Chapter 11

Thermal Conductivity of Graphite-Based Polymer Composites

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Abstract

It is well known that polymers are insulators, which limit their usage in other applications where thermal conductivity is essential for heat to be efficiently dissipated or stored. In the past, the improvement in the thermal conductivity of polym.rs with conductive fillers has been investigated by researchers. Carbon-based materials such as graphite, graphene and carbon nanotube, which feature excellent properties such as a high mechanical strength, a high thermal conductivity and a tailorable electronic configuration, have been added to different polymer matrices to enhance their thermal conductivity. Amongst others, graphite more especially expanded graphite merits special interest because of its abundant availability at a relatively low cost and lightweight when compared to other carbon allotropes. Herein, we describe the thermal conductivity of polymer/graphite composites and their applications.

Keywords: polymer, graphite composites, thermal conductivity, functionalization, applications

1. Introduction

Polymers can be moulded into various shapes and forms which afford their application in different fields [1–3]. This is owing to their unique properties such as lightweight, durability and low production cost. Polymers have substituted natural materials (e.g. steel and glass) in most of their former uses [1–3]. Besides these unique features, their success in certain applications is hindered by their poor electrical, thermal and mechanical properties. The incorporation of different fillers has been subject to researchers and scientists as a suitable solution to overcome these limitations. However, the resulting composite properties were found to be directly dependent on several aspects such as matrix-type, filler-type, interaction between the filler and polymer as well as the distribution of the filler within the polymeric matrix [4].

Research has escalated on the use of conductive fillers to improve not only the electrical and thermal conductivities but also the overall physical properties of the resulting composite product. Different conductive fillers such as metal powder, carbon black, carbon nanotubes (CNTs) and natural graphite were employed as reinforcing fillers of various polymeric materials [5, 6]. Amongst all these fillers, graphite garnered in much interest owing to its unique properties such as abundant availability, low cost and easy functionalization [7].

The polymer/graphite composites exhibited a high thermal conductivity and an electrical conductivity at a fairly low concentration. Polymer/graphite composites have been used in many applications including structural, aerospace and sporting goods. Most recently, researchers have focused their attention on the development of polymer/graphite composites for applications whereby thermal conductivity is needed [8, 9]. It is documented [7] in the study that the significance of thermal conductivity and/or thermal diffusivity in polymer composites is related to the need for considerable levels of thermal conductivity in circuit boards and heat exchangers. According to the studies [10], conductive composites are frequently used in wide applications such as heating elements, temperature-dependent sensors, self-limiting electrical heaters, switching devices, antistatic materials for electromagnetic interferences and shielding of electronic devices. This chapter reviews recent development on the thermal conductivity of polymer/graphite composites.

2. Graphite

Graphite is a carbon-based layered material whose structure is composed of successive layers of graphene sheets (carbon) and received much interest owing to its exceptional thermal, mechanical and electrical properties [5, 11, 12]. It is thermodynamically stable and soft with the successive layers being parallel to the base plane. The layers are bonded together by van der Waals forces. Graphite consists of carbons that are hexagonally bound to each other by covalent bonds with an interatomic separation of 0.142 nm and an interlayer separation of 0.335 nm. It is sp^2-hybridized with three of four valence electrons of hexagonally attached carbons that are linked to the valence electrons of the neighbouring carbon by σ-bonding. Therefore, the fourth electron resonates freely within the graphene layer but it is no longer interacting with a specific carbon atom. Van der Waals forces acting between adjacent graphene layers result from the delocalization of π-electrons. Thus, the interatomic interaction within the single graphene layer is stronger, that is, 75 times when compared to the interaction between the adjacent layers [11]. Hence, there has been much graphite modification that takes place in between the layers in order to improve its dispersion in different polymeric materials. Graphite can be classified into two types: natural and synthetic graphite as shown in **Figure 1**.

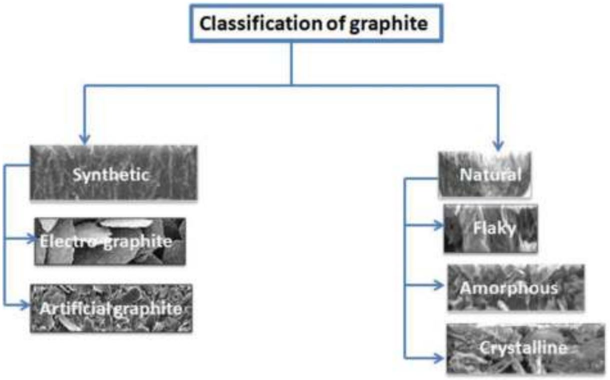

Figure 1. Schematic representation of graphite classification.

2.1. Natural graphite

Naturally occurring abundant graphite is classified into three categories depending on the geological environment, that is, amorphous, flake and highly crystalline [11]. Amorphous graphite has a content of graphite ranging from 25 to 85% depending on the geological conditions. It is usually derived from mesomorphic environment such as shale, slate and coal. Amorphous graphite is regarded as the less pure form of graphite with lack of considerable ordering and presence of microcrystalline structure. It has been applied in different applications where graphite is often utilized; however, its utilization depends on the degree of purity. Flake graphite is formed in either metamorphic or igneous geologic environments. It is obtained through froth floatation which results in 80–90% graphite. Flake graphite is less abundant as compared to amorphous graphite and has good electrical properties. It has been employed in various applications of graphite such as secondary steel manufacture, lubricants, pencils, powder metallurgy and coatings. Despite being found almost all over the world, crystalline (Vein/lump) graphite is commercially mined in Sri Lanka. It originates from crude oil deposits that through time, temperature and pressure were converted to graphite. As reflected by its name, it has a higher degree of crystallinity due to its direct deposition from a high-temperature fluid phase and its purity is more than 90%. Thus, it has good electrical and thermal conductivity. Vein graphite enjoyed its success in different applications such as batteries, lubricants, grinding wheels and powder metallurgy.

2.2. Synthetic graphite

Synthetic graphite is produced by treating carbonaceous precursors such as coal, petroleum and synthetic or natural organic chemicals in inert atmosphere to temperatures above 2400°C as well as thermal treatment of nongraphitic carbons, graphitization or chemical vapour deposition (CVD) from hydrocarbons under temperatures of 1883°C [11]. High temperatures are often employed to facilitate solid-state phase transition effect in order to produce graphite crystals. The production method is the primary factor that influences the resulting graphite properties. Synthetic graphite can also be categorized into two, that is, electro-graphite and artificial graphite. Electro-graphite is a pure carbon-shaped graphite produced from coal tar pitch and calcined petroleum pitch in the electric furnace, while artificial graphite results from the thermal treatment of calcined petroleum pitch at 2800°C. In general, the synthetic graphite has a low density, a high electrical resistance and porosity. Synthetic graphite is employed in different applications such as energy storage, carbon brushes and aerospace. Further modifications are often not required for its application in various fields. To avoid confusion, graphite will be used in this document without discriminate, whether it is synthetic or natural-based.

3. Modification of graphite

Modification of graphite has been subject of research in order to afford interaction with large polymer molecules and to achieve a better graphite dispersion [5, 11]. Many efforts have been done to overcome the absence of functional groups on the surface of graphite (or graphene sheets) and space between the sheets. There are three classic forms of modified graphite, that is, graphite-intercalated compounds (GICs), graphene oxide (graphite oxide (GO)) and expanded graphite (EG).

Graphite-intercalated compounds (*GICs*): GICs result from the insertion of atomic or molecular layers of different chemical species called intercalant between graphene sheets of the host graphite material [5, 12–14]. GIC can be categorized into two depending on the character of their bonding, that is, covalent GICs and ionic GICs. Covalent GICs include graphite oxide (GO), carbon monofluoride and tetracarbon monofluoride, whereas ionic GICs include graphite salts, graphite-alkali-metal compounds, graphite-halogen compounds and graphite-metal chloride compounds. Ionic GICs received much interest due to the capability of changing the electronic properties of graphite. The latter result in the presence of π-bonds in graphite that can accept/donate electrons from/to the intercalation. Further classification of ionic GICs depends on the staging of the GIC which is associated with the number of graphite layers between each intercalant layer. In the first stage (stage 1), the intercalant and graphite layers are alternating in which one layer of graphite is separated by one layer of intercalant. In a stage 2 GIC, there are two adjacent layers of graphite sheets between each intercalant layer. The intercalation of graphite results in increasing its interlayer spacing, weakening the interlayer interactions. The latter facilitate the exfoliation of the GICs by mechanical or thermal treatments.

Graphite oxide (*GO*): GOs are known as pseudo-two dimensional solid materials with covalent between the layers. Graphite oxide is often prepared by heat treatment of graphite flakes with oxidizing agents such that polar groups are introduced on the graphite surface [5, 15, 16]. This treatment also widens the interlayer spacing between the graphene sheets.

Expanded graphite (*EG*): The exposure of intercalated graphite to thermal treatment beyond critical temperature or microwave radiation leads to a large expansion of graphite flakes along the *c*-axis than in-plane direction as shown in **Figure 2**. The resulting material, which is known

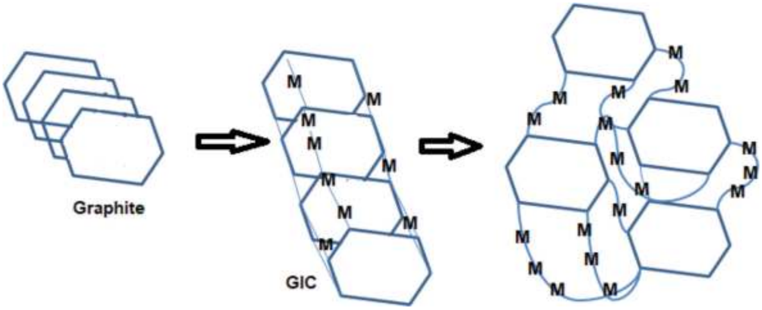

Figure 2. Schematic presentation of the preparation of expanded graphite (EG).

as expanded graphite (EG), has a vermicular or a worm-like structure with a low density, a high-temperature resistance and a high conductivity [6, 17, 18]. A mixture of sulphuric acid and nitric acid is usually employed for graphite intercalation followed by heat or microwave treatment to produce expanded graphite [5, 19].

Graphene: Graphene is a monolayer of sp^2-hybridized carbon atoms arranged in a two-dimensional lattice. It has been produced using different methods such as growth by chemical vapour deposition (both of discrete monolayers onto substrate and agglomerated powders), micro-mechanical exfoliation of graphite, and growth on crystalline silicon carbide [5]. These methods afford defect-free material with excellent physical properties; however, the yield is not large enough for use as a composite filler. The thermal conductivity of graphene ranges between 600 and 5000 $W\ m^{-1}\ K^{-1}$ with Young modulus of 1 TPa and a tensile strength of 130 GPa [20].

4. Graphite composites

In order to broaden the applications of polymers, the incorporation of a suitable filler with required functionality is the most cost-effective and reliable method [17]. Some of the polymers fall short when it comes to electrical, thermal and mechanical as compared to ceramics and steel. However, the unique properties of polymers such as lightweight and mouldability into different shapes make them suitable candidates for various applications. Amongst other fillers, graphite features unique properties such as a high thermal and electrical conductivity, a low coefficient of thermal expansion, an exceptional thermal resistance, a high thermal shock resistance, improved stiffness and an increased strength. It is abundantly available and easily functionalized to afford various applications. The thermal conductivity of the graphite and/or its composites is of significant importance considering the demands as thermal conductance in heat exchangers, circuit boards, machinery, electronic appliances and many other applications as explained in Section 1.

4.1. Preparation of graphite composites

Beside the modification of graphite, the major contributor to the distribution of graphite in the polymeric matrix relies on the selected preparation method. Classic preparation methods for graphite/polymer composites are *in situ* polymerization, melt intercalation and solution-casting techniques [21–24]. Complete dispersion of the graphite particles leads to poor thermal conductivity due to lack of conductive network path within the composite product. **Figure 3** shows a schematic presentation of the resulting morphologies depending on the preparation method.

4.1.1. In situ polymerization

In situ polymerization involves the polymerization of monomer (or/and oligomer) in the presence of the filler [6, 21, 24–26]. This method is one of the most effective processes to facilitate the dispersion of the filler in the polymeric material. Moreover, it enhances strong interaction between the composite component; hence, the mechanical properties of the resulting composite are superior to the composite prepared by either solution casting or melt intercalation [25]. This technique, however, is associated with some limitations such as polymer and filler selection and limited to laboratory scale. Moreover, it is environmentally unfriendly process which makes it not feasible for composite preparation.

4.1.2. Solution casting

In solution casting, the polymer is dissolved in suitable solvents and then the filler is added into the polymer solution [22, 27]. In order to improve the dispersion of the fillers, the sonication step is usually adopted [27, 28]. Some polymers are, however, not soluble in most available solvents which then limit the choice of a polymer for this technique. This process is not environmentally friendly due to the fact that the solvent has to be evaporated from the system which can be harmful except if the solvent is water. For industrial production, this technique will be expensive with regard to the recovery of the solvent used. Nevertheless, the mechanical

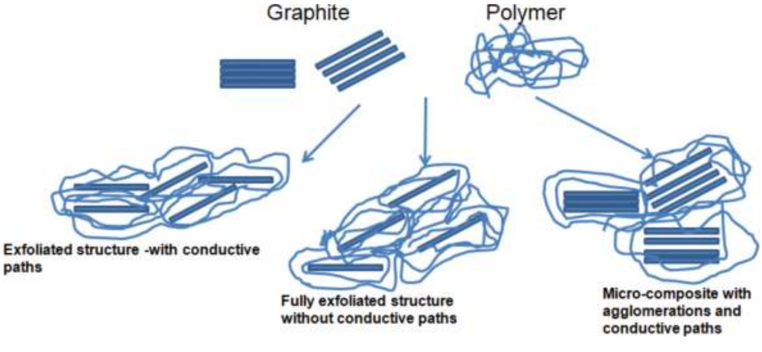

Figure 3. Different types of composites arising from and interaction between the host polymer and graphite layers obtained from different preparation methods.

properties of the resulting composites are superior to melt intercalation due to the sufficient time given for the filler to interact with each other as well as the polymeric matrix. A comparison between solution casting as well as solution casting followed by melt pressing was conducted by Bai et al. [22]. It was reported that solution-casted samples had high ability to form the percolated filler network as compared to solution casting followed by melt pressing. The percolation network is essential for the conduction paths within the composite material. However, the appropriate solvent can be chosen to avoid the formation of micro-voids within the composite [29]. The solution casting followed by hot pressing serves as a good procedure to eradicate the voids within the composite material [29].

4.1.3. Melt intercalation

Melt intercalation is the most favourable process with regard to industrial and environmental perspectives [23, 30, 31]. Polymer and filler are mixed together in the melt-compounding technique which leads to exposure to high shear and heat. The mixture is heated to a temperature above the melting temperature of the polymer for certain period to allow homogeneity. Classic compounding techniques include a single-screw extruder, a twin-screw extruder and an internal mixer. All these techniques can be utilized alone or in combination to afford better dispersion of the fillers. Injection moulding and/or melt pressing are usually used to mould the composite for characterization. In general, the percolation threshold is little bit higher than the other processing techniques, that is, solution casting and in situ polymerization [30]. Interestingly, the balance between the mechanical properties and other properties such as electrical conductivity can be achieved through this method which is of significance towards the commercialization of the resulting composite products. Its limitations involve the choice of polymer/filler, limited filler distribution and thermal degradation of the host polymer [23]. The properties of the polymer such as molecular weight, viscosity and chain length play a major role on the properties of the resulting composite product, hence influencing conclusions reached by different authors [11].

4.1.4. Other processing techniques

The combination of solution casting followed by melt intercalation/pressing has also been reported [28, 32, 33]. The main was to ensure the interaction between the fillers in order to promote the conductance path network within the host matrix. On the other hand, electrospun graphite composites were also reported in the study [34]. Despite the advantages associated with these techniques, *viz*. cost-effective, possibility of scaling up, control over the morphology of the resulting fibres and almost all polymers can be processed, there are only few studies based on the electrospun graphite composites [34, 35]. In situ melt mixing was carried out by mixing low-temperature expendable graphite with LDPE [36]. The expandable graphite expanded during the mixing process which is of significant importance considering the contact between the graphite particles. It is, however, recognized that such a process can lead to a large number of agglomeration with an increase in the filler’s content. In the case of adhesive resins (e.g. epoxy resin), curing at a certain temperature over a certain period is usually utilized to prepare the composite products [37, 38].

5. Thermal conductivity

5.1. Graphite composites

Numerous researchers studied the thermal conductivity of polymer composites with regard to their importance to reach appreciable levels of thermal conductance in circuit boards, heat exchangers, appliances and machinery as summarized in **Table 1** [7, 17, 39]. Amongst all thermal conductive fillers, graphite merits special interest not only due to its high thermal conductivity, that is, 25–470 W m^{-1} K^{-1}, but high thermal stability, exceptional chemical resistance and mechanical properties [40]. A comparative study of the thermal conductivity between graphite and other conductive fillers (*viz*. copper powder (Cu), aluminium powder (Al), silver powder (Ag), zinc oxide (ZnO), boron nitride (BN), aluminium oxide (Al_2O_3) and diamond) particles was done by Fu et al. [37]. It was reported that the highest thermal conductivity was obtained at the filling load of 44.3 wt% of graphite due to the layered structure of graphite forming heat pathways within the matrix. The thermal conductivities of diamond (29.14%), Cu (68.25%), Al (69.69%), Al_2O_3 (67%) and BN (35.5%) were 0.35, 0.74, 1.11, 0.57 and 0.59 W m^{-1} K^{-1}, respectively. Although the resulting thermal conductivities were not true reflection of the thermal conductivity of the particles, this was related to the different structural arrangement within the particles which controls the contact between them. The

System	Maximum particle content	Preparation method	Thermal conductivity (W m^{-1} K^{-1})	Refs.
LDPE/graphite	10 vol.%	Melt mixing	6.5	[39]
HDPE/graphite	7%	Melt mixing	1.59	[40]
LDPE/low-temperature expandable graphite	50 wt%	Melt mixing followed by pan milling and dilution with neat LDPE	5.04	[51]
LDPE/untreated low-temperature expandable graphite	50 wt%	Melt mixing	7.02	[51]
LDPE/low-temperature expandable graphite (LTEG)	37 vol% (60 wt%)	Melt mixing	11.24	[36]
Ethylene vinyl acetate/natural graphite	7.5	Melt mixing	~0.29	[52]
Ethylene vinyl acetate/expanded graphite (EG)	7.5	Melt mixing	~0.31	[52]
Ethylene vinyl acetate/expanded graphite (EG)	4 phr	Solution casting followed by melt pressing	0.87	[33]
Ethylene vinyl acetate/natural graphite (NG)	4 phr	Solution casting followed by melt pressing	0.48	[33]
Epoxy resin/graphite	44.3 wt%	Oven curing	1.68	[37]
Epoxy resin/graphite	4.5 wt%	Oven curing	1.0	[38]
Epoxy resin/graphite	2 wt%	Oven curing	1.0	[50]

Table 1. Selected studies based on the thermal conductivity of graphite composites.

graphite being a cheaper material performed better than other expensive conductive particles. In general, the thermal conductivity increases almost linearly with an increase in graphite content, regardless of processing method as shown in **Figure 1** [39–43]. This can be attributed to the high thermal conductivity of the graphite when compared to pristine polymeric matrix.

Mu and Feng [41] prepared graphite/silicone rubber composites using solution-casting and melt-mixing processing techniques. They reported that the thermal conductivity increased with an increase in graphite content; however, solution-casted composites had a high conductivity as compared to melt-mixed ones. The authors reported that the thermal conductivity of solution-casted composites reached a value of 0.32 W m^{-1} K^{-1} at 9 per hundred rubber (phr) of graphite, whereas for melt-mixed it was only 0.24 W m^{-1} K^{-1}, which is the conductivity level similar to solution-casted composite at 4 phr. This was attributed to the conducting path networks created by contact between the graphite layers at a fairly low content in the case of solution casting compared to the reduction of surface-to-volume ratio in the case of melt mixing as shown in **Figure 4**. The latter resulted in a higher content of graphite required so that they can abut or contact in order to form the conducting paths. A comparison between two commercial graphite (EG-10, synthetic graphite, SGL Carbon, UK, and KS-15, synthetic graphite, Lonza, Switzerland) in two different polymeric matrices (high-density polyethylene (HDPE) and polystyrene (PS)) was conducted by Krupa and Chodák [7]. They reported a nonlinear increase of thermal conductivity with an increase in graphite content regardless of matrix and graphite type. It was, however, reported that the graphite KS displayed higher thermal conductivities than the thermal conductivities of EG-filled material especially for PS composites at a higher graphite content. The graphite KS had smaller particles with a narrow particle size distribution as well as a higher specific surface than graphite EG which corroborate the fact that the size of the particles did not influence the thermal conductivity, however, the contact between the graphite particles even if they are agglomerated. In another study, it was reported that the crystallinity of the polymer also plays a major role on the thermal conductivity of the resulting composite product [44]. It was reported that high-density polyethylene (HDPE)-based composites displayed high thermal conductivities over the whole graphite composition as compared to less crystalline low-density polyethylene (LDPE). Similarly, Deng et al. investigated the effect of chain structure on the thermal conductivity of expanded graphite/polymer composites [45]. Expanded graphite (EG) was blended with three different polymers, that is, polyphenylene sulphide (PPS), syndiotactic polystyrene (sPS) and amorphous polystyrene (aPS). The thermal conductivities of the neat aPS, sPS and PPS

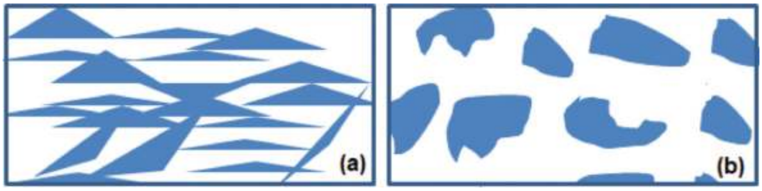

Figure 4. Schematic presentation of the proposed mechanism for thermal conductive paths for (a) solution-casted and (b) melt-mixed samples.

samples were reported as 0.18, 0.23 and 0.24, respectively. This was ascribed to the crystallinity of polymers. Similar result of observation was reported elsewhere in the study [46, 47]. The EG/PPS composites showed the highest thermal conductivity throughout the whole range in comparison to the two counterpart composites (**Figure 5**). The observed behaviour was attributed to the difference in polymer matrices with varied chain structures which may result in different crystallizations and interactions of composites.

Sefadi et al. [48] studied the influence of graphite treatment with sodium dodecyl sulphate (SDS) in water on the thermal conductivity. Moreover, the authors exposed the samples to 50-KGy electron beam irradiation to improve the interaction between graphite and ethylene vinyl acetate (EVA), as host matrix. They reported an increase in thermal conductivity with an increase in filler content due to high conductivity of graphite, regardless of the treatment. However, the thermal conductivity of the irradiated samples was slightly lower than unirradiated samples. This was attributed to the restriction of the polymer chains *via* cross-linking which reduced the vibration of phonons. There are a number of factors which contribute to the overall thermal conductivity of a composite product such as the dispersion of filler, matrix crystallinity and crystal structure, degree of interfacial thermal contact between the components, and scattering of phonons. Thus, these factors may counterbalance each other such that the obtained thermal conductivity does not reflect the percentage of the conductive filler added into the host matrix. For instance, Shen et al. [49] reported that the

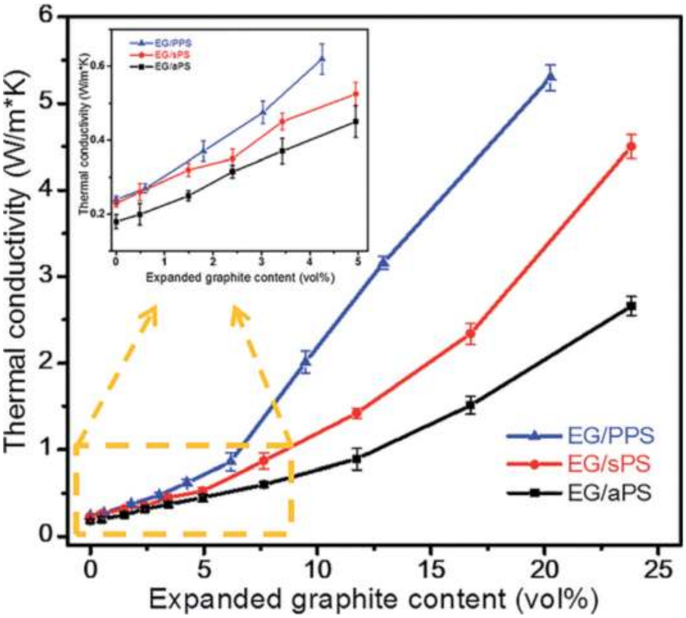

Figure 5. The thermal conductivity of EG/polymer composites as a function of EG volume contents (the error bar is marked). The inset shows the thermal conductivity at a low content [45].

functionalization of the filler can promote dispersion as well as interaction between composite components, but at the expense of thermal conductivity. Hence, it is of significant importance to choose functionalization of the filler while taking into account the lateral size of the filler for high thermal conductive materials. Li et al. [50] also reported that the treatment of the graphite with UV/O_3 did not have an influence on the thermal conductivity of the resulting composite materials. On the contrary, Wang and Tsai [20] reported that functionalized fillers exhibited superior thermal enhancements more than pristine filler. This was attributed to the increase in interfacial thermal conductivity (ITC) between the filler and the host matrix.

5.2. Graphite with other fillers (ternary systems)

There has been an ever-increasing interest in incorporating additional conductive filler into a graphite composite product to overcome the limitation of these materials [22, 31, 53–55]. It can be argued that the maximum thermal conductivity value achieved in graphite composites is 11.24 W m^{-1} K^{-1} (see **Table 1**). It is envisaged that the incorporation of the second filler can further enhance the thermal conductivity of the resulting composite products [31, 53, 56]. Lebedev et al. [53] reported that the inclusion of 1 wt% of carbon nanotubes (CNT) into polylactic acid (PLA)/natural graphite composites improved thermal conductivity by more than 40% of magnitude. The thermal conductivity was increased from 0.93 W m^{-1} K^{-1} for neat polymer to 2.73 W m^{-1} K^{-1} after the addition of 30 wt% graphite, whereas after the inclusion of 1 wt% CNT, the thermal conductivity value reached 3.8 W m^{-1} K^{-1}. This is ascribed to the additional CNT bridges which closely adjoin the surface of graphite. A similar study using HDPE as the polymeric matrix was recent conducted by Che et al. [31]. The authors reported that the thermal conductivity further increased with the addition of CNT compared to that with EG composites. In another study, it was demonstrated that a small content of a second filler, that is, below 2 wt%, has no significant influence on the thermal conductivity when compared to EG composites due to the fillers being wrapped in between the graphite layers [57]. A maximum increase of 38.5% compared to single filler-based composite was achieved at 5 wt% of the second filler. Self-hybrid composites of EG by crushing EG using a high-speed crusher to obtain different particle sizes were recently studied by Kim et al. [54]. The composites were prepared by mixing the crushed EG and raw EG with polycarbonate (PC) using melt extrusion. Hybrid composites (10 wt% crushed EG and raw EG) displayed a higher thermal conductivity by 12 and 20.7% compared to 20 wt% raw EG and crushed EG composites. The thermal conductivity value reached 2.62 W m^{-1} K^{-1} compared to 2.34 and 2.17 W m^{-1} K^{-1} for raw-EG and crushed EG-based composites due to synergistic effect. Various thermal conductive particles rather than carbon-based ones can also be used to enhance the thermal conductivity. Kostagiannakopoulou et al. [58] also reported that the thermal conductivity of the epoxy system increased significantly by increasing the filler content. However, the inclusion of the second filler, that is, multiwalled carbon nanotubes (MWCNTs) did improve the thermal conductivity at a higher graphite content (5, 10 and 15%). The highest enhancement percentage was 48 at 15% of graphite. The highest increase of ~176 was achieved in the case of 15% wt of the filler. A combination of graphite and aluminium nitride (AIN) was reported by Yuan et al. [59] and the thermal conductivity reached a value of

2.77 W m^{-1} K^{-1} that was 14.6 times that of neat polymeric matrix by combining only 50 wt% AIN and 6 wt% graphite.

6. Conclusions and remarks

The design of composites from graphite is inexpensive and available in abundance. This has initiated new ideas in the field of science for the development of a wide range of novel functional materials. Generally, the addition of graphite improved the thermal conductivity of the host polymer matrix irrespective of filler functionalization, the type of polymer and the method of preparation. Various processing techniques such as solvent casting melt blending and pan milling and masterbatch melt mixing have been used for the preparation of graphite composites. The type of mixing method seemed to have had an effect on the resultant thermal conductivity of the graphite/polymer composites. For instance, solution-casted composites had a high thermal conductivity as compared to melt-mixed system. It is understood that during solution casting, the EG particles will have a sufficient surface-to-volume ratio; as a result, they can contact easily and form conducting path networks at low EG contents. However, for melt mixing, one is of the idea that the EG particles' shape is changed during the melt-mixing process, resulting in a decrease of surface-to-volume ratio. Therefore, only a higher content of EG can contact and form conductive paths. Furthermore, the type of polymer had an influence on the thermal conductivity of the polymer/graphite composites, with the crystalline polymers having a higher thermal in the composites. It was further observed that the type of treatment on the graphite or its polymer composites also played a significant role in the improvement or non-improvement of the thermal conductivity of the polymer graphite composites. For example, the silane-treated graphite composites showed a higher thermal conductivity than the non-silane-treated graphite composites. In some cases, the treatment of the graphite with UV/O_3 did not have an influence on thermal conductivity of the resulting composite materials. Lately, the incorporation of the second filler with graphite can further enhance the thermal conductivity of the resulting composite products and widen the application of graphite composites.

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References

[1] Ho BT, Roberts TK, Lucas S. An overview on biodegradation of polystyrene and modified polystyrene: The microbial approach. Critical Reviews in Biotechnology. 2017;**38**(2):308-320. DOI: 10.1080/07388551.2017.1355293

[2] Restrepo-Flórez J-M, Bassi A, Thompson MR. Microbial degradation and deterioration of polyethylene-a review. International Biodeterioration & Biodegradation. 2014;**88**:83-90. DOI: 10.1016/j.ibiod.2013.12.014

[3] Wei R, Zimmermann W. Microbial enzymes for the recycling of recalcitrant petroleum-based plastics: How far are we? Microbial Biotechnology. 2017;**10**(6):1308-1322. DOI: 10.1111/1751-7915.12710

[4] Yasmin A, Luo J-J, Daniel IM. Processing of expanded graphite reinforced polymer nanocomposites. Composites Science and Technology. 2006;**66**(9):1182-1189. DOI: 10.1016/j.compscitech.2005.10.014

[5] Potts JR, Dreyer DR, Bielawski CW, Ruoff RS. Graphene-based polymer nanocomposites. Polymer. 2011;**52**(1):5-25. DOI: 10.1016/j.polymer.2010.11.042

[6] Chen G, Weng W, Wu D, Wu C. PMMA/graphite nanosheets composite and its conducting properties. European Polymer Journal. 2003;**39**(12):2329-2335. DOI: 10.1016/j.eurpolymj.2003.08.005

[7] Krupa I, Chodák I. Physical properties of thermoplastic/graphite composites. European Polymer Journal. 2001;**37**(11):2159-2168. DOI: 10.1016/S0014-3057(01)00115-X

[8] Ezquerra T, Kulescza M, Balta-Calleja F. Electrical transport in polyethylene-graphite composite materials. Synthetic Metals. 1991;**41**(3):915-920. DOI: 10.1016/0379-6779(91)91526-G

[9] Blaszkiewicz M, McLachlan DS, Newnham RE. The volume fraction and temperature dependence of the resistivity in carbon black and graphite polymer composites: An effective media-percolation approach. Polymer Engineering & Science. 1992;**32**(6):421-425. DOI: 10.1002/pen.760320606

[10] Klason C, MCQueen DH, Kubát J. Electrical Properties of Filled Polymers and Some Examples of Their Applications, Macromolecular Symposia. Manhattan, America: Wiley Online Library. 1996;**24**(2):110-117. DOI: 10.1002/masy.1996108012

[11] Nasir A, Kausar A, Younus A. Polymer/graphite nanocomposites: Physical features, fabrication and current relevance. Polymer-Plastics Technology and Engineering. 2015;**54**(7): 750-770. DOI: 10.1080/03602559.2014.979503

[12] Dresselhaus MS, Dresselhaus G. Intercalation compounds of graphite. Advances in Physics. 2002;**51**(1):1-186. DOI: 10.1080/00018730110113644

[13] Smith RP, Weller TE, Howard CA, Dean MP, Rahnejat KC, Saxena SS, Ellerby M. Superconductivity in graphite intercalation compounds. Physica C: Superconductivity and Its Applications. 2015;**514**:50-58. DOI: 10.1016/j.physc.2015.02.029

[14] Xu J, Dou Y, Wei Z, Ma J, Deng Y, Li Y, Liu H, Dou S. Recent progress in graphite intercalation compounds for rechargeable metal (Li, Na, K, Al)-ion batteries. Advanced Science. 2017;**4**(10):1-14. DOI: 10.1002/advs.201700146

[15] Olanipekun O, Oyefusi A, Neelgund GM, Oki A. Synthesis and characterization of reduced graphite oxide–polymer composites and their application in adsorption of lead. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2015;**149**:991-996. DOI: 10.1016/j.saa.2015.04.071

[16] Shin HJ, Kim KK, Benayad A, Yoon SM, Park HK, Jung IS, Jin MH, Jeong H-K, Kim JM, Choi J-Y, Lee YH. Efficient reduction of graphite oxide by sodium borohydride and its effect on electrical conductance. Advanced Functional Materials. 2009;**19**(12):1987-1992. DOI: 10.1002/adfm.200900167

[17] Mochane MJ, Motaung TE, Motloung SV. Morphology, flammability, and properties of graphite reinforced polymer composites. Systematic review. Polymer Composites. 2017. DOI: 10.1002/pc.24379

[18] Tsai K-C, Kuan H-C, Chou H-W, Kuan C-F, Chen C-H, Chiang C-L. Preparation of expandable graphite using a hydrothermal method and flame-retardant properties of its halogen-free flame-retardant HDPE composites. Journal of Polymer Research. 2011;**18**(4): 483-488. DOI: 10.1007/s10965-010-9440-2

[19] Shen X, Lin X, Jia J, Wang Z, Li Z, Kim J-K. Tunable thermal conductivities of graphene oxide by functionalization and tensile loading. Carbon. 2014;**80**:235-245. DOI: 10.1016/j.carbon.2014.08.062

[20] Wang T-Y, Tsai J-L. Investigating thermal conductivities of functionalized graphene and graphene/epoxy nanocomposites. Computational Materials Science. 2016;**122**:272-280. DOI: 10.1016/j.commatsci.2016.05.039

[21] Milani MA, González D, Quijada R, Basso NR, Cerrada ML, Azambuja DS, Galland GB. Polypropylene/graphene nanosheet nanocomposites by in situ polymerization: Synthesis, characterization and fundamental properties. Composites Science and Technology. 2013; **84**:1-7. DOI: 10.1016/j.compscitech.2013.05.001

[22] Bai Q-q, Wei X, Yang J-h, Zhang N, Huang T, Wang Y, Zhou Z-w. Dispersion and network formation of graphene platelets in polystyrene composites and the resultant conductive properties. Composites Part A: Applied Science and Manufacturing. 2017;**96**:89-98. DOI: 10.1016/j.compositesa.2017.02.020

[23] Anandhan S, Bandyopadhyay S. Polymer nanocomposites: From synthesis to applications. In: Nanocomposites and Polymers with Analytical Methods. Rijeka: InTech; 2011. DOI: 10.5772/17039

[24] Ding P, Su S, Song N, Tang S, Liu Y, Shi L. Highly thermal conductive composites with polyamide-6 covalently-grafted graphene by an in situ polymerization and thermal reduction process. Carbon. 2014;**66**:576-584. DOI: 10.1016/j.carbon.2013.09.041

[25] Patole AS, Patole SP, Kang H, Yoo J-B, Kim T-H, Ahn J-H. A facile approach to the fabrication of graphene/polystyrene nanocomposite by in situ microemulsion polymerization. Journal of Colloid and Interface Science. 2010;**350**(2):530-537. DOI: 10.1016/j.jcis.2010.01.035

[26] Zheng G, Wu J, Wang W, Pan C. Characterizations of expanded graphite/polymer composites prepared by in situ polymerization. Carbon. 2004;**42**(14):2839-2847. DOI: 10.1016/j.carbon.2004.06.029

[27] Guo H, Li X, Li B, Wang J, Wang S. Thermal conductivity of graphene/poly (vinylidene fluoride) nanocomposite membrane. Materials & Design. 2017;**114**:355-363. DOI: 10.1016/j.matdes.2016.11.010

[28] Zhang W-B, Zhang Z-x, Yang J-H, Huang T, Zhang N, Zheng X-T, Wang Y, Zhou Z-W. Largely enhanced thermal conductivity of poly (vinylidene fluoride)/carbon nanotube composites achieved by adding graphene oxide. Carbon. 2015;**90**:242-254. DOI: 10.1016/j.carbon.2015.04.040

[29] Ding P, Zhang J, Song N, Tang S, Liu Y, Shi L. Anisotropic thermal conductive properties of hot-pressed polystyrene/graphene composites in the through-plane and in-plane directions. Composites Science and Technology. 2015;**109**:25-31. DOI: 10.1016/j.compscitech.2015.01.015

[30] Han Y, Wu Y, Shen M, Huang X, Zhu J, Zhang X. Preparation and properties of polystyrene nanocomposites with graphite oxide and graphene as flame retardants. Journal of Materials Science. 2013;**48**(12):4214-4222. DOI: 10.1007/s10853-013-7234-8

[31] Che J, Wu K, Lin Y, Wang K, Fu Q. Largely improved thermal conductivity of HDPE/expanded graphite/carbon nanotubes ternary composites *via* filler network-network synergy. Composites Part A: Applied Science and Manufacturing. 2017;**99**:32-40. DOI: 10.1016/j.compositesa.2017.04.001

[32] Xiao Y-j, Wang W-y, Chen X-j, Lin T, Zhang Y-t, Yang J-h, Wang Y, Zhou Z-w. Hybrid network structure and thermal conductive properties in poly (vinylidene fluoride) composites based on carbon nanotubes and graphene nanoplatelets. Composites Part A: Applied Science and Manufacturing. 2016;**90**:614-625. DOI: 10.1016/j.compositesa.2016.08.029

[33] George JJ, Bhowmick AK. Ethylene vinyl acetate/expanded graphite nanocomposites by solution intercalation: Preparation, characterization and properties. Journal of Materials Science. 2008;**43**(2):702-708. DOI: 10.1007/s10853-007-2193-6

[34] Huang Z-X, Liu X, Wong S-C, Qu J-p. Electrospinning polyvinylidene fluoride/expanded graphite composite membranes as high efficiency and reusable water harvester. Materials Letters. 2017;**202**:78-81. DOI: 10.1016/j.matlet.2017.05.067

[35] Tu Z, Wang J, Yu C, Xiao H, Jiang T, Yang Y, Shi D, Mai Y-W, Li RKY. A facile approach for preparation of polystyrene/graphene nanocomposites with ultra-low percolation

threshold through an electrostatic assembly process. Composites Science and Technology. 2016;**134**:49-56. DOI: 10.1016/j.compscitech.2016.08.003

[36] Wu H, Lu C, Zhang W, Zhang X. Preparation of low-density polyethylene/low-temperature expandable graphite composites with high thermal conductivity by an in situ expansion melt blending process. Materials & Design (1980-2015). 2013;**52**:621-629. DOI: 10.1016/j.matdes.2013.05.056

[37] Fu Y-X, He Z-X, Mo D-C, Lu S-S. Thermal conductivity enhancement with different fillers for epoxy resin adhesives. Applied Thermal Engineering. 2014;**66**(1-2):493-498. DOI: 10.1016/j.applthermaleng.2014.02.044

[38] Wang Z, Qi R, Wang J, Qi S. Thermal conductivity improvement of epoxy composite filled with expanded graphite. Ceramics International. 2015;**41**(10):13541-13546. DOI: 10.1016/j.ceramint.2015.07.148

[39] Lebedev SM, Gefle OS. Evaluation of electric, morphological and thermal properties of thermally conductive polymer composites. Applied Thermal Engineering. 2015;**91**:875-882. DOI: 10.1016/j.applthermaleng.2015.08.046

[40] Ye CM, Shentu BQ, Weng ZX. Thermal conductivity of high density polyethylene filled with graphite. Journal of Applied Polymer Science. 2006;**101**(6):3806-3810. DOI: 10.1002/app.24044

[41] Mu Q, Feng S. Thermal conductivity of graphite/silicone rubber prepared by solution intercalation. Thermochimica Acta. 2007;**462**(1-2):70-75. DOI: 10.1016/j.tca.2007.06.006

[42] Mochane M, Luyt A. The effect of expanded graphite on the flammability and thermal conductivity properties of phase change material based on PP/wax blends. Polymer Bulletin. 2015;**72**(9):2263-2283. DOI: 10.1007/s00289-015-1401-9

[43] Mochane M, Luyt A. The effect of expanded graphite on the thermal stability, latent heat, and flammability properties of EVA/wax phase change blends. Polymer Engineering & Science. 2015;**55**(6):1255-1262. DOI: 10.1002/pen.24063

[44] Krupa I, Novák I, Chodák I. Electrically and thermally conductive polyethylene/graphite composites and their mechanical properties. Synthetic Metals. 2004;**145**(2-3):245-252. DOI: 10.1016/j.synthmet.2004.05.007

[45] Deng S, Wang J, Zong G, Chen F, Chai S, Fu Q. Effect of chain structure on the thermal conductivity of expanded graphite/polymer composites. RSC Advances. 2016;**6**(12):10185-10191. DOI: 10.1039/c5ra26272k

[46] Hay J, Luck D. The conformation of crystalline poly (phenylene sulphide). Polymer. 2001;**42**(19):8297-8301. DOI: 10.1016/S0032-3861(01)00335-4

[47] Langer L, Billaud D, Issi J-P. Thermal conductivity of stretched and annealed poly (p-phenylene sulfide) films. Solid State Communications. 2003;**126**(6):353-357. DOI: 10.1016/S0038-1098(03)00110-8

[48] Sefadi JS, Luyt AS, Pionteck J, Piana F, Gohs U. Effect of surfactant and electron treatment on the electrical and thermal conductivity as well as thermal and mechanical properties of

ethylene vinyl acetate/expanded graphite composites. Journal of Applied Polymer Science. 2015;**132**(32). DOI: 10.1002/app.42396

[49] Shen X, Wang Z, Wu Y, Liu X, Kim J-K. Effect of functionalization on thermal conductivities of graphene/epoxy composites. Carbon. 2016;**108**:412-422. DOI: 10.1016/j.carbon.2016.07.042

[50] Li J, Sham ML, Kim J-K, Marom G. Morphology and properties of UV/ozone treated graphite nanoplatelet/epoxy nanocomposites. Composites Science and Technology. 2007;**67**(2):296-305. DOI: 10.1016/j.compscitech.2006.08.009

[51] Wu H, Sun X, Zhang W, Zhang X, Lu C. Effect of solid-state shear milling on the physicochemical properties of thermally conductive low-temperature expandable graphite/low-density polyethylene composites. Composites Part A: Applied Science and Manufacturing. 2013;**55**:27-34. DOI: 10.1016/j.compositesa.2013.08.009

[52] Tavman I, Çeçen V, Ozdemir I, Turgut A, Krupa I, Omastova M, Novak I. Preparation and characterization of highly electrically and thermally conductive polymeric nanocomposites. Archives of Materials Science. 2009;**40**(2):84-88

[53] Lebedev S, Gefle O, Amitov E, Berchuk DY, Zhuravlev D. Poly (lactic acid)-based polymer composites with high electric and thermal conductivity and their characterization. Polymer Testing. 2017;**58**:241-248. DOI: 10.1016/j.polymertesting.2016.12.033

[54] Kim HS, Na JH, Jung YC, Kim SY. Synergistic enhancement of thermal conductivity in polymer composites filled with self-hybrid expanded graphite fillers. Journal of Non-Crystalline Solids. 2016;**450**:75-81. DOI: 10.1016/j.jnoncrysol.2016.07.038

[55] Kim HS, Kim JH, Yang C-M, Kim SY. Synergistic enhancement of thermal conductivity in composites filled with expanded graphite and multi-walled carbon nanotube fillers via melt-compounding based on polymerizable low-viscosity oligomer matrix. Journal of Alloys and Compounds. 2017;**690**:274-280. DOI: 10.1016/j.jallcom.2016.08.141

[56] Yu A, Ramesh P, Sun X, Bekyarova E, Itkis ME, Haddon RC. Enhanced thermal conductivity in a hybrid graphite nanoplatelet–carbon nanotube filler for epoxy composites. Advanced Materials. 2008;**20**(24):4740-4744. DOI: 10.1002/adma.200800401

[57] Wu K, Xue Y, Yang W, Chai S, Chen F, Fu Q. Largely enhanced thermal and electrical conductivity via constructing double percolated filler network in polypropylene/expanded graphite-multi-wall carbon nanotubes ternary composites. Composites Science and Technology. 2016;**130**:28-35. DOI: 10.1016/j.compscitech.2016.04.034

[58] Kostagiannakopoulou C, Fiamegkou E, Sotiriadis G, Kostopoulos V. Thermal conductivity of carbon nanoreinforced epoxy composites. Journal of Nanomaterials. 2016;**2016**:1-12. DOI: 10.1155/2016/1847325

[59] Yuan W, Xiao Q, Li L, Xu T. Thermal conductivity of epoxy adhesive enhanced by hybrid graphene oxide/AlN particles. Applied Thermal Engineering. 2016;**106**:1067-1074. DOI: 10.1016/j.applthermaleng.2016.06.089