

Thermal Management in Polymer Composites: A Review of Physical and Structural Parameters

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Contrary to expectation, the thermal conductivity of carbon-polymer nanocomposites has been reported to be low near the lower boundary of the rule of mixtures. Various dispersing processes have been developed to achieve uniform dispersion of the nanocarbon fillers, including an in situ polymerization process based on ring-opening polymerizable oligoesters. However, even if the nanofiller is well dispersed, phonon scattering due to the interfacial thermal resistance at the nanofiller-matrix interface and the contact thermal resistance at the nanofiller-nanofiller interface is inevitable, and this is the main cause of the low thermal conductivity of the nanocomposite. When the nanofiller is incorporated in a high content, the interfacial thermal resistance can be overcome by forming a contacted three-dimensional (3D) filler network between the fillers. Recently, thermal percolation behavior has been reported to occur in composite materials with sufficiently high carbon filler content. Also, the thermal conductivity can be synergistically improved by the simultaneous incorporation of fillers of different sizes and shapes, forming a contacted 3D filler network. It can be concluded that large fillers with high thermal conductivity are suitable for thermally conductive composites, while nanofiller is advantageous for heat-insulating composites.

1. Introduction

Thermal management and control of heat transfer are critically important to solve the potential problems caused by miniaturization and integration of electronic devices.^[1] Lightweight

materials with excellent thermal conductivity and processability are required for the construction of miniaturized electronic devices to smoothly transfer the heat generated from various sources integrated in its limited space. Various studies have been performed on polymer composites containing thermally conductive fillers that are expected to satisfy such demands.^[2]

Polymer-based composites are well known for their light weight, ease of processing, and low cost.^[3] In recent years, studies have been carried out to replace metal materials with polymer-based composites with improved thermal conductivity due to incorporation of thermally conductive fillers.^[4] Traditionally, metal, ceramic, and carbon materials have been used as the thermally conductive fillers, such as ceramic fillers (boron nitride (BN),^[5,6] silicon carbide (SiC),^[7] zirconium boride (ZrB₂),^[8] and beryllium oxide (BeO)^[9]), metallic fillers^[10] (aluminum oxide (Al₂O₃),^[11] copper (Cu),^[12] aluminum (Al),^[13] titanium dioxide (TiO₂),^[14] aluminum nitride (AlN)^[15]), and carbon-based fillers^[16] (graphite,^[17] carbon fiber (CF),^[18] carbon black (CB),^[19] carbon nanotubes (CNTs),^[20,21] graphene^[22]). The inherent thermal conductivity of these fillers is one of the most important physical parameters to improve the thermal conductivity of the polymer composites.

Polymer composites filled with ceramic fillers have been used in electronic applications. The thermal conductivity of ceramic fillers is reported in the range from tens to hundreds of W mK⁻¹^[23]; that is, BN: 250–300 W mK⁻¹, SiC: 75–125 W mK⁻¹, and BeO: 260 W mK⁻¹. The thermal conductivity of polymer composites containing the ceramic fillers are known to be affected by packing density,^[24] mixing method,^[25] surface treatment,^[26] and size distribution and particle size.^[27]

Polymer composites filled with metallic fillers show excellent thermal and electrical conductivities. However, the polymer composites have limited use in applications requiring lightweight construction due to the high density.^[28] The thermal conductivity of metallic fillers is reported to be over tens of W mK⁻¹; that is, gold (Au): 345 W mK⁻¹, Cu: 483 W mK⁻¹, and Al: 204 W mK⁻¹.

Recent studies have reported on the thermal conductivity of polymer composites based on carbon fillers, which show

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relatively high thermal conductivity values compared to those of ceramic and metal fillers. The thermal conductivity of graphite is reported to span the wide range of 119–165 W mK⁻¹.^[29–32] CF is known to exhibit anisotropic thermal conductivities along the axial and transverse directions. For example, A CF mat showed a high thermal conductivity of 2000 W mK⁻¹ in the axial direction but a relatively low thermal conductivity of 10–110 W mK⁻¹ in the transverse direction.^[33,34] The thermal conductivity of nanocarbons such as CNTs^[2] and graphene^[35,36] has been reported to be 1800–6500 W mK⁻¹. Specifically, the thermal conductivity of single-walled carbon nanotubes (SWCNTs) is reported to be 2800–6000 W mK⁻¹,^[28] while multi-walled carbon nanotubes (MWCNTs) show a thermal conductivity of 3000 W mK⁻¹ or higher.^[37]

Most of the reported thermal conductivity results of the polymer composites containing nanocarbon fillers have been reported to be near the lower boundary of the rule of mixtures, as shown in **Figure 1**, that is, without synergistic improvement.^[2] In this review, we summarize the heat transfer mechanism in crystalline and amorphous materials, and then discuss the thermal conductivities of polymer composites filled with carbon fillers. Also, we address physical factors affecting the low thermal conductivity of polymer composites filled with the nanocarbon fillers, such as dispersion, filler size and shape, thermal percolation, synergistic enhancement. Finally, we introduce examples by which using nanofiller can improve thermal insulation properties.

2. Heat Conduction Mechanism

A fundamental understanding of the heat transfer mechanism in crystalline materials is needed to manage thermal conduction in polymer composites. **Figure 2** shows a schematic of heat transfer in a crystalline material.^[38] External heat energy is transferred to the atoms on the surface of the crystalline material and then converted to vibration energy. This vibration energy transfers the thermal energy in wave form to surrounding atoms at the same speed. When the vibrational

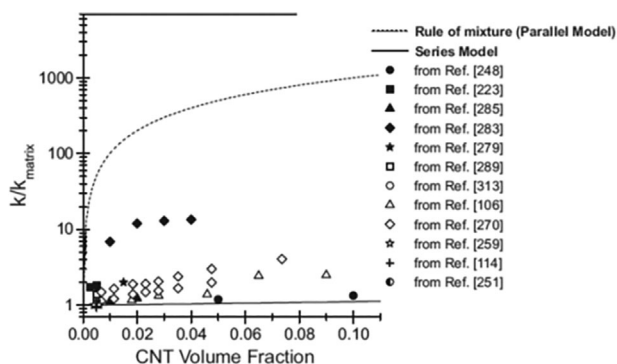


Figure 1. Overview of published data on thermal conductivity enhancement compared with reference matrix, versus CNT loading. The Y axis uses a logarithmic scale, enlarging differences between low thermal conductivity values. Reproduced with permission.^[2] Copyright 2011, from Elsevier Ltd.



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energy reaches atoms on the opposite surface, heat conduction is completed.^[38,39]

Unlike crystalline materials, heat transfer in amorphous polymers is achieved by the heat diffusion mechanism, as shown in **Figure 3**.^[38] First of all, the heat reaches the surface atoms closest to the external heat source. The heat is transferred to adjacent atoms, but does not proceed in a wave form; instead, it slowly diffuses, causing disorderly vibration

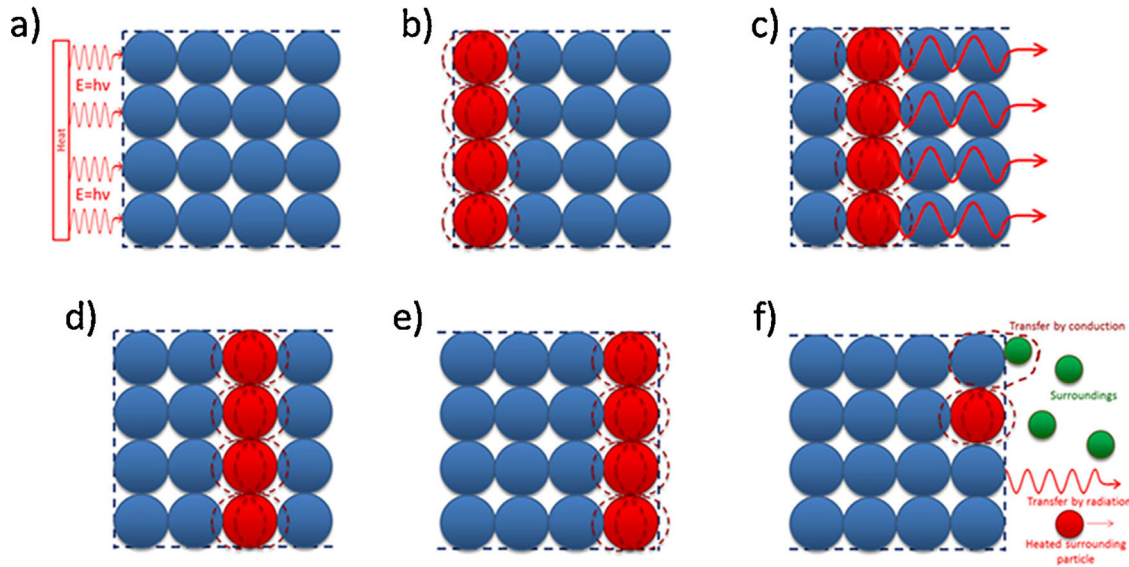


Figure 2. Mechanism of thermal conduction in a crystalline material. Reproduced with permission.^[38] Copyright 2016, Elsevier Ltd.

and rotation in atoms of all polymer chains, and then is dispersed into adjacent chains.

In general, the thermal conductivity of non-crystalline materials is lower than that of highly crystalline materials such as metals, ceramics, and carbon materials.^[4] For example, the thermal conductivity of amorphous polymers such as polymethylmethacrylate and polystyrene is about 0.2 W mK^{-1} , while the thermal conductivity of highly crystalline high-density polyethylene is 0.5 W mK^{-1} .^[40] In addition, the thermal conductivity of polytetrafluoroethylene, which is a semi-crystalline polymer, increases in proportion to its crystallinity.^[41] These results indicate that crystallinity is an important physical factor in determining the thermal conductivity of a material. However, in actual experimental results, it is difficult to reveal the relationship between thermal conductivity and crystallinity because the crystallinity can be affected by many parameters such as defects, bond strength, processing conditions, temperature, molecular weight, etc.^[42]

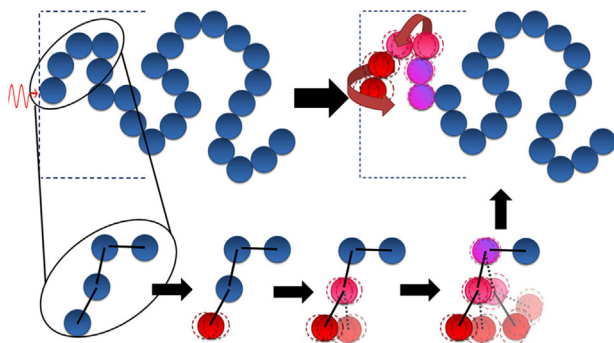


Figure 3. Mechanism of thermal conduction in an amorphous polymer. Reproduced with permission.^[38] Copyright 2016, Elsevier Ltd.

3. Physical Factors Determining Thermal Conductivity of Polymer Composites Containing Carbon Fillers

The inherent thermal conductivity of the incorporated carbon filler is one of the most important parameters determining the thermal conductivity of carbon-based polymer composites. In addition, structural characteristics of the carbon filler, such as defect level, dispersion, and shape of the filler, can be important parameters. Structural defects in the carbon filler cause scattering, reflections, diffraction, or refraction of phonons, which interfere with free movement and reduce the

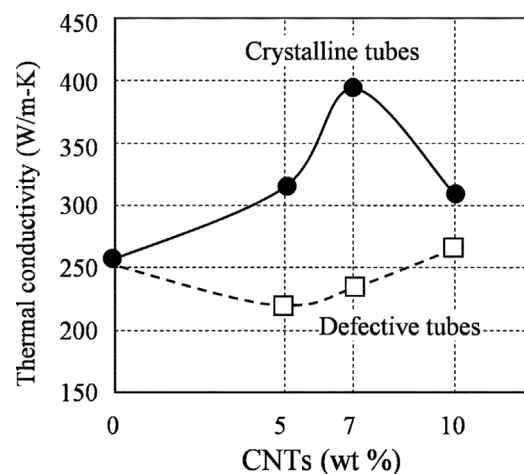


Figure 4. Thermal conductivities of carbon fiber/phenolic resin composites containing either highly crystalline MWCNTs or defective MWCNTs, respectively, as a function of the amount of the added MWCNTs, respectively. Note that the maximum value of the thermal conductivity for the composite with the crystalline MWCNTs is exactly the same as that of copper. Reproduced with permission.^[45] Copyright 2007, AIP publishing.

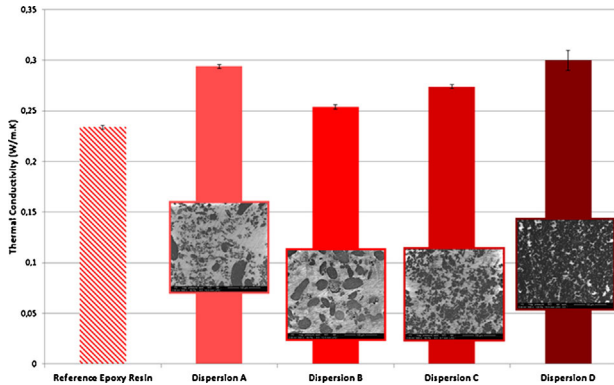


Figure 5. Experimental thermal conductivity versus filler dispersion. Reproduced with permission.^[38] Copyright 2016, Elsevier Ltd.

thermal conductivity. High temperature heat treatment is well known as an efficient way to increase the structural integrity of carbon fillers.^[43,44] Weisenberger et al.^[43] investigated the relationship between graphitization temperature and CF structure. Also, it has been reported that treatment of CF at 2500 °C reduces impurities and increases crystallinity.^[44] Kim et al.^[45] observed that high-crystalline CNTs exhibited higher thermal conductivity than defective CNTs, as shown in **Figure 4**.

Filler dispersion is another important physical factor affecting the thermal conductivity of a carbon-polymer composite. Song et al.^[46] observed that excellent dispersion of CNTs positively affects the thermal conductivity of a CNT/epoxy composite. **Figure 5** shows the relationship between the dispersion of carbon nanofibers (CNFs) and the thermal conductivity of polymer composites fabricated by various processes and the excellent dispersion of CNFs was the important factor to improve the thermal conductivity of the composite.^[38] However, Dos Santos et al.^[47] reported that the effect of dispersion on thermal conductivity is insignificant in composites filled with CNT content of more than 8 vol%, and the result was due to the

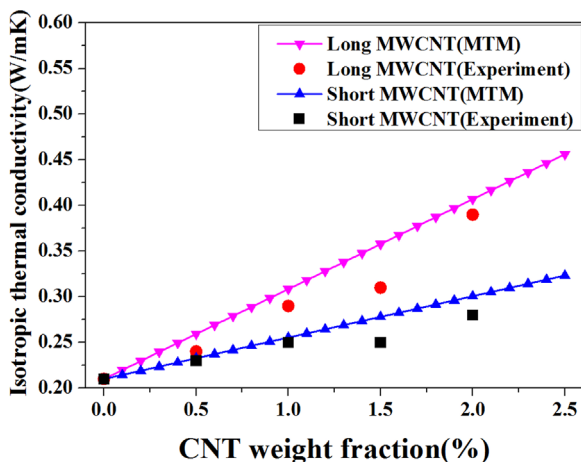


Figure 6. Isotropic thermal conductivity of polymer composites filled with short and long MWCNTs. Reproduced with permission.^[48] Copyright 2015, Elsevier Ltd.

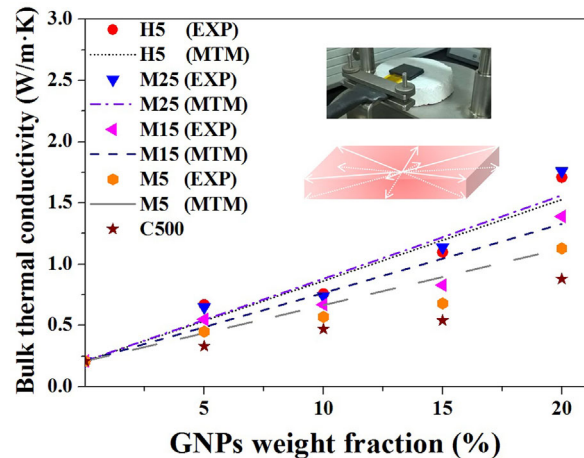


Figure 7. Bulk thermal conductivity of polymer composites filled with GNPs. Reproduced with permission.^[49] Copyright 2016, Nature Publishing Group.

agglomeration of CNTs above a certain content threshold. Therefore, the composites filled with a high content of carbon filler has recently become an active research interest.

The shape of the carbon filler is also an important factor affecting thermal conductivity of the composite. To clearly identify the effect of MWCNT length on thermal conductivity, experiments were designed to control other physical factors such as filler content, dispersion, and functionality. MWCNT/polycarbonate (PC) composites were prepared by melt blending with the MWCNT content set to within 2 wt% to induce good dispersion without added dispersants.^[48] The long and short MWCNTs used in the experiment showed similar defect levels, functionalities, and wall thicknesses. As shown in **Figure 6**, the thermal conductivities of composites filled with long MWCNTs were higher than those of composites filled with short MWCNTs.^[48] Another study investigated the effects of the lateral size and thickness of graphene nanoplatelets (GNPs) on the thermal conductivity of GNP/PC composites, as shown in **Figure 7**.^[49] Similar to previous experiments, physical factors other than GNP geometry, such as filler content, dispersion, and functionality were controlled to minimize their effects. The results showed that greater lateral size and thicker thickness of GNP induced higher thermal conductivity of the GNP/PC composites.^[49]

4. High Dispersion of Carbon Fillers Based on In Situ Polymerizable Oligoester

Typical composite manufacturing methods are melt blending, solution mixing, in situ polymerization, and etc.^[50–57] The melt blending is an economical and convenient process with low cost, rapid production, and environmental benefits. High temperatures and high shear forces applied during the processing are ideal for mixing fillers with high melt viscosity thermoplastics. However, excellent dispersion is not expected when high filler content is used, because the viscosity of the polymer melt is much higher than that of the solvent. In contrast, the solution

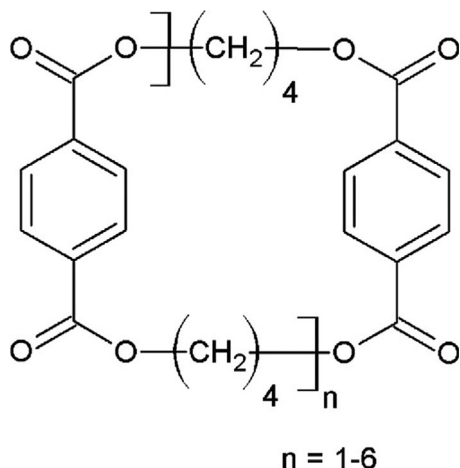


Figure 8. Chemical structure of CBT oligomers. Reproduced with permission.^[60] Copyright 1998, American Chemical Society.

mixing can be expected to provide good dispersion due to the low viscosity of the solvent. However, it is necessary to remove the solvent, which is a time-consuming process and causes re-agglomeration of the carbon filler during the drying process. Finally, the in situ polymerization is a method in which fillers are dispersed among small molecules such as monomers and oligomers, and then they are polymerized; this process can lead to excellent filler dispersion similar to that occurring in solution mixing. The in situ polymerization can also incorporate various chemical reactions to induce covalent bonds between polymer matrices and functionalized fillers, which can help improve the interfacial and mechanical properties of composites.^[58,59]

Cyclic butadiene terephthalate (CBT) is an oligoester with two to seven repeating units, as shown in **Figure 8**, and can be used as a matrix for in situ polymerization.^[60] It softens at about 140 °C due to ring-opening of the oligomer, and completely melts at a temperature of 160–190 °C.^[61] When the oligomer is melted prior to the in situ polymerization, the viscosity of the molten oligomer is low enough to cause excellent filler dispersion.^[62,63] Since the oligomer is converted to a polymer during the in situ polymerization by continuous heating above 160 °C, the melting temperature after the in situ polymerization increases to 240 °C.^[64]

Figure 9 shows the fabrication process for CBT-based composites filled with well-dispersed nanocarbons.^[65,66] Noh et al.^[66] developed a technique for fabricating composites in

which GNP particles are well dispersed using both solvent-free powder mixing of the GNP filler and CBT powder and in situ polymerization of the low-viscosity CBT matrix. GNP/polymerized CBT (pCBT) composites were fabricated and the filler dispersion was evaluated by calculating the filler to filler distance using image processing of scanning electron microscopy (SEM) images. The results showed that introduction of either the oxidation group or the phenyl group positively influenced uniform dispersion of GNP fillers.

Composites containing nanocarbon fillers such as MWCNT and GNP were prepared using a CBT oligomer matrix, and their thermal conductivities investigated.^[65–68] In addition, thermal conductivities of pCBT composites containing the carbon fillers were theoretically calculated on the basis of the modified Mori-Tanaka model, and those values were in good agreement with the experimentally-obtained results.^[67,68] In the case of MWCNT/pCBT nanocomposites, the increase in the thermal conductivity was small regardless of the filler content, but the in-plane thermal conductivity of the pCBT composite containing 20 wt% GNP was 1.98 W mK⁻¹.^[67,68] Thermal conductivity was maximized by the formation of an efficient filler network, that is, advantageous for phonon transmission.^[65–68]

5. Interfacial Thermal Resistance and Contact Thermal Resistance

The outstanding intrinsic thermal conductivity of carbon fillers was described in the introduction part; in particular, nanocarbons such as CNT and graphene exhibit the highest thermal conductivity among known materials. However, considering the excellent thermal conductivity of nanocarbons, the overall thermal conductivity results of polymer composites filled with highly dispersed carbon fillers were reported to be lower than expected near the lower boundary of Figure 1.^[2] The thermal conductivity values lower than expected ones are due to interfacial thermal resistance between the polymer matrix and the filler, and also to the contact thermal resistance between the fillers, as shown in **Figure 10**.^[2,69–73]

Theoretically, phonon transmission through the phase interface depends on the vibration frequencies of the two phases making up the interface; phonon scattering is caused by vibration frequency mismatches due to the presence of interfacial thermal barriers.^[70,71] Interfacial thermal resistance occurs when phonon transmission occurs through the interface between two different phases.^[2,69–71] The interfacial thermal resistance is also caused by

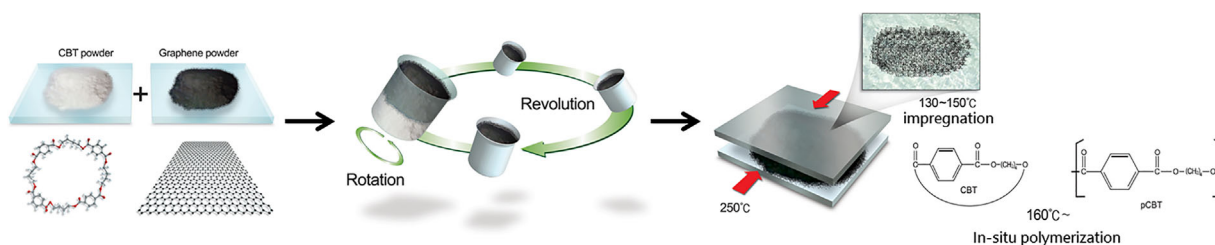


Figure 9. Schematic diagram of the solvent-free process for the preparation of graphene-polymer composites with excellent dispersion based on simple powder mixing and in situ polymerization of CBT oligomers. Reproduced with permission.^[66] Copyright 2015, Nature Publishing Group.

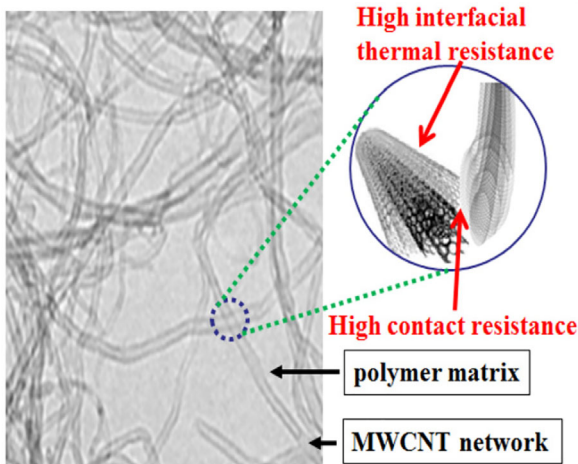


Figure 10. Schematic diagram explaining the low thermal conductivity of polymer/CNT composites. The small contact area between CNTs results in high contact resistance, while high interfacial thermal resistance is caused by the barrier to heat flow associated with the differences in the phonon spectra of the two phases and the imperfect physical contact between CNT and the polymer matrix. Reproduced with permission.^[69] Copyright 2012, Elsevier Ltd.

incomplete physical contact between the two phases,^[70,71] which can result in heat loss. In carbon/polymer composites, the interfacial thermal resistance occurs at the interface between the carbon filler and the polymer matrix. When two similar or different fillers are in contact and form a junction, only a small portion of the actual surface area is involved due to the non-planarity and roughness of the contact surface; this causes contact thermal resistance.^[72,73] At this time, heat transfer at the junction can only occur through the actual contact area.

Experiments investigated the effect of interfacial thermal resistance by observing the thermal conductivity of composites filled with various carbon allotropic fillers.^[74] The thermal conductivities of polymer composites filled with carbon fillers of different sizes and shapes such as CB, MWCNT, GNP, graphite, expanded graphite (EG), and pitch-based carbon fibers (PCFs) were measured and compared, as shown in **Figure 11**. Regardless of the type of filler, the thermal conductivity increased linearly with filler contents up to 20 wt%. Although the intrinsic thermal conductivity of nanocarbon filler is the highest, the thermal conductivity of composites filled with the nanocarbon fillers was not significantly enhanced. This is due to the quantitative increase in interfacial area of the filler-polymer matrix due to the large surface area of the nanocarbon filler, resulting in increased interfacial thermal resistance. On the other hand, the thermal conductivity of composites filled with micro-sized one-dimensional PCF and EG including intercalation spacing was effectively enhanced. In other words, it was confirmed that the thermal conductivity of composites filled with micro-sized carbon filler was more efficiently increased than that of composites incorporated with nano-sized carbon filler. Since the surface area of the micro-sized filler is much smaller than that of the nanofiller, the interfacial area of the filler-polymer matrix is greatly reduced, which reduces the interfacial thermal resistance and is advantageous for phonon transport.

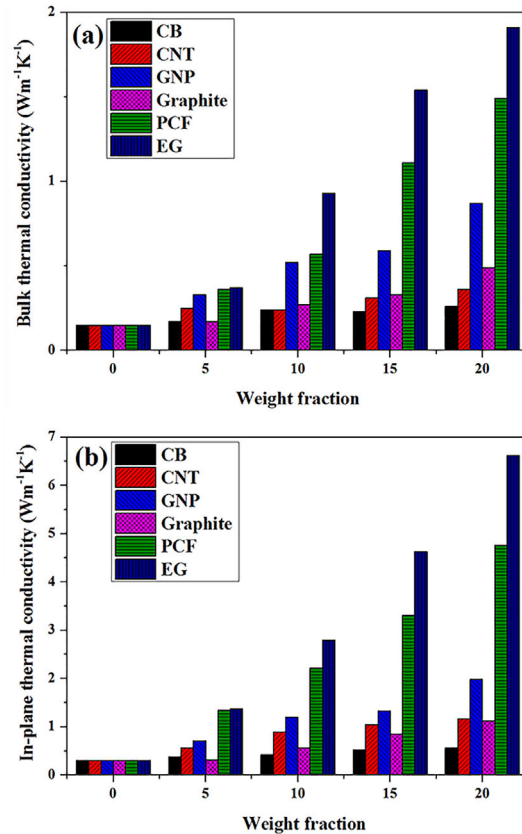


Figure 11. Thermal conductivities of the carbon filler/pCBT composites with respect to filler weight fraction: a) bulk; b) in-plane. Reproduced with permission.^[74] Copyright 2016, WILEY-VCH Verlag GmbH & Co.

6. Thermal Percolation

There is still debate as to whether there is a thermal percolation phenomenon that dramatically increases the thermal conductivity of the composite beyond a certain amount.^[72–77] Some studies reported that thermal conductivity of the composite was improved linearly with increasing filler content.^[75,76] However, other studies^[77–84] reported that the thermal percolation

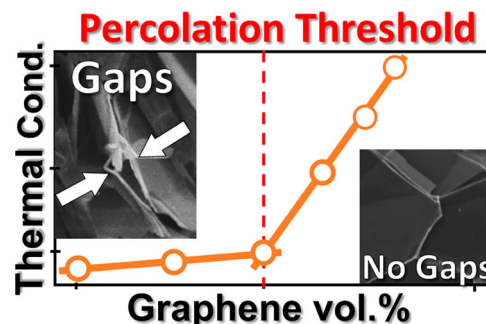


Figure 12. Thermal percolation behavior in GNP filled composites. Reproduced with permission.^[79] Copyright 2015, American Chemical Society.

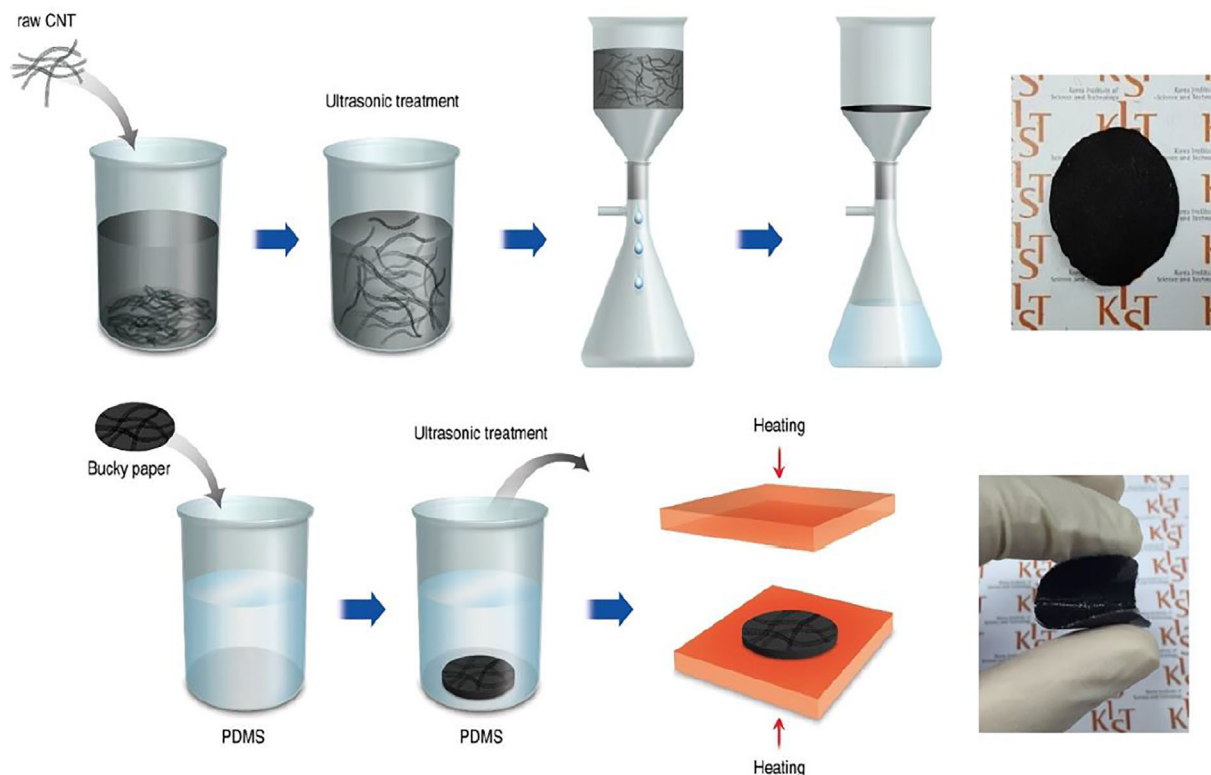


Figure 13. Schematic of two-step process involving buckypaper fabrication and vacuum filtration of MWCNTs. Reproduced with permission.^[85] Copyright 2016, MDPI.

behavior occurs at a specific filler content, leading to sudden increase of the thermal conductivity. Shtein et al.^[79] identified thermal percolation behavior in polymer composites filled with GNPs, and insisted that the cause is direct contacts between fillers, as shown in **Figure 12**. Kim et al.^[80] quantitatively revealed the relationship between the degree of direct contacts between fillers and the degree of enhancement in the thermal conductivity. In general, because phonon scattering due to interfacial thermal resistance is known to be larger than that caused by contact thermal resistance, increasing the degree of direct contacts between fillers can be an effective way to enhance the thermal conductivity of composites.^[2,80]

While the excellent properties of CNTs lead to them being widely used for enhancing the thermal conductivity of composites, it is difficult to obtain the CNT-based composites with excellent thermal conductivity due to the poor dispersion of the fillers in the polymer matrix. Many studies have been performed on chemical treatments of CNTs and the manufacturing methods of the CNT-based composites in attempts to solve the poor dispersion.^[2,65,69] Of the various types of CNT based materials, buckypaper exhibits excellent electrical, thermal, and mechanical properties and can effectively control the dispersion of large quantities of CNTs. Cha et al.^[85] fabricated continuous MWCNT buckypaper by the vacuum filtration method, and then impregnated the buckypaper with polydimethylsiloxane (PDMS) resin to produce a flexible composite film with enhanced thermal conductivity and mechanical properties, as shown in

Figure 13. The thermal conductivity of the buckypaper/PDMS composites were enhanced up to 75% compared to individual MWCNT/PDMS composites because the MWCNTs in the buckypaper were in direct contact and formed an efficient three-dimensional (3D) network that was advantageous for phonon transmission.

Buckypapers and graphene papers have limited commercial use due to the relatively high cost of raw nanocarbon material, long fabrication time, and high fabrication cost. In contrast, expanded graphite is suitable as a filler for thermally conductive composites due to its high conductivity, ease of processing and low manufacturing cost.^[80] **Figure 14** shows the unique structural characteristics of EG (\approx interlayer spacing), which are advantageous for the effective formation of direct contacts between EG fillers inside a composite. Expandable graphite (EaG), a precursor of EG, is generally prepared by the acid treatment of graphite and the EaG expands more as it is treated at higher temperatures. EaG was expanded up to 800% as it is treated at 800 °C. The thermal conductivity (10.77 W mK^{-1}) of the epoxy composite filled with 20 wt% of the 800% EG was enhanced by 673%, compared to that (1.6 W mK^{-1}) of epoxy composites filled with 20 wt% of untreated EaG. The internal structures of EG/epoxy composites were observed using a 3D non-destructive method, micro-computed tomography (CT), as shown in **Figure 15**. The expansion of the EG caused direct contacts between the EG fillers, forming a larger and more-connected filler network, which leading to the dramatic increase of the thermal conductivity.

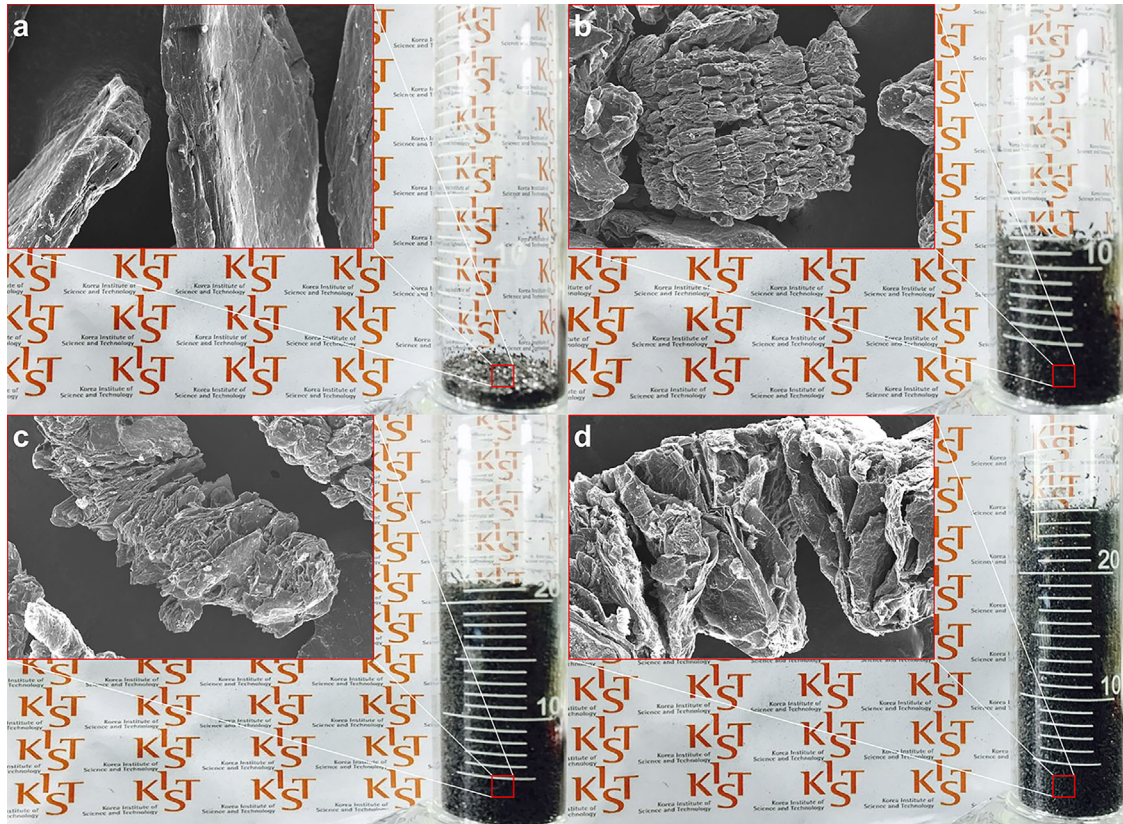


Figure 14. Inductively coupled plasma (ICP) treated EG a) before treatment, b) at 400 °C, c) at 600 °C, and d) at 800 °C. Reproduced with permission.^[80] Copyright 2017, Elsevier Ltd.

7. Synergistic Enhancement by Simultaneously Filling Fillers of Various Size and Shape

The thermal conductivity of composites has been reported to be synergistically enhanced by the simultaneous incorporation of different types of thermally conductive fillers.^[68,69,79,86–88] In EG- and CF-based composites, the synergistic enhancement was particularly clear.^[86–88] The thermal conductivity of PC composites filled with EG of 9.9wt% and MWCNT of 0.1wt% simultaneously was found to be 49% higher than that of PC composites incorporating 10 wt% of EG alone.^[86] Similarly, the thermal conductivity of pCBT composites can be enhanced by the simultaneous incorporation of PCF and GNP. The isotropic and in-plane thermal conductivities of the pCBT composites filled with 5 wt% PCF and 15 wt% GNP were 82% and 183% higher than those of pCBT composites filled with 20wt% of GNP alone.^[87] In PC composites filled with EG of two different sizes, synergistic enhancement based on self-hybridization has also been reported.^[88] The thermal conductivity of PC composites simultaneously filled with 10 wt% EG of two different sizes was enhanced by 20.7%, compared to that of PC composites containing 20 wt% EG of a single size.

Such synergistic improvements resulting from the simultaneous incorporation of fillers are determined by factors such as the effective formation of a heat transfer network that minimizes interfacial thermal resistance and phonon scattering. Recently, as shown in **Figure 16**, a theoretical modeling based on

micromechanics was developed that can illustrate the synergistic improvement of the thermal conductivity of composites by the simultaneous incorporation of GNP and MWCNT nanofillers.^[89] However, the topic on the synergistic enhancement should be studied more clearly both phenomenologically and theoretically.

8. Thermally Insulating Composites Based on Nanofillers

So far, this review has focused on using thermally conductive fillers to improve the thermal conductivity of a composite. Contrary to expectations, the thermal conductivity of nanocomposites filled with nanocarbon fillers was not significantly enhanced due to interfacial and contact thermal resistances. In contrary to, the application of nanofiller to polymer composites can be advantageous for the development of insulating composites because it maximizes the interfacial and contact thermal resistances.

Thermally insulating polymer composites are beneficial in various applications related to energy conservation and environmental protection, including clothing and building materials. The lightest and most highly porous solids, aerogels, were discovered by Kistler in the early 1930s.^[90] The silica aerogel is an open cell structure composed of nanoparticles that exhibits high specific surface area (500–1200 m²g⁻¹), low

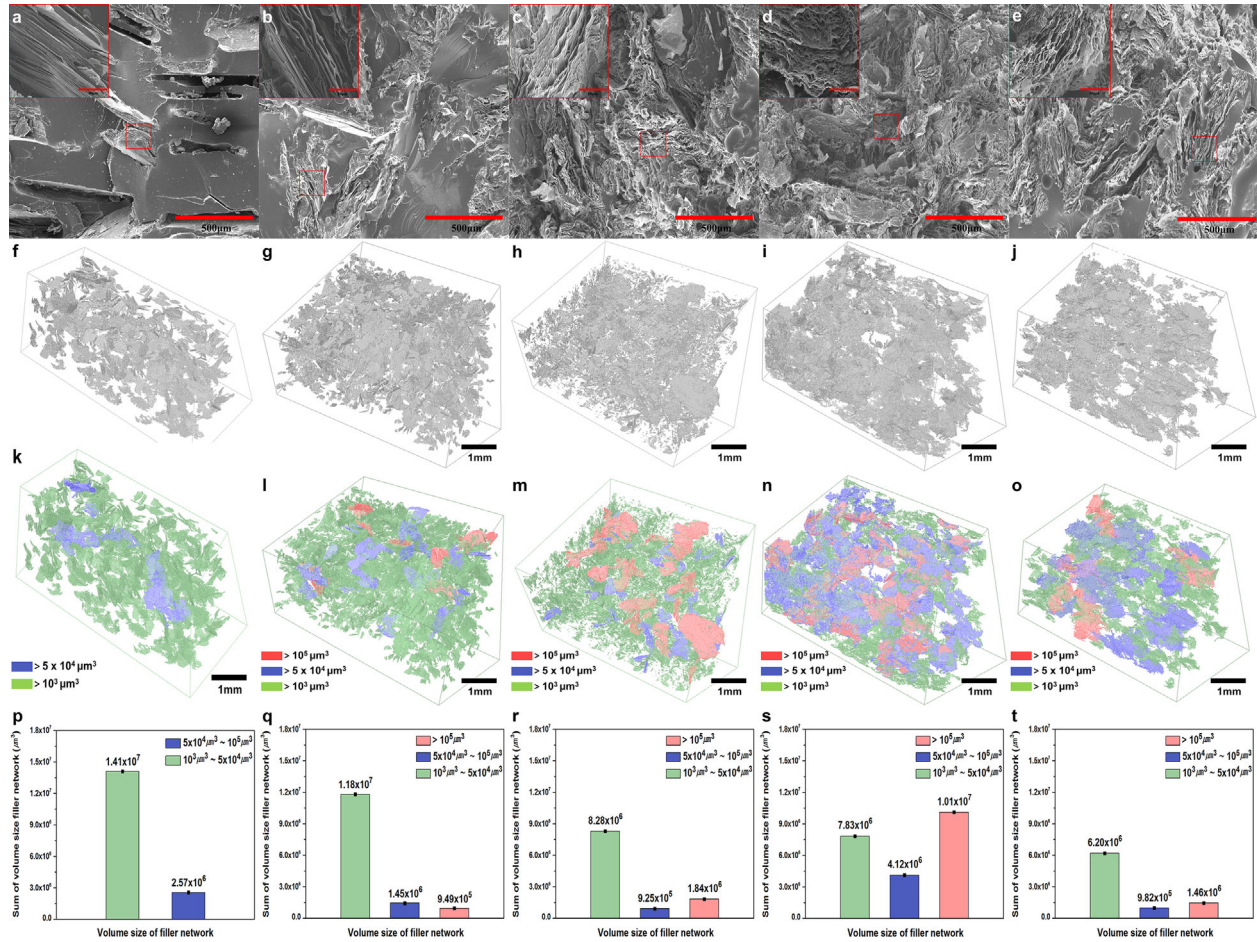


Figure 15. SEM and micro-CT images of epoxy/EG composites with respect to ICP treatment temperature and EG filler content. Reproduced with permission.^[80] Copyright 2017, Elsevier Ltd.

density ($0.003\text{--}0.1 \text{ g cm}^{-3}$), low dielectric constant ($1.1\text{--}2.0$), and low thermal conductivity ($0.013\text{--}0.014 \text{ W mK}^{-1}$). Due to high thermal insulation capability of the silica aerogels, they are used where insulation performance is needed, such as in

acoustic and electronic applications, space shuttles, and nuclear reactors.^[90–96]

The thermal conductivity of epoxy composites filled with silica aerogels is shown in Figure 17a.^[97] As shown in Figure 17a, the measured thermal conductivity values were not proportional to the silica aerogel content. This was considered to result from the porous open cell structure of silica aerogels capable of external inflow. Since the epoxy resin impregnated the aerogel pores during the manufacturing process, the thermal conductivity of the composite exhibited higher than expected. Therefore, maintaining the porosity of the silica aerogel was an important factor for lowering the thermal conductivity of a composite.

In order to maintain pores of the silica aerogels, pre-mixing with ethanol was performed as shown in Figure 17b.^[97] Incorporation of ethanol into the pores protects them from impregnation of the epoxy resin during composite fabrication. The pores of the aerogels are restored by evaporating the ethanol during the curing process. The thermal conductivity of epoxy composites in which the silica aerogel pores were restored, was lowered to 0.04 W mK^{-1} .

In order to develop polymer composites with further improved heat resistance, a fabrication method for polyimide composites filled with silica aerogels was designed as shown in Figure 18.^[98] When silica aerogels were mixed with polyamic

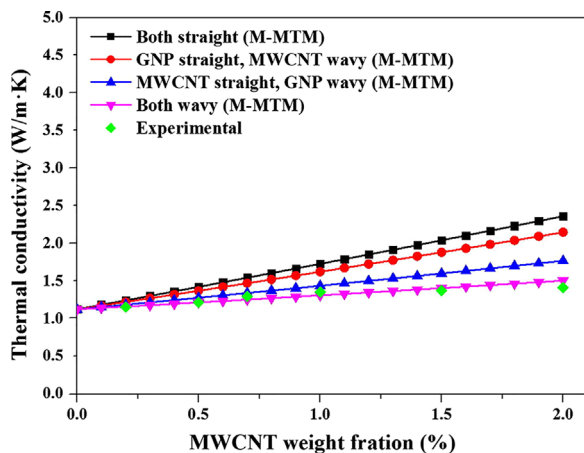


Figure 16. Thermal conductivities of composites filled with 20 wt% hybrid fillers using varying MWCNT and GNP fractions. Reproduced with permission.^[89] Copyright 2016, Elsevier Ltd.

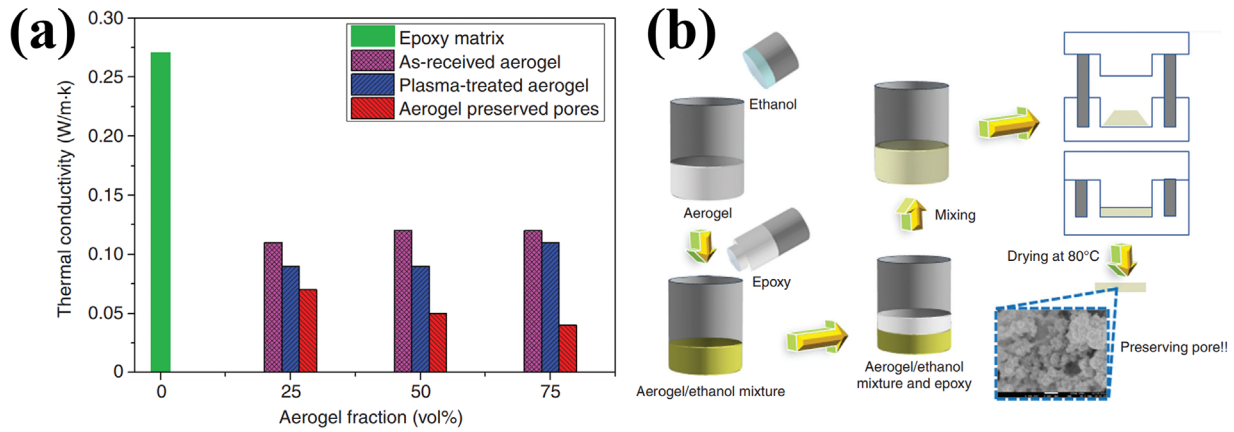


Figure 17. a) Thermal conductivities of the aerogel/epoxy composites with respect to the volume fraction of the aerogel; and b) schematic diagram of the processing method for preserving aerogel pores. Reproduced with permission.^[97] Copyright 2015, De Gruyter.

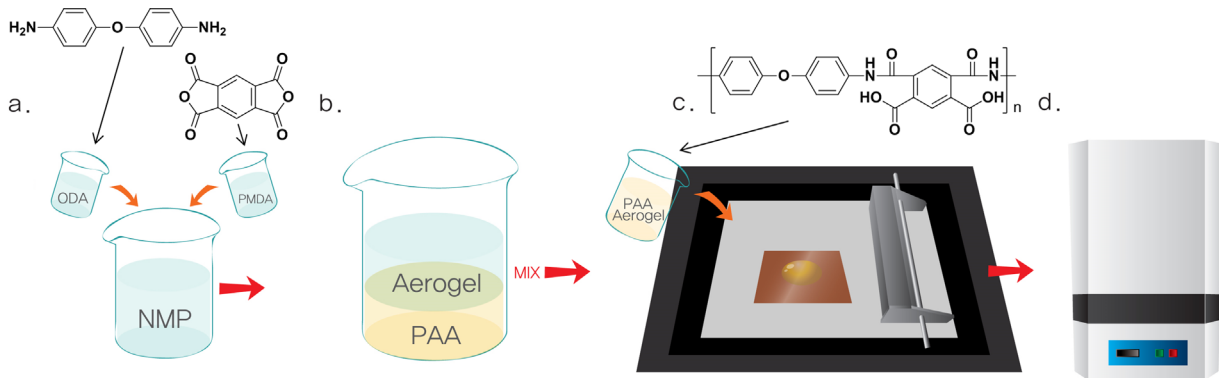


Figure 18. A new method for the preparation of the silica aerogel powder/polyimide (converted from PAA) composite that reserves the pores in the aerogel using a multi-step drying process. Reproduced with permission.^[98] Copyright 2014, Springer International Publishing AG.

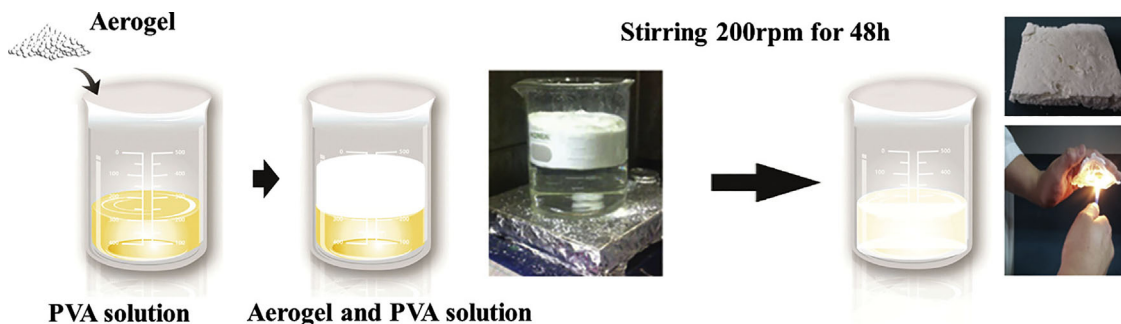


Figure 19. Processing procedures for the preparation of silica aerogel/PVA composites. Reproduced with permission.^[99] Copyright 2015, Elsevier Ltd.

acid (PAA), a precursor of polyimide resin, the solvent fills the aerogel pores. Thereafter, when the polyimide was synthesized through various stages of curing, its penetration into the pores was prevented by the solvent, and the solvent was vaporized and removed. The thermal conductivity of a polyimide composite containing the pore-restored silica aerogel was lowered to

0.03 W mK⁻¹ and heat resistance of the composite was maintained at 400 °C.

In order to minimize the thermal conductivity of the composites filled with silica aerogels, the pore preservation method, not the pore restoration method, was designed as shown in **Figure 19**.^[99] When super-hydrophobic silica aerogels

were mixed with a hydrophilic polyvinyl alcohol (PVA) solution, light silica aerogels floated on the surface of the PVA solution. As the PVA solution was evaporated while stirring, the precipitated PVA polymer was mixed with the silica aerogels at the surface to fabricate composites. The pores of the silica aerogels inside the composites were preserved without being impregnated with the PVA polymer, and the lowest thermal conductivity of the composite was 0.022 W mK^{-1} .

9. Conclusion

In this review, the principles of heat transfer in polymer composites and the major physical factors affecting the thermal conductivity of composites were discussed, and thermal management methods for the composites are summarized. In general, excellent filler dispersion is known to be beneficial for improving the thermal conductivity of composites. However, even in the cases of composites containing uniformly dispersed fillers, most of the thermal conductivity results were reported to be low near the lower boundary of the rule of mixtures. This unexpected result was known to be caused by the interfacial and contact thermal resistances.

Larger fillers are more effective at fabricating thermally conductive composites because the interfacial area of the filler-polymer matrix is greatly decreased, which reduces the interfacial thermal resistance and is advantageous for phonon transport. Increasing direct contacts between fillers can be a good solution to improve the thermal conductivity of composites, leading to thermal percolation behavior, because heat loss and phonon scattering due to the contact thermal resistance is less than those caused by the interfacial thermal resistance. Also, the direct contacts between the fillers can be induced by simultaneously incorporating thermally conductive fillers of different sizes and shapes, resulting in synergistic improvement of the thermal conductivity.

Recently, there has been a growing interest in insulating composites based on aerogels, which are the lightest of solids and show the lowest thermal conductivities. It is important to maintain the pores of the aerogels in order to lower the thermal conductivity of the composite filled with aerogels. Both a method of restoring the pores after filling with the solvent and a method of preserving the pores using an incompatible material system have been proposed, and excellent thermal insulating properties can be achieved by these methods. In nanocomposites, the interfacial thermal resistance is maximized because of the increased amount of the interface between the filler and the matrix. Therefore, nanofillers are more suitable for the development of thermally insulating composites than of thermally conductive composites.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

aerogel, carbon, composite, thermal conductivity

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