

# Thermal Conductivity of Nanoparticles Filled Polymer Nanocomposites: Review

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**Abstract**— Thermally conductive polymer nanocomposites offer new possibilities for replacing metal parts in several applications, including power electronics, electric motors and heat exchangers etc., thanks to the polymer advantages such as high strength to weight ratio, corrosion resistance and ease of processing. Current interest to improve the thermal conductivity of polymers is focused on the selective addition of nanofillers with high thermal conductivity. This article is intended to review the status of worldwide research in the thermal conductivity of various nanoparticles and their polymer nanocomposites. The dependence of thermal conductivity of polymer nanocomposite on the atomic structure, surface area, the morphology, the defect and the purification of nanofillers are reviewed. The roles of particle/polymer and particle/particle interfaces on the thermal conductivity of polymer nanocomposites are discussed with the help of modelling in details, as well as the relationship between the thermal conductivity and structure of the composites.

**Key words:** Thermal Conductivity, Polymer Nanocomposite, Modelling, Nanofillers, Crystallinity

## I. INTRODUCTION

Polymers are generally known as better insulators because of their low thermal conductive as compared to metals or ceramic materials. Polymers typically have very low intrinsic thermal conductivity. Thermally conductive polymers can find a wide range of applications in the field of electronics packaging and encapsulations, satellite devices and in areas where good heat dissipation and low density materials are required. Now days polymers reinforced with thermally conductive fillers, organic or inorganic, are becoming most popular for these types of the applications.[1-4] Increased thermal conductivity of polymers can improve the processing and fabrication of polymers due to good heat transport properties of polymers. Subsequently the improved physical properties of the polymeric materials due to improved and controlled cooling and annealing process. One example is crystallinity of polymer can be significantly changed with the speed of cooling, which is careful consideration in designing polymer processing is vital to achieve desired properties.

For one-dimensional and rectilinear heat flow, the steady state heat transfer in polymeric materials can be described by the Fourier’s law of heat conduction:

$$q = -k \, dt/dx \tag{1}$$

Where, q is the heat flux (i.e. the heat transfer rate per unit area normal to the direction of flow), x is the thickness of the material, Dt/dx is the temperature gradient per unit length and proportionality constant k is known as the thermal conductivity.

The units for thermal conductivity k are expressed as:

S. No	Systems	Unit
1	SI units	W/(mK)
2	English units	Btu in./(ft <sup>2</sup> h°F)
3	cgs units	Cal/(cm s°C)

Table 1: Units for thermal conductivity

The corresponding units for heat flux are expressed as W/(m<sup>2</sup>), Btu/(ft<sup>2</sup> h), and cal/(cm<sup>2</sup> s), resp.

Typically in solids heat transfer involves the transport of energy from one place to another by phonons, electrons, or photons. Phonons, quantized modes of vibration occurring in a rigid crystal lattice, are the primary mechanism of heat conduction in most polymers since free movement of electrons is not possible. (Mujumdar, 1998). In view of theoretical prediction, the Debye equation is usually used to calculate the thermal conductivity of polymers. (Han & Fina, 2010)

$$\lambda = (C_p \, v \, l) / 3 \tag{2}$$

Where, Cp is the specific heat capacity per unit volume;

v is the average phonon velocity;

l is the phonon mean free path.

For amorphous polymers, a very low thermal conductivity of polymer results due to extremely small value of l (phonon mean free path is few angstroms) due to phonon scattering from numerous defects [5].

Materials	Thermal Conductivity at 25 °C (W/mK)
Low density polyethylene (LDPE)	0.30
High density polyethylene (HDPE)	0.44
Polypropylene (PP)	0.11
Polystyrene (PS)	0.14
Polymethylmethacrylate (PMMA)	0.21
Nylon-6 (PA6)	0.25
Nylon-6.6 (PA66)	0.26
Poly(ethylene terephthalate) (PET)	0.15
Poly(butylene terephthalate) (PBT)	0.29
Polycarbonate (PC)	0.20
Poly(acrylonitrile-butadiene-styrene) copolymer (ABS)	0.33
Polyetheretherketone (PEEK)	0.25

Table 1: Displays the thermal conductivities of some polymers. [6-8]

## II. METHODS FOR THERMAL CONDUCTIVITY MEASUREMENTS

Several steady state and non-steady state methods have been developed and used for the measurements of thermal conductivity of polymer composites [9-10]. In classical steady-state methods, the temperature difference across the specimens in response to an applied heating power as an absolute value or by comparison with a reference material put in series or in parallel to the sample is measured. Classical steady state methods however required bulky

specimens and is time consuming as compared to other methods.

Non -steady-state methods generally includes hot wire and hot plate methods, temperature wave method and laser flash techniques [11]. Laser-flash thermal diffusivity measurement is a relatively fast method, using small sample size and is widely used [11-13]. In this method, a very short laser pulse irradiates the sample surface and the temperature difference is measure on the other side of the specimen. The thermal conductivity is then calculated according to equation to eq. 3

$$k = \dot{\alpha} C_p \rho \quad (3)$$

Where  $\dot{\alpha}$  = thermal diffusivity,  $C_p$  = heat capacity and  $\rho$  = density of the material.

Differential scanning Calorimetry (DSC) methods are also used by applying an oscillary [14] or step temperature profile [15] and analyzing the dynamic response.

Significant experimental error may be involved in thermal conductivity measurements, due to difficulties in controlling the test conditions such as the thermal contact resistance with the sample, leading to accuracy of thermal conductivity measurements typically in the range of 5~10%. In indirect methods, such as those calculating the thermal conductivity from thermal diffusivity, experimental errors on density and heat capacity values will also contribute to experimental error in the thermal conductivity.

### III. MODELING OF THERMAL CONDUCTIVITY IN COMPOSITES

Rule of mixture and the series model are the upper bound and the lower bound thermal conductivity of composites. Rule of mixture are also called as parallel model assumed that the each phase contribute independently to the overall conductivity, proportionality to its volume fraction (Eq. 4)

$$K_c = k_p \Phi_p + k_m \Phi_m \quad (4)$$

Where  $K_c$ ,  $k_p$ ,  $k_m$  are the thermal conductivity of the composite, particle, matrix respectively and  $\Phi_p, \Phi_m$  volume fractions of particles and matrix, respectively.

The parallel model maximizes the contribution of the conductive phase and implicitly assumes perfect contact between particles in a fully percolating network. This model has some relevance to the case of continuous fiber composites in the direction parallel to fibers, but generally results in very large overestimation for other types of composites.

On the other hand, the basic series model assumes no contact between particles and thus the contribution of particles is confined in the region of matrix embedding the particle. The conductivity of composites accordingly with the series model is predicted by equation 5.

$$K_c = \frac{1}{(\varphi_m + k_m) + (\varphi_p + k_p)} \quad (5)$$

Most of the experimental results were found to fall in between the two models. However, the lower bound model is usually closer to the experimental data compared to the rule of mixture [16], which brought to a number of different models derived from the basic series model, generally introducing some more complex weighted averages on thermal conductivities and volume fractions of particles and matrix. These so-called second order models including equations by Hashing and Shtrikman, Hamilton

and Crosser, Hatta and Taya, Agari, Cheng and Vachon as well as by Nielsen [17-19], appear to reasonably fit most of the experimental data for composites based on isotropic particles as well as short fibers and flakes with limited aspect ratio, up to loadings of about 30% in volume.

### IV. CRYSTALLINITY AND TEMPERATURE DEPENDENCE

Thermal conductivity of amorphous Polymers such as polymethylmethacrylate (PMMA) or polystyrene (PS) is relatively low 0.2 W/mK [7]. This shows increased in crystallinity of polymer increase the thermal conductivity. Price et al., showed that the thermal conductivity of semi-crystalline polymer increases with crystallinity [20].

Thermal conductivity of polymer does not only depend upon crystallinity but on many factors which explains the large scatter in the reported data and some contradictory results. Chemical constituents, molecular structure, bonding associated, molecular weight, density, defects or structural faults, processing conditions and temperatures also contribute to variation in thermal conductivity of polymers. [21]

Semi crystalline and amorphous polymers also vary considerably in the temperature dependence of thermal conductivity. At low temperature, semi crystalline polymers display a temperature dependence similar to that obtained from highly imperfect crystals, having a maximum in the temperature range near 100 K which shifts to lower temperatures and higher thermal conductivities as the crystallinity increases [22-23], while amorphous polymers display temperature dependence similar to that obtained for inorganic glasses with no maximum but a significant plateau region at low temperature range [24]. The thermal conductivity of an amorphous polymer increases to the glass transition temperature ( $T_g$ ) with increasing temperature, while it decreases above  $T_g$  [25-26]. The study of the thermal conductivity of some amorphous and partially crystalline polymers (PE, PS, PTFE and epoxy resin) as a function of temperature in a more common-use range (273-373 K) indicates that the conductivity of amorphous polymers increases with temperature and that the conductivity is significantly higher in the crystalline regions than in the amorphous regions [27].

### V. FILLERS FOR THERMALLY CONDUCTIVE COMPOSITES

Traditionally the thermal conductivity of polymers has been enhanced by the addition of thermally conductive fillers, including carbon – based; metallic or ceramic particles (see Table 2)

Materials	Thermal conductivity at 25°C (W/mk)
Graphite	100~400 (on plane)
Carbon black	6~174
Carbon Nanotubes	2000~6000
Copper	483
Silver	450
Gold	345
Aluminum	204
Nickel	158
Boron Nitride	250~300
Aluminum nitride	200
Beryllium oxide	260

Table 2: Thermal conductivities of some thermally conductive fillers. [28-32]

Several factors like filler purity, crystallinity and particle size affect the thermal conductivity of the filler materials results in the significant scattering of data reported. In the case of fibers and layers anisotropic behavior plays an important role in thermal conductivity of such materials. These materials can show high conductivity if measure along a main axis as compared to perpendicular direction. High filler loadings (>30 vol. %) is required to achieve the appropriate level of thermal conductivity in the polymer composites which represents a great challenge in the composite processing and fabrication. Also high filler loadings alter the mechanical behavior of the polymer composite. For these reason, polymer composites with more than 4 W/mK thermal conductivity is very challenging at present with usual processing techniques. [21]

## VI. NANOCOMPOSITES FOR THERMAL CONDUCTIVITY

Polymers nanocomposites are commonly defined as the combination of a polymer matrix and the additives that have at least one dimension in the nanometer range. The additives can be one-dimensional (example include nanotubes and fibers), two-dimensional (which include layered minerals like clay), or three- dimensional (including spherical particles). Over the past decade, polymer nanocomposites have attracted considerable interests in both academia and industry, owing to their outstanding mechanical properties like elastic stiffness and strength with only a small amount of the nanoadditives. This is caused by the large surface area to volume ratio of nanoadditives when compared to the micro- and macro- additives. Other superior properties of polymer nano- composites include barrier resistance, flame retardancy, scratch/wear resistance, as well as optical, magnetic, thermal conductivity and electrical properties. Polymer based nanocomposites can be obtained by the addition of nanoscale particles which are classified into three categories depending on their dimensions: nanoparticles, nanotubes and nanolayers. The interest in using nanoscaled fillers in polymer matrices is the potential for unique properties deriving from the nanoscopic dimensions and inherent extreme aspect ratios of the nanofillers [33-34] summarizes six interrelated characteristics of nanocomposites over conventional micro composites:

- 1) Low percolation threshold (about 0.1 - 2 vol. %)
- 2) Particle – particle correlation (orientation and position) arising at low volume fractions (less than 0.001),
- 3) Large number density of particles per particle volume (106 to 108 particle /  $\mu\text{m}^3$ ),
- 4) Extensive interfacial area per volume of particles( 103 to 104  $\text{m}^2/\text{ml}$ ),
- 5) Short distance between particles (10-50 nm at 1-8 vol.%)
- 6) Comparable size scales among the rigid nanoparticles inclusion, distance between particles have been used to improve thermal conductivity of polymers.

As a few examples, HDPE filled with 7 vol. % nanometer size expanded graphite has a thermal conductivity of 1.59 W/mK twice that of micro composites (0.78 W/mK) at the same volume content [35]. Poly (vinyl butyral) (PVB) PS, PMMA and poly (ethylene vinyl

alcohol) (PEVA) based nanocomposites with 24 wt.% boron nitride nanotubes (BNNT) have thermal conductivities of 1.80, 3.61, and 2.50 W/mK, respectively.[36] Carbon nanofibre was also reported to improve the thermal conductivity of polymer composites [37-38]. However, the most widely used and studied nanoparticles for thermal conductivity are certainly carbon nanotubes (either single wall-SWCNT or multiwall-MWCNT), which have attracted growing research interest. Indeed, CNT couples very high thermal conductivity with outstanding aspect ratio, thus forming percolating network at very low loadings.

Droval and co-workers [39] investigated the effect of boron nitride (BN), tale ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ), aluminum nitride (AlN) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ) particles, and their impact on thermal properties. Lewis and Nielson, Cheng and Vachon, Agari and Uno models were used to predict the evolution of thermal conductivity with filler and were found to describe correctly thermal conductivity. Only BN shows a real exponential increase of conductivity over 20% v/v filler. Consequently, in best conditions introducing 30% v/v of BN allows the thermal conductivity to be multiplied by six.

## VII. CONCLUSION

As electronic devices tend to become slimmer and more integrated, heat management become central task for device design and application. Similar issues are faced in several other applications, including electric motors and generators, heat exchangers in power generation , automotive , etc. metallic materials are widely used as heat dissipation materials, but there have many attempts to replace the metallic materials with highly thermally conductive based composites due to their lightweight, corrosion resistance, easy processing and lower manufacturing cost. Thermally conductive polymer based composites are tentatively prepared by the incorporation of thermally conductive fillers. The outstanding thermal conductivity of mentioned fillers makes them promising candidates to obtain highly conductive polymer based composites.

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