy silane) was first added into 1000 ml of the water/ethanol mixture. The mixture temperature was raised to 80 °C and then 10 g of exfoliated graphite was added. The grafting was achieved under shearing for 5 h at 80 °C. The reaction product was filtered and washed six times using a mixture of water/ethanol and freeze dried. The obtained product was ground and placed in sealed container for characterization.

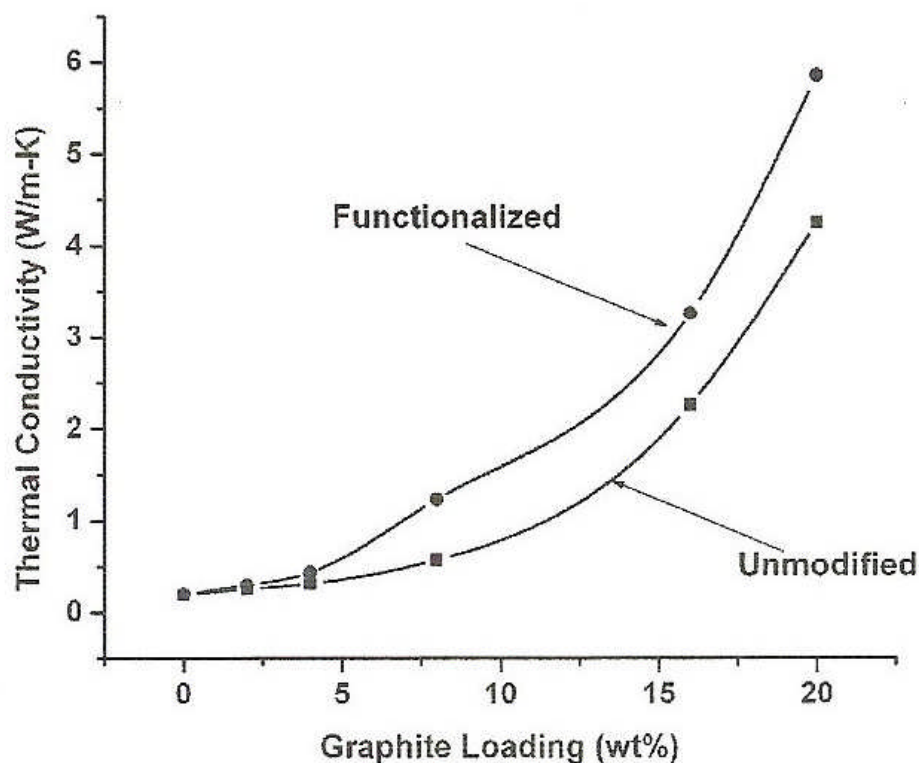


FIGURE 4 Thermal conductivity as a function of Graphite loading of EG/epoxy (unmodified) and FN/epoxy (functionalized) composites (taken from Ganguli S. et al, 2008)

Thermal conductivity of EG/epoxy and FN/epoxy composites was measured by the Netzsch laser flash diffusivity system LFA 457 with 5 mm thick POCO graphite specimen as reference heat capacity material. The thermal conductivity of neat Epon 862/W epoxy resin is around 0.2 W/m K. Figure 4 shows no significant change in thermal conductivity for composites with 2% and 4% of exfoliated graphite. At 8%, the thermal conductivity was seen to increase to 0.5 W/m K. As the filler concentration increased the conductivity was seen to increase. The composite with 20% filler concentration showed 19-fold enhancement in conductivity compared to neat resin.

Functionalized exfoliated graphite composites showed similar low conductivity for 2 and 4% but for higher loading of functionalized exfoliated graphite, the conductivity is seen to increase and was higher than EG/epoxy composites (Fig 4). The composite with 20 % of functionalized exfoliated graphite was measured to be 5.8 W/m K which is 28-fold improvement in comparison to neat resin. The mode of thermal conduction in amorphous polymers is primarily by phonons. In order to enhance thermal transport in filled amorphous polymeric systems, the acoustic impedance mismatch between the filler and the polymeric matrix has to be reduced. Functionalisation seems to improve this interfacial heat transfer between the graphite platelets and the epoxy matrix. This improvement is attributed to the covalent bonds formed between the graphite platelets and the epoxy matrix as a result of chemical functionalisation which reduce the acoustic mismatch impedance and enhance thermal conductivity.

Aiping Yu et al (2007) dispersed expanded graphite in acetone by high shear mixing for 30 min followed by bath sonication for 24 h and prepared GNP dispersions at a concentration of 2 mg/ml. Composites of GNP / epoxy were prepared by adding epoxy resin to the GNP suspension and subjecting it

to high-shear mixing for 30 min. The solvent was then removed in vacuum oven at 50 °C and the curing agent (Diethyltoluenediamine, EPI-CURE W) was added in a ratio 100:26 (Epoxy: curing agent) by weight while the mixture was continuously stirred. The mixture containing the homogenously dispersed GNP was degassed and cured in vacuum in a stainless steel mold. The composite was initially cured at 100 °C for 2 h and then further cured at 150 °C for another 2 h to complete the curing cycle.

Composites with different loading levels of GNP ranging from 0.1 to 10 % by volume were prepared (Aiping Yu et al, 2007). The thermal conductivity of GNP/epoxy composite was compared with graphite macroplatelet (GMP)/epoxy composite. With 5.4% of GMP filler (GMP aspect ratio of length \approx 30 μ m, thickness \approx 10 μ m) at 30 °C was found to show a thermal conductivity of 0.54 W/m K which was comparably higher than pristine epoxy (K= 0.201 W/m K). Composites with \sim 5% volume of GNP (prepared with 800 °C exfoliating temperature) in composite showed thermal conductivity of \approx 1.45 W/m K which compares very favorably with current available thermal interface materials which require about 10 times (i.e. 50 - 70 %) filler volume to achieve similar thermal conductivity.

The researchers studied GNP prepared from exfoliated graphite using different shock temperatures namely 200, 400 and 800 °C. The thermal conductivity was seen to enhance with both the volume fraction of the filler content in the composite and the shock treatment temperature (Fig. 5a). Further studies on GNP (prepared from 800 °C shock treatment temperatures) composites with 25 % of filler showed the thermal conductivity of these composites increased with temperature for a given volume fraction of the filler. The highest thermal conductivity achieved with these GNP composites with 25 % volume fraction of filler was 6.44 W/m K which corresponds to an enhancement of more than 100 % per 1 volume % loading (Fig. 5b). These composites when used in computer processor that usually operate at elevated temperatures could show thermal conductivity as high as 6.87 W/m K

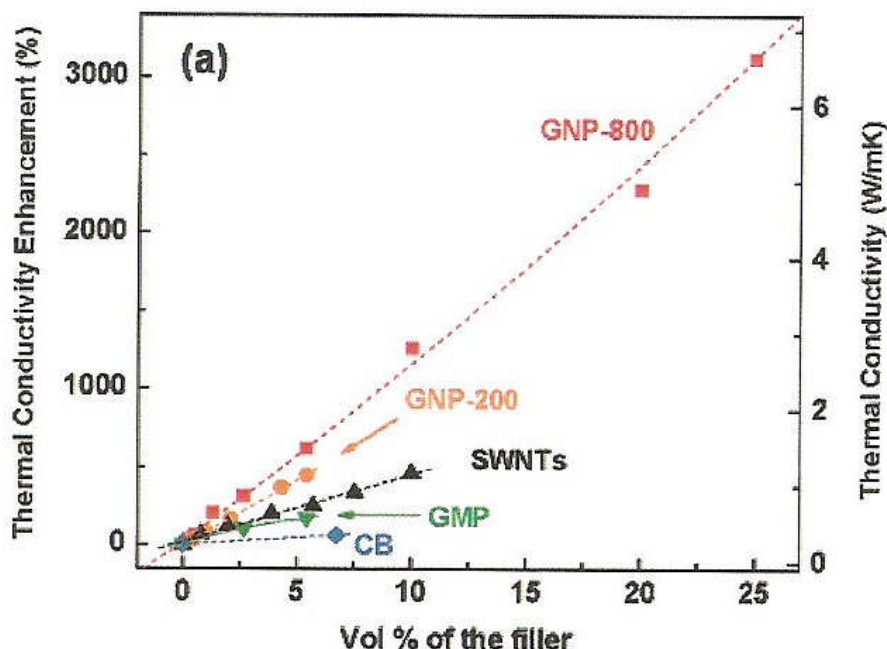


FIGURE 5 a Thermal conductivity enhancement % of epoxy based composites at 30 °C with graphitic fillers: graphite microparticles (GMT), GNPs at 200 °C (GNP-200) and GNPs at 800 °C (GNP-800), carbon black (CB) and purified single walled nanotubes (SWNTs) (taken from Aiping Yu et al, 2007)

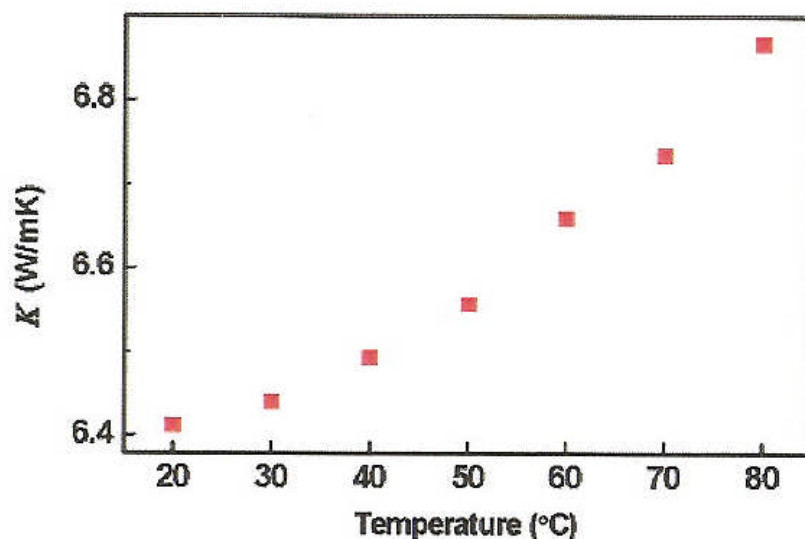


FIGURE 5b Temperature dependence of thermal conductivity (K) for the composites with 25 % loading of GNP-800 by volume (taken from Aiping Yu et al, 2007)

1.1.3 Graphite/silicone rubber composite to enhance thermal conductivity and storage modulus

Nylon 6/layered silicate nanocomposites were first prepared by intercalation polymerization. Since then, layered silicate nanocomposites have progressed and methods have been identified to homogeneously disperse layered silicates such as montmorillonite in polymeric matrix in nanosheets to improve desirable properties of the matrix such as poor electrical and thermal conductivity (Alexandre M. & Dubois P., 2000; Saujanya C. and Radhakrishnan S., 2001; Weng W. P. and Pan C.Y., 2004).

Mu Q. and Feng S. (2007) studied silicone/EG nanocomposites prepared via solution intercalation and normal melt mixing with methylvinylsilicone gum (M_n 5.8×10^5 ; mole content of vinyl group, 0.15%), silica and 2,5-bis(tert-butyl peroxy) 2,5-dimethyl hexane (DBPMH) and EG of average diameter 300 μm .

For melt mixing (MM) method, methylvinylsilicone gum, silica, EG and some other additives were rolled on a twin-roller at room temperature (RT) for certain time. They were then compress molded at 190 $^{\circ}\text{C}$ under a pressure of 9.8 MPa for 20 min to obtain 120 mm x 40 mm plates with thickness of 2 mm.

In solution intercalation (SI) method, the EG was dispersed in toluene to prepare a suspending dispersion with certain EG content. The methylvinylsilicone gum was dissolved in toluene by heating to a backflow temperature of toluene (~ 100 $^{\circ}\text{C}$). The EG suspending dispersion was added drop by drop into the methylvinylsilicone gum solution at the backflow state. After a backflow of 2 h, the heating was stopped and a portion of toluene was extracted under vacuum during the cooling process. The resultant mixture was dried under vacuum and pressed to composites under similar condition as MM method.

Composites of different EG filler content were prepared by the two methods. The thermal conductivity of the composites prepared using these two methods (MM and SI) were measured at 50 $^{\circ}\text{C}$ by using Fourier law with the assumption that the heat flows only in the direction of measurement (i.e. one-direction). Figure 6 shows that the thermal conductivity increases as the EG content increases. However, the composites prepared by SI method showed higher thermal conductivity compared to the composites prepared by MM method with same EG content. For 9 per hundred rubber (phr), the thermal conductivity of composite prepared using SI method was calculated to be 0.32 W/m K whereas the composite at same

phr prepared using MM method showed thermal conductivity of 0.24 W/m K which is the conductivity level of composed prepared by SI method at 4 phr (Mu Q. and Feng S., 2007). This was attributed to the surface-to-volume ratio which in SI prepared composites was found to be larger than MM prepared composites. Hence, in SI prepared composites, the EG having larger surface-to-volume ratio can abut or contact and then form a conducting path network at a lower EG content thus playing an important role in improving thermal conductivity of the composites (Mu Q. and Feng S., 2007).

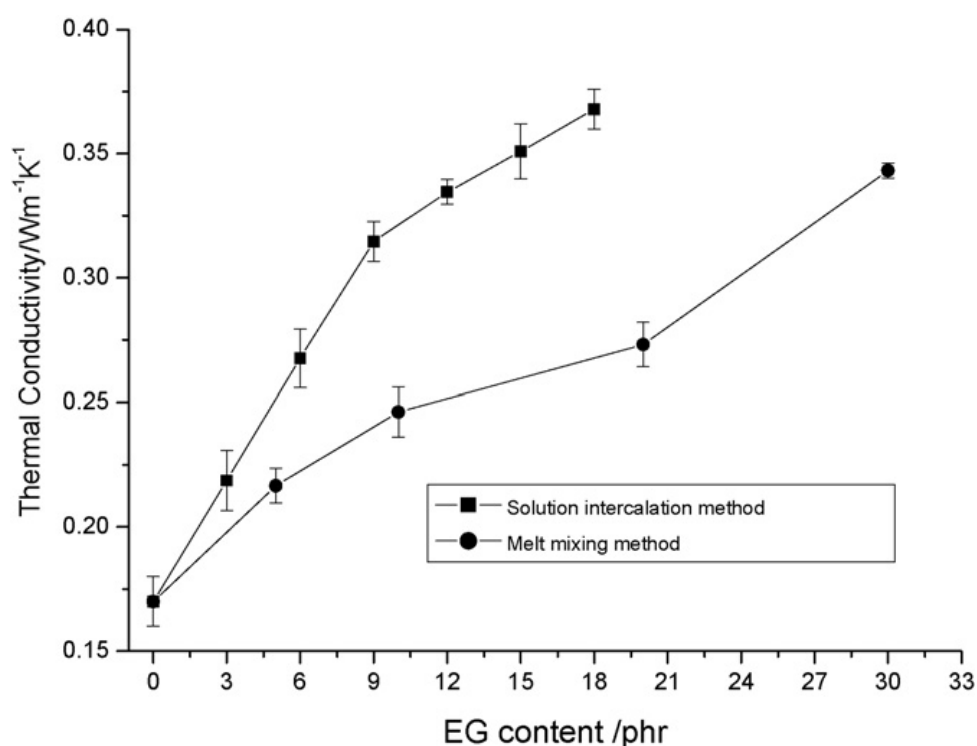


FIGURE 6 Thermal conductivity versus fraction of expanded graphite for silicone/EG composites prepared by two methods at 50 °C (taken from Mu Q. and Feng S., 2007).

Similarly, storage modulus E' for composites prepared using SI method at 10 phr were relatively higher than the E' of composites prepared using MM method at same phr (Fig. 7). It has been reported that there exists a correlation between the conductivity network formation and the stiffening effect arising from the EG dispersion in the polymer solution (Zheng W. & Wong S.C., 2003).

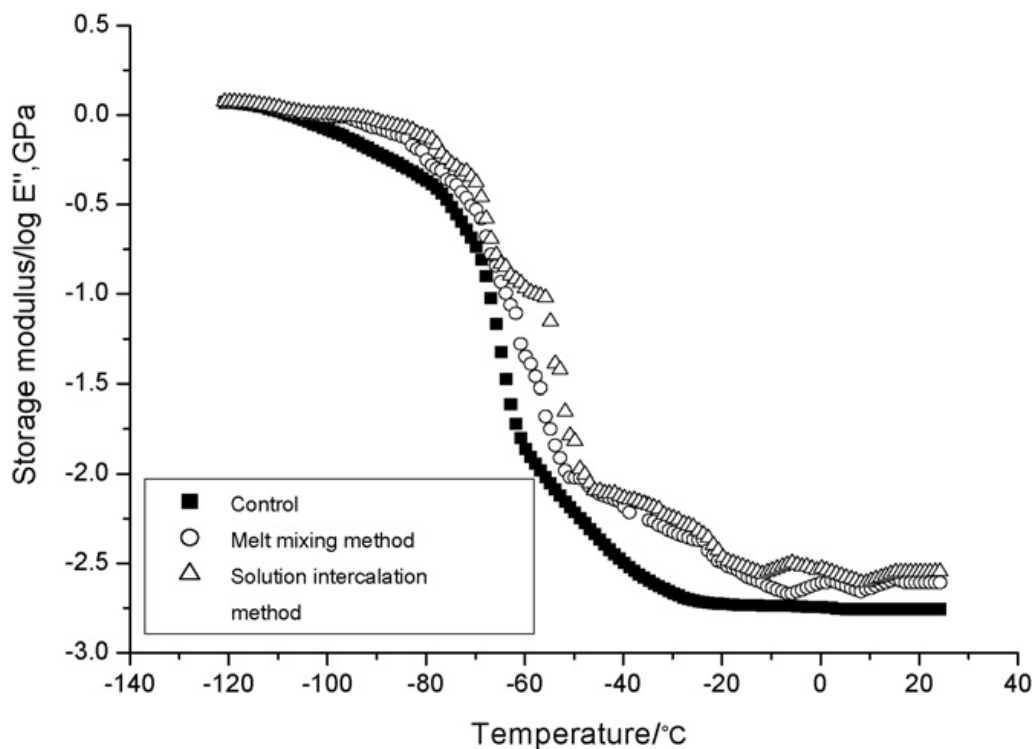


FIGURE 7 Storage modulus at 10 phr EG content as a function of temperature for the samples prepared by two methods (taken from Mu Q. and Feng S., 2007)

1.1.4 Exfoliated graphite nanoplatelet/paraffin composites to enhance thermal conductivity in PCMs

Paraffin wax is one of the most attractive materials for latent heat storage PCM as it is not only commercially available but has desirable properties of high latent heat, chemical inertness and no phase segregation. However, due to its low thermal conductivity, it decreases the overall power of the thermal storage device (Sharma A. et al, 2009; Zalba B., Marin J. M. and Cabeza LF., 2003; Farid MM. et al, 2004). Attempts to improve the thermal conductivity by adding metal foams or fins to paraffin wax increases the weight of the composite and cost to the storage systems and some such methods of enhancements are not compatible with PCMs (Sharma A. et al, 2009; Lafdi K., Mesalhy O. and Shaikh S., 2007).

Many studies have been carried out where EG is reported to be inserted into the paraffin wax to improve thermal conductivity (Karaipekli A. et al, 2007; Zang Z. and Fang X., 2006; Alawadhi E.M. and Amon C.H., 2003; Mills A. et al., 2006; Pincemin S. et al, 2008; Zang Y. et al, 2006). Kim S and Drzal L.T. (2009) prepared composites with xGnP (exfoliated graphite nanoplatelet) with varying mass fraction (1%, 2%, 3%, 5% and 7%) in paraffin wax to understand the relationship between the thermal conductivity of the composite PCM and the mass fraction of graphite nanoplatelets. The paraffin wax was melted by heating it at 75 °C and then the xGnP was mixed into the liquid paraffin. After being filtered and dried, the paraffin/xGnP composite PCM was obtained. To ensure the availability of PCMs as continuous PCMs, the samples were remelted and electrical and thermal conductivity of the samples was measured. The electrical resistivity was found to show a sharp transition from electrical insulator to an electrical conductor (Fig. 8). The resistivity of the second melted sample showed similar behaviour as first melted samples.

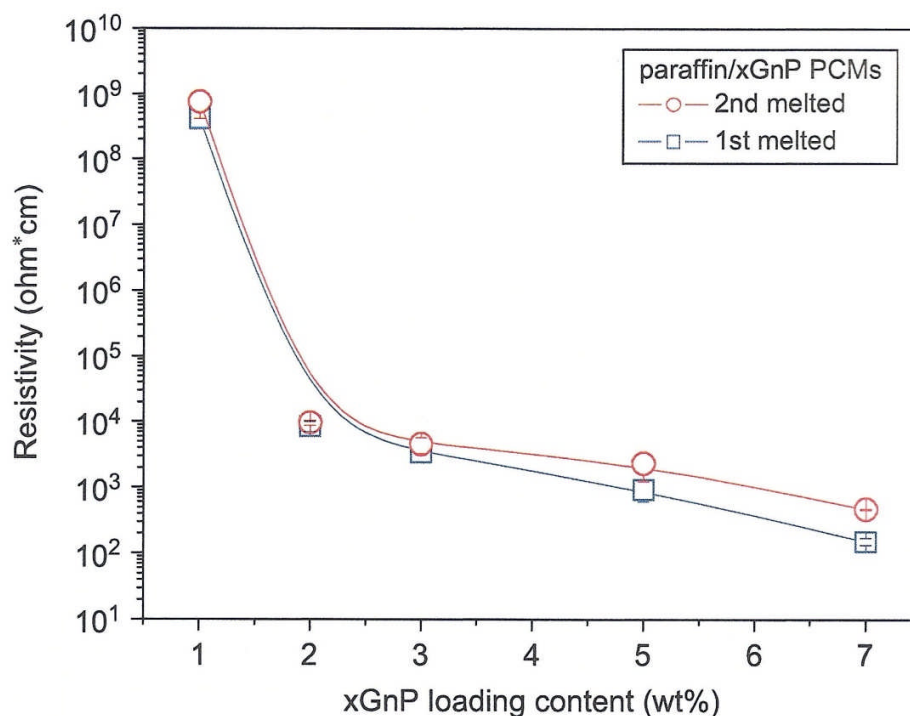


FIGURE 8 Resistivity of paraffin/xGnP composite PCMs by melting times (taken from Kim S and Drzal L.T., 2009)

The thermal conductivity of the xGnP/paraffin PCM composite is found to significantly improve compared to that of pure paraffin and increase with an increase in xGnP content. For 7% wt of xGnP, the conductivity went up to 0.8 W/m K (pure paraffin $k=0.26$ W/m K). Paraffin/xGnP composites PCMs as continuous PCMs for thermal conductivity were remelted and the second melted samples showed higher conductivity than the first samples (Fig. 9).

Although, previous results showed a decrease in latent heat with an increase in graphite loading content (Zang Z. and Fang X., 2006; Cai Y. et al, 2008), the latent heat of the paraffin/xGnP composites PCMs showed no significant difference from the latent heat of the pure paraffin. Hence, xGnP can be considered as an effective heat diffusion promoter to improve thermal conductivity of PCMs without reducing its latent heat storage capacity.

Zong Y. et al (2010) prepared composites with compressed expanded natural graphite (CENG) with different densities in paraffin wax of thermal conductivity 0.35 W/m K, melting point 50 °C and latent heat of 167 J/g. The expanded graphite was placed in a cubical mode and pressed to obtain CENG of varying bulk densities ranging from 0.07 to 0.26 g/cm³. The CENG prepared were wrapped in paraffin wax and heated above the melting point of paraffin wax in vacuum oven for 3 h. When the CENG were submerged in the melted paraffin wax, the system was allowed to cool until the wax solidified under normal atmosphere. Depending on the bulk density of the CENG matrix, mass ratio of the paraffin wax in these composites varied from 74% to 92%. The dispersion of the expanded graphite in the paraffin wax was found to be uniform and the interfaces of the two phases (expanded graphite/paraffin wax) were seen to compactly combine due to the high wetting ability of paraffin wax. The pore structure and the thermal

conductivity were found to be anisotropic for the CENG matrix. The thermal conductivity in both, the direction perpendicular to the pressing direction (axial direction) and parallel to the direction of pressing (radial direction) was measured by using a steady state method. As expected, the thermal conductivity of the composite was found to increase with an increase in the bulk density of the CENG. An almost linear relationship was seen between the density and the thermal conductivity and the plot represents that the correlation coefficient R is 0.98 (Zong Y. et al, 2010) (Fig. 10).

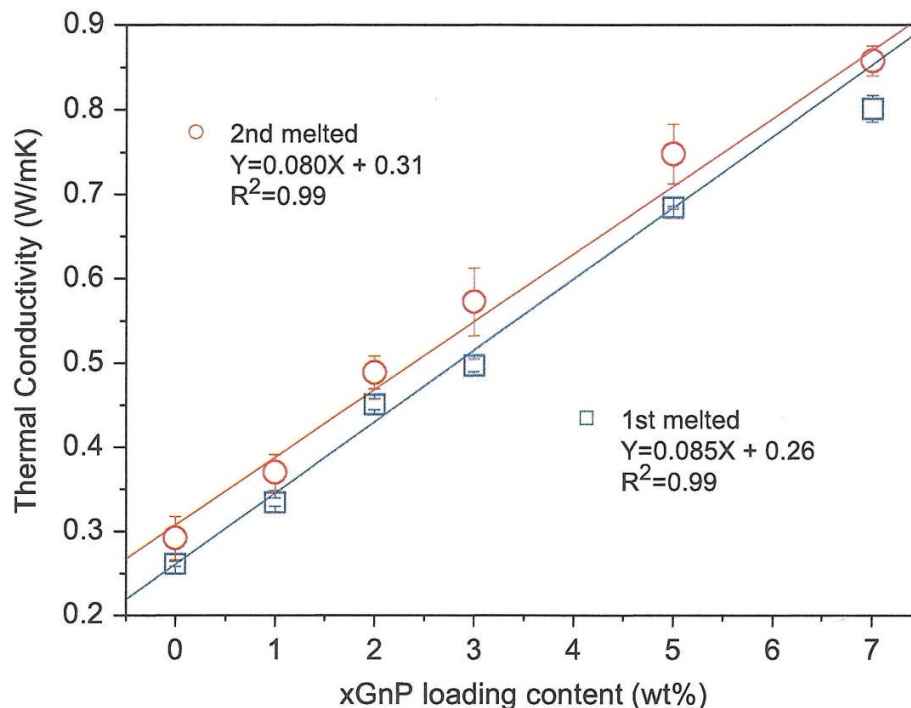


FIGURE 9 Thermal conductivity of paraffin/xGnP composite PCMs by melting times (taken from Kim S and Drzal L.T., 2009)

To measure the temperature distribution as a function of time, the samples were heated on a hot plate with a constant temperature of 70 °C (higher than the melting point of paraffin wax). A photo shot of the samples was taken every 3 s interval by thermal imager (IR Flex Cam Thermal Imager Ti45HT-20). At a given time, the conductivity of the composite in the two directions (axial and radial) was measured by comparing the thermal images of composites with heat transferred perpendicular to the compression force and along the direction of compression. When the thermal conductivity in the two directions (axial and radial) was compared, the temperature response was same in both directions for first 380 s as the temperature of the composite was below the melting point of paraffin wax. However, as the response time increased, the thermal conductivity was found to be dominated by the direction of orientation of the pores in the CENG matrix. Zong Y. et al (2010) concluded that it was due to this anisotropy of the pores and the existence of natural convection that significantly reduces the melting time of the paraffin wax and thus increases the thermal conductivity of the CENG.

1.1.5 EG/pitch composites to enhance conductivity

Pitches are known to be excellent binding materials in carbon/carbon composites due to their high carbon yield, high fluidity and excellent capacity for producing graphitisable materials (Mendez A. et al., 2005).

They are made of hundreds of polycyclic aromatic compounds and hence making them an insulator with specific resistance being $\sim 10^{11} \Omega\text{m}$ (Zander M., 1987; Grigoriev I. S., 1991). Hence, Afanasov I. M. et al (2009) prepared composites of coal tar pitch with exfoliated graphite to improve the thermal and electrical conductivity of the pitch.

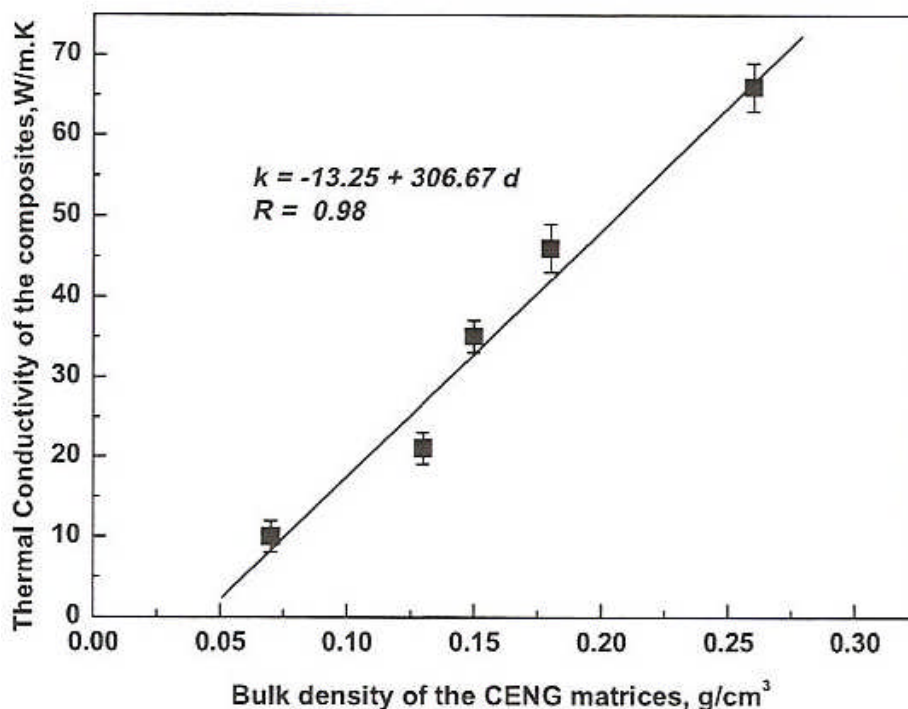


FIGURE 10 Variation in thermal conductivity of the composites with the bulk density of CENG matrices (taken from Zong Y et al, 2010)

Three types of EG with different bulk densities were prepared and referred to as EG1, EG2 and EG3. The fourth type was prepared by mechanically crushing EG1 and referred to as EG4. Two commercial binder coal tar pitches CPT1 and CPT2 were used which were milled to obtain a pitch powder with an average size of less than $500 \mu\text{m}$. The EG and pitch were mixed by direct stirring of EG and pitch for 1 min in ambient temperature with 0.3- 10 wt % of EG. The mixture was kept at $200 \text{ }^\circ\text{C}$ for 3 h to ensure formation of uniform composite (Afanasov I. M. et al, 2009).

The volume resistance with different weight content of EG was studied for composites prepared with pitches CPT1 and CPT2. It can be seen from figure 11 that there is no significant difference in volume resistance based on the type of EG in the composites (CPT1/EG2, CPT1/EG3 and CPT1/EG4). However, there was decrease of 10 magnitudes when $\sim 1.5\%$ weight of EG is incorporated in the pitch matrix which is similar to the variation in resistivity seen in paraffin/xGnp composites (Fig. 8). This sudden decrease was attributed to the conductive network made by EG particles. The higher aspect ratio of the exfoliated graphite plays an important role in the formation of the conductive network within the pitch matrix. With further increase in EG content, the electrical resistance decreased slowly. Since, there is a close relationship between electrical resistance and thermal conductivity, it can be concluded that these composites showed similar pattern in thermal conductivity.

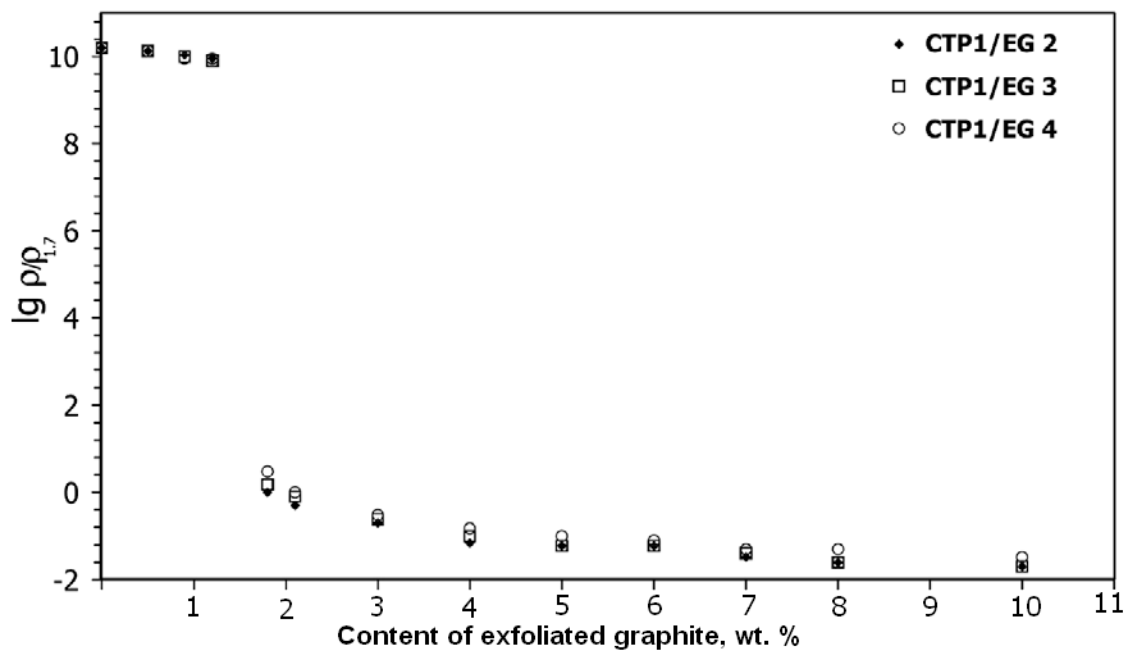


FIGURE 11 Volume resistance of the composites of CTP1 with different exfoliated graphite versus the EG content (taken from Afanasov I.M. et al., 2009).

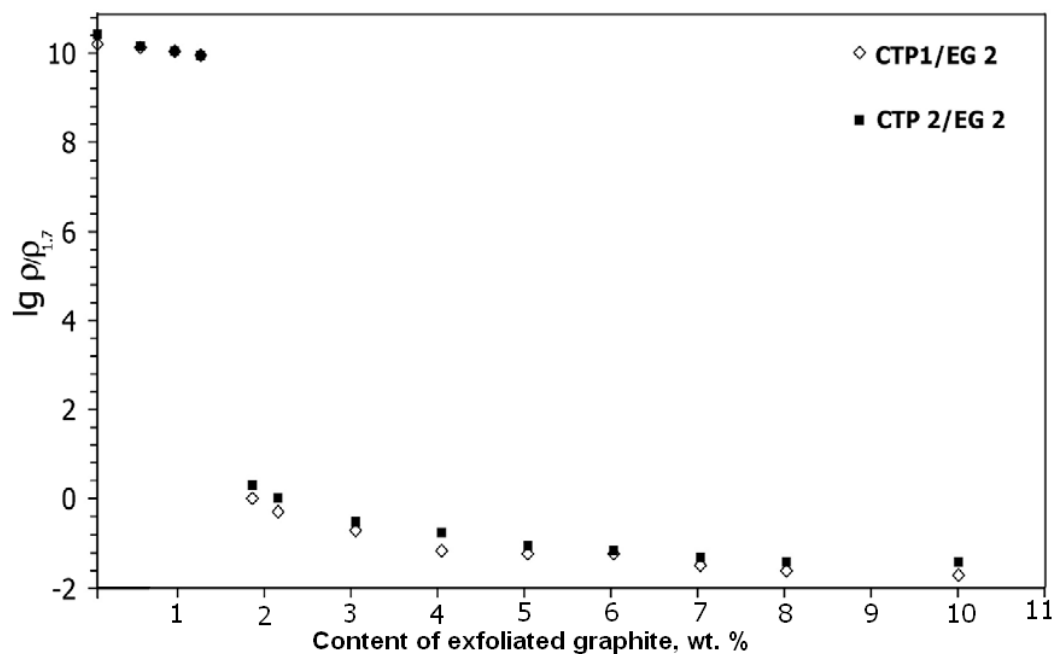


FIGURE 12 Volume resistances of the composites of two coal tar pitches with EG2 versus EG2 content by weight (taken from Afanasov I.M. et al., 2009)

When compared to composites with CPT2 Fig. 12, similar trend was seen that is, a sudden decrease in electrical resistance in composites with EG ranging between 1.2- 1.7%. Hence, it can be concluded that the type of coal tar pitch and type of EG did not have significant role in the behaviour of conductivity. It was the critical weight content of EG in the composite that showed a sudden decrease in the resistance in the composite (Afanasov I.M. et al., 2009).

The thermal gravimetry (TG) graphs of the initial pitches and composites prepared from EG2 is shown in Fig. 13. It can be seen that the composite with 1.2% EG shows onset of degradation 20 °C higher than the pure matrix and with 10 % wt of EG, the degradation is almost 50 °C higher than that of pure matrix for both pitches. Hence, addition of EG showed higher thermal stability compared to pure pitch. This was assumed to be due to the heat shielding effect achieved from EG or the polymerisation processes of the pitch components on the EG particles (Afanasov I.M. et al., 2009).

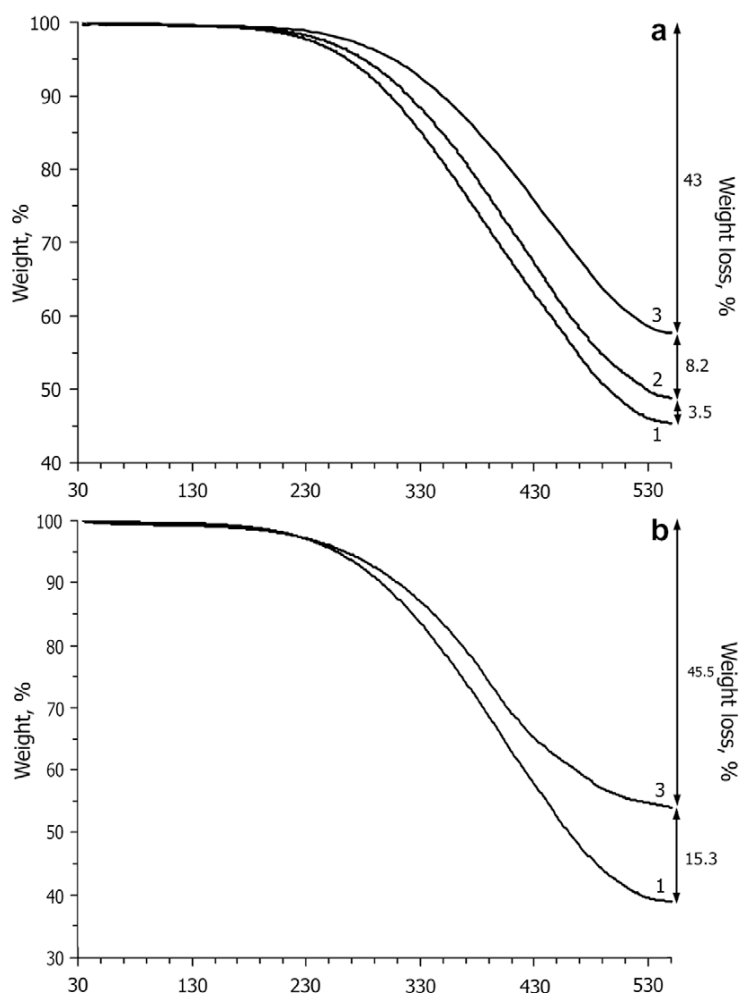


FIGURE 13 TG curves of pure coal tar pitches and CTP/EG2 composites for CTP1 (a) and CTP2 (b): pure CTP (1), CTP with 2 wt.% EG2 (2) and CTP with 10 wt.% EG2 (3) (taken from Afanasov I.M. et al., 2009)

1.1.6 Natural graphite flakes, ammonium lingo-sulfonate and mesophase based composites

Desai S. (2006) prepared and studied composites with natural graphite three different average flake sizes; small (avg. flake size: 180 μm), medium (avg. flake size: 300 μm) and large (avg. flake size: 600 μm). The mesophase pitch supplied in the form of pellets was ground into fine powder and passed through a sieve of 35 micron. The composites were made by mixing graphite flakes of known average flake size, mesophase pitch powder and ammonium ligno-sulfonate (ALS). The mixture was degassed at 350 $^{\circ}\text{C}$ for 90 min and hot-pressed to obtain a composite.

Composites were prepared with a given flake size and same starting volume fraction of graphite (75%) and a set of composites were prepared with varying starting volume fraction of large flakes graphite using same procedure. The composites were heat treated to different temperatures (1000 $^{\circ}\text{C}$, 1600 $^{\circ}\text{C}$ and 2400 $^{\circ}\text{C}$ /graphitization temperature) and characterized at room temperature.

Thermal conductivity of the composite was calculated using the relation between thermal diffusivity, bulk density and specific heat. The specific heat of the samples was estimated using Spencer's formula, the density was calculated from the weight and dimensions of the sample and the thermal diffusivity was measured using the conventional laser flash method at Tyndall Institute, Cork.

Thermal conductivity of composites with 75% starting volume fraction of graphite heat-treated to 1000 $^{\circ}\text{C}$ prepared from medium and large flakes were found to have diffusivities in the range between $14 \times 10^{-5} \text{ m}^2/\text{s}$ to $15 \times 10^{-5} \text{ m}^2/\text{s}$ and $21 \times 10^{-5} \text{ m}^2/\text{s}$ to $25 \times 10^{-5} \text{ m}^2/\text{s}$ respectively. The samples prepared from small flakes and heat-treated to 1000 $^{\circ}\text{C}$ are assumed to have poor conductivity since no signal could be detected while measuring thermal diffusivity. Thermal diffusivities and the estimated thermal conductivities of the samples heat-treated to 1600 $^{\circ}\text{C}$ are summarized in Table 1. It can be again seen that the thermal diffusivity and hence the thermal conductivity increases significantly with the flake size.

TABLE 1 Diffusivity and estimated thermal conductivity of samples HT to 1600 $^{\circ}\text{C}$ of different flake sizes

Flakes forming of the composite	Average diffusivity ($\times 10^{-5} \text{ m}^2/\text{s}$)	Thermal conductivity of the sample (W/m K)
S	4.54 \pm 01	52
M	15.47 \pm 01	220
L	24.98 \pm 01	325

When the thermal conductivity of the graphitized composites was calculated, it was seen that the thermal conductivity increases as the flake size increases (Fig. 14). The graphitised samples prepared using large flakes were found to have thermal conductivity of $\sim 655 \text{ W/m K}$ which is more than one and half times that of copper and with density of only one fourth of that of copper.

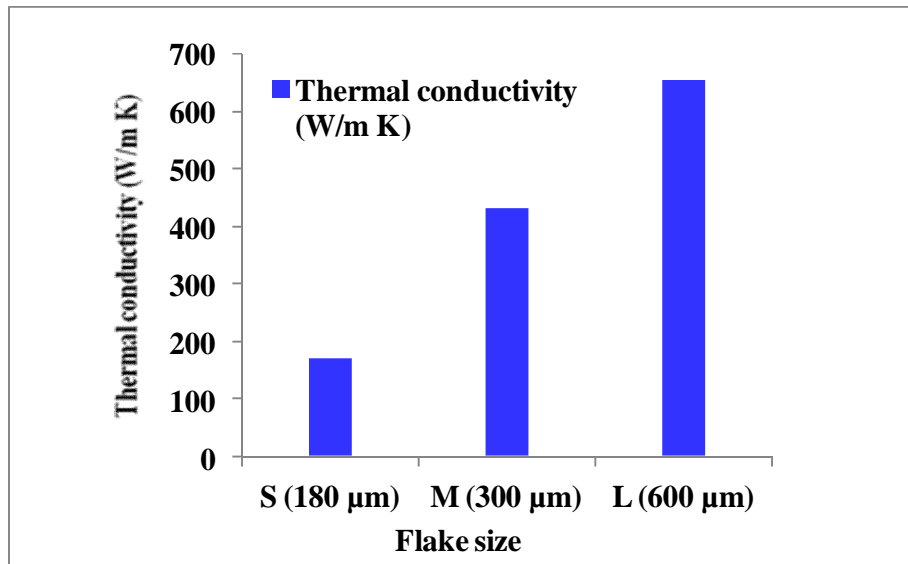


FIGURE 14 Thermal conductivity of graphitised composites (75% starting volume fraction of graphite) versus flake sizes (taken from Desai S., 2006)

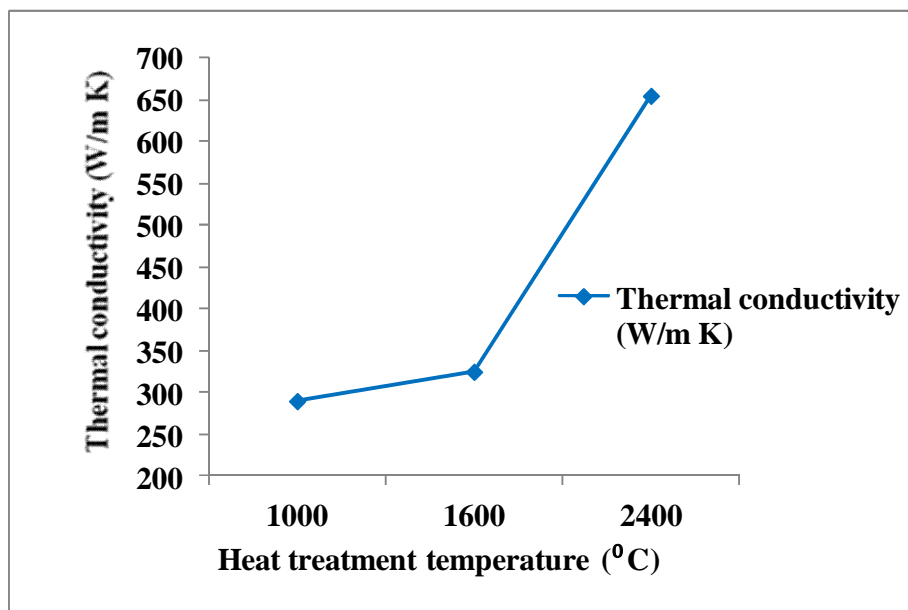


FIGURE 15 Graph of thermal conductivity versus heat-treatment temperature of samples fabricated using large flakes (taken from Desai S., 2006)

The conductivity of the composite prepared from same average flake size and heat-treated to different temperatures was studied. It was found that the conductivity of a composite for a given flake size increases as the heat-treatment temperature increases (Fig. 15). A significant increase in conductivity was observed when the heat-treatment temperature increased from 1600 °C to graphitization temperature. This

large improvement in the thermal conductivity is attributed to the graphitization of the binder which provides thermally conducting links.

The graphitised composites with varying starting volume fraction of graphite flakes (large) showed that the thermal conductivity increases with an increase in starting volume fraction of graphite (Desai S., 2006).

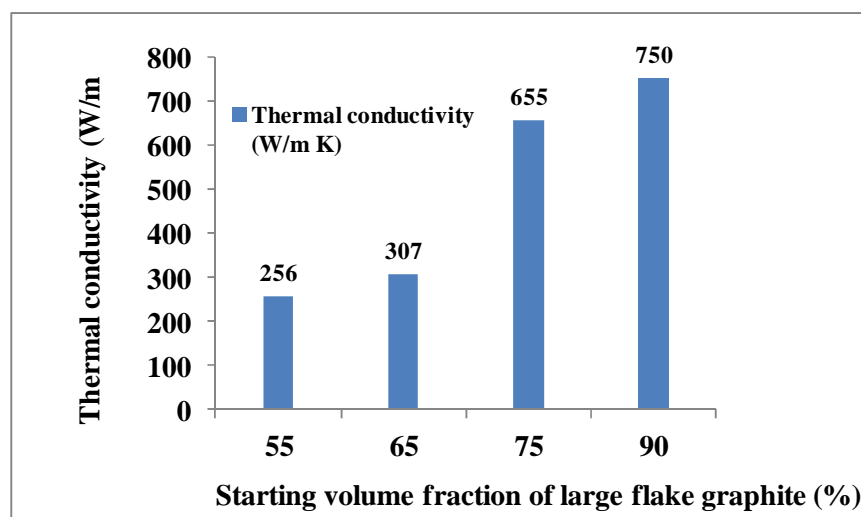


FIGURE 16 Thermal conductivity of large flake graphitised composites prepared with different starting volume fraction of flakes (taken from Desai S., 2006)

Desai S. (2006) concluded that the thermal conductivity was dominated by the flake sizes and heat-treatment temperature. As the volume fraction of graphite increases in the composite, superior properties are observed (Fig 16). The thermal conductivity of sample prepared from 90% starting volume fraction of flakes is found to have a thermal conductivity as high as ~750 W/m K which is nearly twice that of copper with density(1.78 g/cc) approximately one fourth that of copper. Hence, this material is particularly attractive for thermal management problems.

1.1.7 Graphene based composites

Since materials scientists are continuously examining materials with improved properties that will dimensionally be more suitable in the field of nano-science and technology. The discovery of graphene and graphene-based polymer nanocomposites is an important step forward. Graphene is regarded as the thinnest material in the universe with tremendous application potential due to its remarkable properties such as superior mechanical properties, high electrical transport properties and high thermal conductivity (Geim A. K. and MacDonald A. H., 2007; Si Y. and Samulski T., 2008; Wang G. et al, 2008 & 2009; Blake P. et al, 2008; Dreyer R.D. et al, 2010). It is the basic structural unit of some carbon allotropes including graphite, carbon nanotubes and fullerenes. In 2004, Geim A. K. and co-workers at Manchester University successfully identified the single layers of graphene and other 2-D crystals.

Although pristine graphene materials are unsuitable for intercalation by large species such as polymer chains (graphene has a tendency to agglomerate in a polymeric matrix), the agglomeration can be prevented by different chemical modification methods (Geng Y. et al, 2009). Initially, graphite oxide is prepared from natural graphite. After oxidation, a number of methods have been identified to obtain soluble graphene. Some of them include covalent modification by the amidation of the carboxylic groups

(Worsley K. A. Et al,2007; Niyogi S. et al, 2006), non-covalent functionalisation of reduced graphene oxide (Bai H. et al, 2009; Salavagione H. J. et al, 2009; Stankovich S. et al, 2006), nucleophilic substitution to epoxy groups (Bourlinos A. B. et al, 2003), diazonium salt coupling (Lomeda JR et al, 2008) and reduction of graphite oxide in a stabilisation medium (Park S. et al, 2008).

Ghosh S. et al. (2008) prepared a large number of graphene layers by the mechanical exfoliation of bulk highly oriented pyrolytic graphite (HOPG) using the standard technique (Geim K. and Novoselov K.S., 2007; Zhang Y.B. et al, 2005). Si/SiO₂ substrate with array of trenches of 300 nm depths and 1-5 μm width were fabricated by reactive ion etching. A long single layer with relatively constant width was placed across the trenches on the Si/SiO₂ wafer. Since conventional thermal conductivity measurement techniques could not be used in this set-up, Ghosh S. et al (2008) developed a non contact technique based on confocal micro-Raman spectroscopy. The graphene flakes in the system were found to have a thermal conductivity ranging between 3080 to 5150 W/m K and the phonon mean free path was calculated to be ~775 nm near RT. Hence, graphene can be looked upon as a thermal management material in future nanocircuits and similar applications that require high thermal transport properties.

2 Conclusion

It can be seen from the above that graphite has become popular in enhancing thermal conductivity of composites with different end applications. The discovery of graphene ‘the thinnest material in the universe’ with superior thermal properties has now attracted researchers to find methods to fully extract the properties of graphene in thermal management applications.

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