Thermal polymer composites of hybrid fillers

S S Samsudin¹, M S Abdul Majid², M J M Ridzuan² and A F Osman¹

¹School of Materials Engineering, Universiti Malaysia Perlis, Jejawi, 02600, Perlis
²School of Mechatronic Engineering, Universiti Malaysia Perlis, Pauh Putra Main Campus, 02600, Perlis

Abstract. Thermal polymer composite materials for heat dissipation purposes have been widely researched over the previous decade due to their ease of processing, electric insulating, low cost and lightweight. These materials, which embedded with high thermal conductive fillers in the polymer matrix, exhibit high electrical insulation and thermal conductivity properties. These materials, however, are very hard to manage because usually it contains more than 70% volume of filler in order to be able to rapidly dissipate heat. Several approaches have been conducted by different research groups to enhance heat transfer through polymers while decreasing its filler contents. This paper presents a systematic review on several approaches which are used for enhancing the thermal properties of polymer composites by incorporating various types of fillers. The primary goal of this review is to identify any future trends in thermal polymer composites that regulate and dictate the method of thermal conduction.

1. Introduction

Since the past half-century, the drive for quicker, cheaper computing and its long-related requirements of growing device density and progressive device miniaturisation have push researchers, scientists and engineers to continuously develop fresh and ever-improving materials, instruments, procedures and design methodologies. Today, as electronic products are chasing light, pocket-sized and large-scale integration, more troubles are raised by heat issues that occur within products.

Outstanding thermal conduction is a must in electronic package and countless industrial processes that involved with heat dissipation using heat sink. To efficiently dissipate heat, thermal composite materials must have excellent thermal conductivity through which heat transfer happens with low contact resistance. The use of thermally conductive material would only be cost-consuming if excellent thermal contacts failed to be produced.

Majority of polymer resins are considered as thermal insulators. Regardless of this disadvantage, polymers are favoured for use in multiple industrial applications including circuit boards in power electronics, heat exchangers, electronic appliances and machinery. This justifies the latest important attempts to overcome the constraints of traditional polymers in studies of thermally conductive composite materials from polymer based.

2. Thermal conductivity of polymers

Polymer usually have thermal heat transfer limitations owing to polymer conductivity properties that depending on many factors, such as the crystallinity, temperature, macromolecular orientation, bonding strength, side groups molecular weight, type and defects or structural defects and processing conditions [1-2]. Polymer crystallinity has a strong effect on thermal conductivity, which means the
thermal conductivity of semi-crystalline polymer was reported to increases with the crystallinity while on the other hand, the amorphous polymer will demonstrate the lowest thermal conductivity. Table 1 lists the typical values for thermal conductivity of common polymers.

Table 1. Thermal conductivity of commercial polymers [2-4].

| Polymer                                | Thermal Conductivity at 25°C (W/mK) |
|----------------------------------------|-------------------------------------|
| Low density polyethylene (LDPE)        | 0.28 – 0.32                         |
| High density polyethylene (HDPE)       | 0.38 – 0.58                         |
| Polypropylene (PP)                     | 0.18 – 0.24                         |
| Polystyrene (PS)                       | 0.13                                |
| Polyvinyl chloride (PVC)               | 0.21                                |
| Polymethyl methacrylate (PMMA)         | 0.25                                |
| Nylon (N6,6)                           | 0.30                                |
| Polyether ether ketone (PEEK)          | 0.30                                |
| Polytetrafluoroethylene (PTFE)         | 0.27                                |
| Phenol resin                           | 0.24 – 0.29                         |
| Epoxy resin                            | 0.17 – 0.21                         |

A new, simple and cost-effective way of improving thermal dissipation from heat source is provided by thermally conductive polymer composites. As regards excellent corrosion resistance, light and processability, thermal polymer composites possess a great deal of potential as compared to traditional thermal conductive metals [5].

3. Thermal conductivity of conductive fillers

Hence the production of a high thermal conductivity polymer-based material involves the introduction of high thermal conductivity filler particles embedded into the polymer matrix. The thermal conductivity of fillers is primarily determined by the way how heat transfers in filler particles. Table 2 lists the thermal conductivity of frequently used thermally conductive fillers.

Table 2. Thermal conductivities of some thermally conductive fillers [6].

| Fillers                      | Category     | Thermal Conductivity (W/mK) |
|------------------------------|--------------|-----------------------------|
| Aluminum                    | Metal        | 234                         |
| Copper                       | Metal        | 386                         |
| Silver                       | Metal        | 427                         |
| Carbon nanotube (CNT)        | Carbon       | 1000–4000                   |
| Carbon fibre                 | Carbon       | 300–1000                    |
| Graphene                     | Carbon       | 2000–6000                   |
| Graphite                     | Carbon       | 100–400                     |
| β-Silicon nitride (β-Si3N4)  | Ceramics     | 103–200                     |
| Hexagonal boron nitride (h-BN)| Ceramics    | 185–300                     |
| Aluminum nitride (AlN)      | Ceramics     | 100–300                     |
| Diamond                      | Ceramics     | 1000                        |
| β-Silicon carbide (β-SiC)    | Ceramics     | 120                         |
| α-Alumina (α-Al2O3)          | Ceramics     | 30                          |

High filler loadings (>70 vol. %) are normally required to attain the suitable value of thermal conductivity in thermally conductive polymer composites, which represents a significant processing challenge. Indeed, the processing capabilities such as the possible extrusion and injection moulding often limit the quantity of fillers in the formulation and thus the efficiency of thermal conductivity [2]. The usual restriction of composite materials is the maximum packing fraction, which mainly caused
problems in terms of processability, mechanical performance characteristics and the case of thermally conductive composite materials is the ability to dissipate heat rapidly and successfully.

4. Thermal polymer composites of hybrid fillers
Therefore, having hybrids compositions of filler is essential for the preparation of the next generation of heat dissipation materials since hybrid fillers system can increase the packing density, lower the system viscosity as well as enhancing the thermal conductivity of the composites. Hybrid filler can be tailored by adding several mixtures of filler with different sizes, shapes, types and dimensionality (1D, 2D or 3D) into polymer-based composites. The effectiveness of hybrid filler consisting of different shapes, types, sizes and dimensional was reported by earlier researchers in their project [7-30] and lists in Table 3.

Table 3. Summary results in hybrid filler for thermal conductivity polymer composites.

| Filler            | Matrix | Filler Fraction | TC (W/mK) | Year | Ref |
|-------------------|--------|-----------------|-----------|------|-----|
| MWCNT/ nano SiC   | Epoxy  | 30 vol%         | 2.000     | 2010 | [7] |
| MWCNT/ micro SiC  | Epoxy  | 5.0/55 wt%      | 7.000     | 2010 | [8] |
| MWCNT@SiO₂        | Epoxy  | 1.0 wt%         | 0.213     | 2011 | [9] |
| BN/MWCNT          | Epoxy  | 30/1.0 vol%     | 1.912     | 2011 | [10]|
| MWCNT/MGP         | Epoxy  | 0.1/0.9 wt%     | 0.320     | 2011 | [11]|
| GO/MWCNT          | Epoxy  | 49.36/0.64 wt%  | 4.700     | 2012 | [12]|
| MWCNT@MgO         | Epoxy  | 2.0 wt%         | 0.290     | 2013 | [13]|
| RGO@SiO₂          | Epoxy  | 1.0 wt%         | 0.322     | 2013 | [14]|
| MWCNT/GO          | PEEK   | 0.45/1.0 wt%    | 0.440     | 2013 | [15]|
| MWCNT/GNP         | Epoxy  | 5.0 wt%         | 0.500     | 2013 | [16]|
| Al₂O₃@GSs         | PVDF   | 40 wt%          | 0.586     | 2013 | [17]|
| GNP/micro SiC     | Epoxy  | 5.0/55 wt%      | 7.060     | 2013 | [18]|
| SiO₂@RGO          | Epoxy  | 30 wt%          | 0.452     | 2014 | [19]|
| SiO₂@MWCNT        | PU     | 1.0 wt%         | 0.310     | 2014 | [20]|
| BN@MWCNT          | PI     | 3.0 wt%         | 0.388     | 2014 | [21]|
| BN/C nano fiber   | Epoxy  | 6.0/8.0 wt%     | 0.600     | 2015 | [22]|
| Graphene/Al₂O₃    | Silicone | 1.0 wt-%/63 vol% | 3.450 | 2015 | [23]|
| SiC nanowires/ GSs | PI     | 7.0 wt%         | 0.580     | 2015 | [24]|
| Alumina fiber/GNP | Epoxy  | 50 vol%         | 1.620     | 2015 | [25]|
| BN/MWCNT          | PE     | 50/1.0 wt%      | 1.641     | 2016 | [26]|
| Al₂O₃@GNP         | Epoxy  | 12 wt%          | 1.490     | 2016 | [27]|
| BNNs/ionic liquid | PMMA   | 34 vol%         | 7.300     | 2017 | [28]|
| Al₂O₃/BT          | PP     | 10 vol%         | 0.900     | 2018 | [29]|
| Graphite/GNP      | Epoxy  | 0.16/ 6.0 vol%  | ~2.500    | 2019 | [30]|

Generally, almost all the investigations performed prepared these composites via solution mixing [7-25,27-28] as well as moulding for thermoplastic matrix [26,29] and high-speed mixing by planetary centrifugal mixer [30]. On the other hand, these researches [7-21,23-25,27-28] were favoured by functionalized fillers and surface modifications on the fillers, with the exclusion of these researches [22,26,29-30], where the fillers as received from the supply were used. Most scientists have utilized surfactants such as coupling agents for a better interaction of fillers and matrix in order to reduce thermal interfacial resistance between matrix and fillers that will enhance thermal conductivity [12]. Interface thermal resistance seems to decrease and suppressed phonon scattering when surface treated fillers are used. Comparing the results between composites with and without surface treated particles,
the former usually demonstrate greater thermal conductivity than the latter. Most of the modified fillers with coupling agent [7-8,10,17-19,25] showed that chemical surface treatment is conducive to the enhancement of thermal conductivity of polymer composites.

For carbon fillers; multiwalled carbon nanotubes (MWCNT) [7-13, 15, 16, 20-21] and graphene nanoplatelets/nanosheets (GnP/GNS) [15], it was reported that the functionalization of the fillers increases interfacial heat transport between the epoxy matrix and the fillers compare to the non-functionalization fillers and facilitates better dispersion of fillers in the matrix, which is beneficial to the enhancement of the thermal conductivity of the composites. In the event of the carbon nanotubes (CNT), Zhou [8] in his study revealed that multiwalled carbon nanotubes (MWCNT) demonstrated the greatest potential for effective thermal conductivity improvement of epoxy compared with single-walled carbon nanotubes (SWCNT) and double-walled carbon nanotubes (DWCNT) due to their relatively lower surface area, higher aspect ratio and better dispersion in an epoxy matrix.

Some of the hybrid fillers [9,13,17,19-21,27-28], however, were designed to thermally conduct but electrically insulate by adapting the coating technique. The highly thermally conductive filler (reduced graphene oxide (RGO), MWCNT and GnP/GNS) will be coated with high electrical insulation filler (silicon dioxide (SiO2), magnesium oxide (MgO), aluminum oxide (Al2O3) and boron nitride (BN). This excellent characteristic makes coating technique a powerful candidate for thermal management in electronic packaging and electronic devices. According to Zhao et al. [20], abundant hydroxyl (-OH) groups on the surface of the SiO2 layer create outstanding compatibility with the polyurethane (PU) matrix, enhancing the interfacial interaction between PU and MWCNTs and decreasing its thermal resistance.

As studied by several researchers [10-12, 24-25,30], the utilization of high aspect ratio filler in tubes, flakes, platelets, sheets, wires and fibres structures also contribute to enhance the thermal conductivity of the composites by increasing the number of heat transfer pathways. The pathways were construct by a long and tortuous bridge that resulting in an increased contact surface area between the hybrid fillers and the matrix. This long bridge will inhibit any filler aggregation leading to reducing the phonon scattering effect at the interface by building a great thermal transfer pathway and effectively reduce interfacial thermal resistance in the composites.

According to Ren et al. [26] and Yao et al. [29], their studies indicated that morphology and fillers size are an important factor in the formation of connected filler networks, which affects the thermal conductivity of the composites. Morphology analysis of the fillers and composites discovered that the variance in size of the 0D fillers is more conducive than 2D fillers towards the formation of effective thermally conductive pathways. 2D fillers was more easily intertwined with other filler and created more compact thermally conducive networks. This enhancement was achieved by the powerful synergistic work of fillers of varying sizes, their compact bond and directional arrangement, which enable elevated thermal conductivity with low filler loading.

5. Conclusions
In summary, thermally conductive polymer composites by using hybrid fillers have been reviewed in this paper. Various fillers produce synergistic impacts, which enhance the efficient thermal conductivity above what models would expect. The synergistic impacts are most frequently based on variation in filler size, which can assist to form percolating networks and enhance their packing ratios, or variation in aspect ratios wherein high aspect ratio fillers will created long bridge networks. The thermal conductivity of hybrid polymer composites is significantly higher than that of polymer composites using any single filling scheme; hybrid filling systems can therefore simultaneously achieve a synergistic impact and reduce costs.

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References

[1] Li A, Zhang C and Zhang Y F 2017 Thermal conductivity of graphene-polymer composites: Mechanisms, properties, and applications Polymers 9 (9) 437.

[2] Han Z and Fina A 2011 Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review Progress in polymer science 36 (7) 914-44.

[3] Tsekmes I A, Kochetov R, Morshuis P H and Smit J J 2013 Thermal conductivity of polymeric composites: A review 2013 IEEE International Conference on Solid Dielectrics (ICSD) 678-681.

[4] Vadivelu M A, Kumar C R and Joshi G M 2016 Polymer composites for thermal management: a review Composite Interfaces 23 (9) 847-72.

[5] Hong J H, Park D W and Shim S E 2010 A review on thermal conductivity of polymer composites using carbon-based fillers: carbon nanotubes and carbon fibers Carbon letters 11 (4) 347-56.

[6] Chen H, Ginzburg V V, Yang J, Yang Y, Liu W, Huang Y, Du L and Chen B 2016 Thermal conductivity of polymer-based composites: Fundamentals and applications Progress in Polymer Science 59 41-85.

[7] Yang K and Gu M 2010 Enhanced thermal conductivity of epoxy nanocomposites filled with hybrid filler system of triethylenetetramine-functionalized multi-walled carbon nanotube/silane-modified nano-sized silicon carbide Composites Part A: Applied Science and Manufacturing 41 (2) 215-21.

[8] Zhou T, Wang X, Liu X and Xiong D 2010 Improved thermal conductivity of epoxy composites using a hybrid multi-walled carbon nanotube/micro-SiC filler Carbon 48 (4) 1171-6.

[9] Cui W, Du F, Zhao J, Zhang W, Yang Y, Xie X and Mai Y W 2011 Improving thermal conductivity while retaining high electrical resistivity of epoxy composites by incorporating silica-coated multi-walled carbon nanotubes Carbon 49 (2) 495-500.

[10] Teng C C, Ma C C, Chiu K C, Lee T M and Shih Y F 2011 Synergetic effect of hybrid boron nitride and multi-walled carbon nanotubes on the thermal conductivity of epoxy composites Materials Chemistry and Physics 126 (3) 722-8.

[11] Yang S Y, Lin W N, Huang Y L, Tien H W, Wang J Y, Ma C C, Li S M and Wang Y S 2011 Synergetic effects of graphene platelets and carbon nanotubes on the mechanical and thermal properties of epoxy composites Carbon 49 (3) 793-803.

[12] Im H and Kim J 2012 Thermal conductivity of a graphene oxide–carbon nanotube hybrid/epoxy composite Carbon 50 (15) 5429-40.

[13] Du F P, Tang H and Huang D Y 2013 Thermal conductivity of epoxy resin reinforced with magnesium oxide coated multiwalled carbon nanotubes International Journal of Polymer Science 2013.

[14] Hsiao M C, Ma C C, Chiang J C, Ho K K, Chou T Y, Xie X, Tsai C H, Chang L H and Hsieh C K 2013 Thermally conductive and electrically insulating epoxy nanocomposites with thermally reduced graphene oxide–silica hybrid nanosheets Nanoscale 5 (13) 5863-71.

[15] Hwang Y, Kim M and Kim J 2013 Improvement of the mechanical properties and thermal conductivity of poly (ether-ether-ketone) with the addition of graphene oxide-carbon nanotube hybrid fillers Composites Part A: Applied Science and Manufacturing 55 195-202.

[16] Safidari M and Al-Haik M S 2013 Synergetic electrical and thermal transport properties of hybrid polymeric nanocomposites based on carbon nanotubes and graphite nanoplatelets Carbon 64 111-21.

[17] Qian R, Yu J, Wu C, Zhai X and Jiang P 2013 Alumina-coated graphene sheet hybrids for electrically insulating polymer composites with high thermal conductivity Rsc Advances 3 (38) 17373-9.

[18] Zhou T, Wang X, Cheng P, Wang T, Xiong D and Wang X 2013 Improving the thermal conductivity of epoxy resin by the addition of a mixture of graphite nanoplatelets and silicon carbide microparticles Express Polym Lett 7 (7) 585-94.
[19] Huang L, Zhu P, Li G, Lu D D, Sun R and Wong C 2014 Core–shell SiO$_2$@ RGO hybrids for epoxy composites with low percolation threshold and enhanced thermo-mechanical properties *Journal of Materials Chemistry A* 2 (43) 18246-55.

[20] Zhao J, Du F, Cui W, Zhu P, Zhou X and Xie X 2014 Effect of silica coating thickness on the thermal conductivity of polyurethane/SiO$_2$ coated multiwalled carbon nanotube composites *Composites Part A: Applied Science and Manufacturing* 58 1-6.

[21] Yan W, Zhang Y, Sun H, Liu S, Chi Z, Chen X and Xu J 2014 Polyimide nanocomposites with boron nitride-coated multi-walled carbon nanotubes for enhanced thermal conductivity and electrical insulation *Journal of Materials Chemistry A* 2 (48) 20958-65.

[22] Raza M A, Westwood A V, Stirling C and Ahmad R 2015 Effect of boron nitride addition on properties of vapour grown carbon nanofiber/rubbery epoxy composites for thermal interface applications *Composites Science and Technology* 120 9-16.

[23] Yu W, Xie H, Yin L, Zhao J, Xia L and Chen L 2015 Exceptionally high thermal conductivity of thermal grease: synergistic effects of graphene and alumina *International Journal of Thermal Sciences* 91 76-82.

[24] Dai W, Yu J, Liu Z, Wang Y, Song Y, Lyu J, Bai H, Nishimura K and Jiang N 2015 Enhanced thermal conductivity and retained electrical insulation for polyimide composites with SiC nanowires grown on graphene hybrid fillers *Composites Part A: Applied Science and Manufacturing* 76 73-81.

[25] Zha J W, Zhu T X, Wu Y H, Wang S J, Li R K and Dang Z M 2015 Tuning of thermal and dielectric properties for epoxy composites filled with electrospun alumina fibers and graphene nanoplatelets through hybridization *Journal of Materials Chemistry C* 3 (27) 7195-202.

[26] Ren P G, Si X H, Sun Z F, Ren F, Pei L and Hou S Y 2016 Synergistic effect of BN and MWCNT hybrid fillers on thermal conductivity and thermal stability of ultra-high-molecular-weight polyethylene composites with a segregated structure *Journal of Polymer Research* 23 (2) 21.

[27] Sun R, Yao H, Zhang H B, Li Y, Mai Y W and Yu Z Z 2016 Decoration of defect-free graphene nanoplatelets with alumina for thermally conductive and electrically insulating epoxy composites *Composites Science and Technology* 137 16-23.

[28] Morishita T and Takahashi N 2017 Highly thermally conductive and electrically insulating polymer nanocomposites with boron nitride nanosheet/ionic liquid complexes *RSC Advances* 7 (58) 36450-9.

[29] Yao J, Hu L, Zhou M, You F, Jiang X, Gao L, Wang Q, Sun Z and Wang J 2018 Synergistic Enhancement of Thermal Conductivity and Dielectric Properties in Al$_2$O$_3$/BaTiO$_3$/PP Composites *Materials* 11 (9) 1536.

[30] Levy I, Wormser E M, Varenik M, Buzaglo M, Nadvir R and Regev O 2019 Graphene–graphite hybrid epoxy composites with controllable workability for thermal management *Beilstein journal of nanotechnology* 10 (1) 95-104.