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Thermal Conductivity of Polypropylene-Based Materials

Antonella Patti and Domenico Acierno

Abstract

In this work, the authors aimed to provide an overview about the thermal conductivity of polypropylene, of its related compounds and the main methods of measurement. The growing spread of polypropylene in the industrial world together with the increasing demand of thermally conductive plastics represented the driving force of studying the heat transport in the polypropylene, and of recent progress and development of the thermal conduction in polypropylene-based materials. At regard, the common approach has been devoted to fill the polymer with thermally conductive materials: metallic, carbon based, ceramic and mineral fillers have been taken into account depending on the need to preserve electrical insulation, lightweight, production increasing or cost saving in the final compositions. Different parameters have been considered in order to optimize the ultimate thermal performances in the realized composites: (i) filler dispersion, (ii) filler/matrix and filler/filler interactions. The introduction of functional groups on the filler surface or in the polymer chain has been tested for acting on the dispersion and on the interfacial interaction. Then, hybrid materials, consisting in two particles different in size and shape combined with the attempt to realize a synergistic effect and to support a conductive network in the matrix, have been investigated.

Keywords: polypropylene, heat transport, measurement methods, enhancement, composites

1. Introduction

Polypropylene (PP), once discovered, immediately has been appreciated for its remarkable and various qualities like low density (the lowest compared to all thermoplastics), excellent chemical and corrosive resistance, dimensional stability, recyclability, flexibility, good processability, and low cost. All these advantages have contributed to make it ideal for a wide range of applications and to be processed thought many converting methods [1].

Injection molding is a very common used technique to work polypropylene, so much to cover about a third of its consumption [2]. In automotive, injection molding represents the main process for realizing vehicle components and PP is one among the conventional used thermoplastic materials. In the car, polypropylene is applied in the interior trim components as pillars, glove box, console bins and console housings, or exterior parts as air inlet panels and wheelhouse liners, or again under the hood for producing a fuse block cover, radiator, and coolant reservoir [3]. Extrusion, instead, is the single most popular process for forming PP in fibers, filaments, sheets and other products, depending on the die profile [4]. PP resins can be

also blow molded or biaxially oriented into thin films; in this case, it is usually used in electronics, packaging and food storage. Many products, such as printings films, magnetic films, decorations films, heat-sealing films, metal electronic deposition films are realized by biaxially oriented PP (BOPP) [5].

Moreover, polypropylene along with others thermoplastics as polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyethylene (PE), polycarbonate (PC), polyphenylene sulphide (PPS), polyphenylene oxide (PPO), has also been considered in heat exchanger applications in order to replace heavier and expensive metals strongly subjected to corrosion problems. Different models of heat exchangers have been also studied as shell and tube, plate, finned tube, and hollow fibers [6]. Yet, the overall heat transmission coefficient in polymer heat exchangers had been lower with respect to that obtained by metals and different approaches have been suggested to improve the heat transport in this field. The first was concerned with the reduction in thickness wall by requiring a new type of design; the second consisted in an increase of the thermal conductivity (TC) of the polymer resins [7].

Unfortunately, most polymers are thermally insulators and an augment of their TC represents one of the challenges of the recent scientific research for the coming benefits in the emerging heat exchangers applications, and also in the electronic and automotive technologies. In fact, plastics are one of the common materials for covering and protecting the electronic components or a better alternative to produce lighter vehicles with reduced fuel consumption. For example, in electronic assembly, miniaturization and higher power density have been experimented in order to achieve more advanced performances: a single chip has been made up of lots of transistors. This led to an intensification of power and a significant heat flow that can negatively affect the lifetime and reliability of the device, if it is not opportune dissipated away in time [8]. In the modern car engine, the electronic control unit (ECU) involves both hardware and software, required to perform the functions as mixture formation, combustion and exhaust gas treatment. In order to accommodate the more stringent standard imposed by the European Community on the emissions of pollutants from cars (Euro 6 standards), new kinds of control unit platform with high capability and reduced weight and size have been studied. Due to an inevitable increase of power density, thermal management has become an important aspect linked to the ability to easily dissipate the heat [9]. In an internal combustion engine, an elevated heat transfer affects performance, efficiency and emissions because it reduces the average combustion gas temperature and pressure, and the work per cycle transferred to the piston, for a given mass of fuel within the cylinder [10]. In automobile components, an improved TC of the constituent materials for engine cover, radiator, and coolant reservoir could be convenient to promote the faster diffusion of the heat, in order to avoid the overheating of the overall system and compromise the respective performances. In injection molding or extrusion, the greater would be the TC of the processed materials, lower would be the heating or cooling time and the operating costs of the overall processes. Moreover, during the cooling phase of these processes, sudden variation of TC could determine shrinkage, stress, delamination or voids in the final products [11].

In improving the heat conduction of the plastics different efforts have been spent in the scientific research with the addition of fillers characterized by a TC superior to the matrix [12–14].

In this work, the authors have focused the main attention on literature studies involving TC of polypropylene and the factors on which it depends as the crystallinity, testing temperature and pressure, polymer chain orientation, and molecular weight. Following, the effect of introducing fillers on the heat transport ability of the PP matrix has also been illustrated. Critical issues in the preparation of thermally conductive plastics, concerning the particles dispersion and the interface

resistance, have been also highlighted. Finally, filler functionalization and hybrid materials have been presented as methods to support the heat conduction in the PP-based composite systems.

2. Thermal conductivity of polypropylene

2.1 Definition of thermal conductivity in polymers

In general, heat transfer takes place through three different mechanisms: convection, conduction, irradiation.

In a solid, the main mechanism of heat transport is the conduction corresponding to the transfer of particle vibration energy to the adjacent particles without any motion of the matter but exclusively due to collision [12].

In steady state condition, Fourier' law (Eq. (1)) [15] describes the heat conduction across a slab of solid material of surface area A and thickness Y whose sides are set at two different temperatures T_1 e T_0 , respectively, in the direction normal to a slab surface (see **Figure 1**):

$$Q = k A \frac{\Delta T}{Y} \quad (1)$$

In Eq. (1), Q is defined as the heat flow required to maintain the temperature difference $\Delta T = (T_1 - T_0)$ between the two opposite surfaces; Y represents the conduction length path; A is the cross-sectional transfer area, and finally k is the TC of the slab material (in W/mK, SI units).

In the 1932, Debye introduced the concept of mean free path of thermal waves, simply called phonons, for explaining the thermal conduction in a dielectric crystal, in which the electrons are not free to move. In this case, the TC has been described through the following expression, also called Debye equation (Eq. (2)):

$$k = \frac{c_p v l}{3} \quad (2)$$

where c_p is the specific heat capacity per unit of volume, l is the phonon mean free path and v is the average phonon velocity.

Usually, the thermal conduction occurs through these phenomena: (i) by charge carriers as electrons and holes, also defined as energized electron motion; (ii) by phonons, i.e., energy quanta of atomic lattice vibrations due to atom interaction and collision and (iii) by photon conductivity verifiable only in the case of high temperature. Depending on the material's nature, the different phenomena do not always

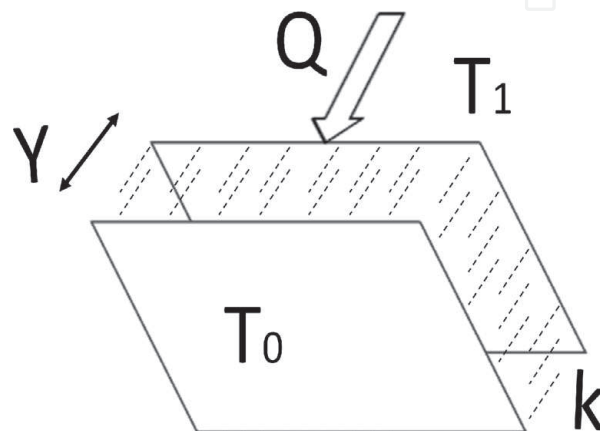


Figure 1.
Heat conduction across a slab of a solid material.

happen simultaneously, but one can dominate over the others. For example, in metals, the electronic contribution exceeds the phonon one; whereas in insulators, phonons contribution prevails over the electrons one [11–14]. Polymers are thermal insulators, and due to defects, grain boundaries, and/or scattering with other phonons the mean free path of phonons (l) is very low and consequently also their TC [16]. For most of thermoplastics, the TC at 25°C falls in the range of 0.11 W/mK (for polypropylene) and 0.44 W/mK (for high density polyethylene) [17].

2.2 Methods for measuring the thermal conductivity of polypropylene-based materials

The classical steady state (SS) and non steady-state (NSS) methods are the two main techniques for evaluating the TC of a material. In the first case, the measurement is carried out after reaching the equilibrium state, while in the second case, the test is performed during the heating phase [18].

The SS mode allows measurements on glass, polymers, insulators, ceramics, metals, composites with an uncertainty of 2–3%; the NSS mode permits to extend the testing also of liquids, gases or powders with an uncertainty up to 10% [12]. However, the first approach is more time consuming and not suitable for shaped samples as concentric cylinder or sphere.

In the SS method, the principle of operation is based on Fourier' law, while in the NSS method, the TC is indirectly evaluated by measuring the thermal diffusivity (α), according to Eq. (3):

$$k = \alpha c_p \rho \quad (3)$$

Here, c_p and ρ are the heat capacity and the density of the tested material, respectively.

The common apparatuses for evaluating the performance in heat transport of PP and its related compounds are: the “Guarded Hot Plate Method (GHPM)” and the “Heat Flow Meter Method (HFMM)”, based on SS approach, or the “Flash Method (FM)” and the “Transient Hot Wire Method (THWM)”, instead based on NSS approach.

The differences among these techniques are found essentially in required time for testing and operation mode [19].

The GHPM (**Figure 2a**) is constituted by a hot plate, placed between two samples of the examining material. The outer side of each specimen is in contact with a cold surface. A known heat flow (i.e., the heating power) is applied to one side of the sample and passes through it by establishing a temperature gradient between the two opposite faces of the sample. At steady-state, the TC is evaluated by measuring the difference in temperature and applying the Eq. (1).

The layout of the HFMM (**Figure 2b**) is very close to the GHPM apparatus designed for a single sample, but the first arrangement is faster and more accurate with respect to the second one [18]. The principal difference concerns the replacement of the main heater with heat flux sensor (HFT) [12].

In the FM (**Figure 2c**), a short but intense energy pulse is sent to one side of the sample and the temperature increase is measured on the opposed side in function of time. The thermal diffusivity can be calculated by Parker Formula (Eq. (4)) [20]:

$$\alpha = \frac{1.38 d^2}{t_{1/2}} \quad (4)$$

where d is the sample's thickness and $t_{1/2}$ is the time required for the signal to reach the 50% of its maximum value.

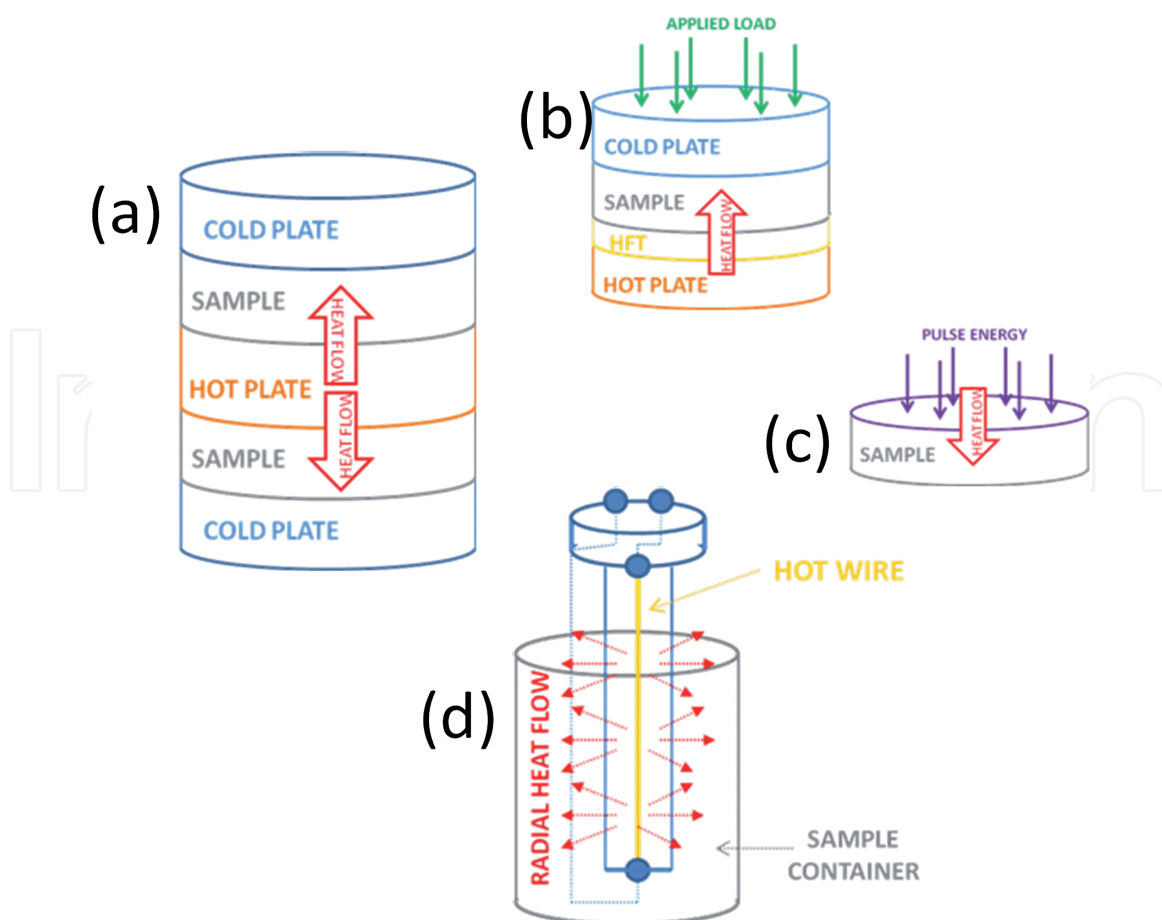


Figure 2.
 Schematic representation of TC measuring devices: (a) GHPM; (b) HFMM; (c) FM; (d) THWM.

The THWM (**Figure 2d**) implicates vertical or cylindrical geometry in which a wire, generally of platinum, is crossed by a constant electric current. A radial heat flow takes place around the wire that spreads in the tested sample. The TC is estimated, knowing the temperature profile on time ($T(t)$) and the heat output by Eq. (5) [21]:

$$k = \frac{q}{4\pi(T(t) - T_0)} \ln\left(\frac{4t\alpha}{r^2 C}\right) \quad (5)$$

in which $\ln C$ is the Euler's constant, q is the applied thermal flow, r is the wire radius and T_0 is the cell temperature.

Finally, also differential scanning calorimetry (DSC) has been considered as a technique for measuring the TC of solid materials. The analysis has been performed by incorporating a temperature sensor [22] or a made in-house accessory into the common apparatus [23]. It is possible also utilized the standard DSC machine, without any special modification or calibration, by setting a specific temperature-time profile and recording the dynamic response of the sample [24].

2.3 Factors affecting the thermal conductivity of polypropylene

The TC of polymers is affected by several factors as crystallinity, chemical constituent, bond strength, molecular weight, side pendent groups, defects or structural faults, processing conditions and temperature [14].

Anderson [16] reported that the TC of polymers decreased as the disorder increased: imperfections, by decreasing the order of the molecular structure, caused a large phonon scattering that reduced the heat transport. Since the polymeric

structure order of the amorphous is lower than of the crystalline, the related thermal behaviour of the former has been expected to be lower compared to the latter, and also TC temperature dependence has changed in different ways depending on substance state. In details, below the glass temperature, as the temperature grew up, the TC of the amorphous remained the same or increased with temperature (probably for the effect of raising chain mobility), while for crystalline the TC initially remained the same and then diminished. Probably, in this second case, a decrease or/and breakup of the crystalline portions have been promoted by higher temperatures after which the conductivity of the amorphous has been risen. These considerations were confirmed by studies of Bashirov et al. [25] and Osswald et al. [26], developed not only on PP, but also on high-density polyethylene (HDPE), low-density polyethylene (LDPE) and other polymers. On the contrary, an opposite trend of the TC of PP against temperature was found by dos Santos et al. [11]. In their work, the authors measured the TC of semi-crystalline and amorphous polymers starting from room temperature and going up to melting temperature (for semi-crystalline polymers) or glass transition (for amorphous polymers). Results showed that initially, as the temperature rose between 25 and 125°C, the TC of PP slight decreased from 0.25 to 0.15 W/mK; then, it underwent a sudden increase reaching a peak of approximately 0.47 W/mK during the melting process, and finally it decreased. In the temperature range of 2–100 K the TC of polypropylene was evaluated by Choy et al. [27]. In the case of isotropic crystalline conditions, an increasing trend that exhibited a maximum near 100 K was detected; then, when the sample was extruded and a marked anisotropy of TC was induced, the heat transport resulted in an order of magnitude increase in the extrusion direction. Finally, a nearly linear temperature dependence without any detectable plateau of the TC of PP copolymer was observed by Barucci et al. in the range of temperature from 0.1 to 4 K [28].

Most of the TC measurements of polymers have been carried out at atmospheric pressure, which is far from the operating process conditions. At regard, some measurements have been reported in order to verify the effect of pressure on TC of polymers. Dawson et al. [29] measured the thermal parameter for polypropylene at pressures of 20, 80 and 120 MPa over the temperature range from 250 to 50°C. For each pressure, the isobaric curve of TC as a function of temperature showed a “Z shaped”, probably attributed to a phase transition (crystallization during cooling). Beyond an increase encountered during this phase, the TC remained fairly constant with the temperature. At an equal temperature, an increase of TC was always verified with pressure, approximately of 20% going from 20 to 120 MPa. Andersson et al. [30] performed measurements of heat conduction of PP at 300°K by changing pressure in the range between 0 and 37 bar. They concluded that, when the pressure was exercised on the sample, a stress in the longitudinal direction was generated, greater than in the radial direction, by leading to anisotropy of the properties in the tested material. Experimental data, related both to atactic and isotactic PP, demonstrated that the TC increased strongly with pressure with a continuous change in the slope of curve until it reached an asymptotic value.

From the above, the actualizing the anisotropy in a sample has implied an influence of its thermal transport behaviour. In fact, when the orientation has been induced in the polymer, its TC became higher in the direction of a molecular orientation and lower in a direction normal to the orientation [31]. This attitude was confirmed in the case of injection molding and extrusion [32] or foaming [33] processes during which a macromolecular orientation of polymer chain was inferred.

Finally, a characterization of the heat transport directly on the melted PP has been carried out because of in a common process the material was usually in the molten state. In fact, in a solid state the TC of semi-crystalline thermoplastics was greater with respect to melt state due to an increase of density upon the solidification. At regard,

Polypropylene	TC (W/mK)
Han et al. [14]	0.11
Goswami et al. [35]	0.12–0.17
Maier et al. [36]	0.17–0.22
Tripathi [4], Guo et al. [37], Birley [38]	0.22

Table 1.
Data reported in literature on TC values of polypropylene.

investigations about the effect of hydrostatic pressure, temperature, and chemical structure on the thermal conduction of melted PP have been performed [26]. These studies confirmed that, as the hydrostatic pressure increased on melt state, also the TC of thermoplastics in general, and of PP in particular, increased for a reduction in free volume. Furthermore, the TC of PP in molten form was not significantly affected by temperature but it appeared to be a complex function of the molecular weight distribution and possible long chain branching [34]. Generally, an increment of the TC of polymers by raising the molecular weight was verified since a larger number of energy transactions took place in a substance with shorter chains [16].

In **Table 1** the TC values for polypropylene are shown.

3. Enhancement of thermal conduction in polypropylene-based materials

3.1 Thermally conductive fillers in polypropylene

In general, the common approach for enhancing the thermal transport behaviour of plastics foresees the addition of thermally conductive particles. By balancing in the polymeric resin the filler content and type, it is possible to obtain the desired features in the final products. Yet, the use of an extremely high percentage of reinforcement (approximately more than 30% in vol.), is needed to achieve the TC values in the composites, required for the modern technologies. This quantity represents a real challenge for the processability of the material and makes difficult or impossible extrusion and injection molding processes [14]. In the last few decades, great attention has been devoted to polymeric nanomaterials, born from the introduction into the matrix of filler having at least one dimension in the order of 1–100 nm. Based on the geometric characteristics, three groups of nanosize particles are distinguished: one-dimensional (nanotubes and nanofibres), two-dimensional (layered minerals), three-dimensional (spherical particles). Small size and large surface area (for a given volume) of nanofiller are considered the key factors for the development of exceptional and unexpected properties with respect to macroworld as in the fields of mechanical properties, barrier resistance, flame retardancy, scratch/wear resistance, as well as optical, magnetic, TC and electrical properties [17]. Thermally conductive fillers can be divided into three categories: metallic powders, ceramic particles and carbon-based materials, and have been chosen depending on the needs to act both on the heat and current transport. For example, by adding carbon-based or metallic particles, the final compounds earned not only in terms of the thermal conduction but also in terms of the electric one; yet, metallic particles, having high specific gravities, could not be applied in the case of the lightweight target and carbon-based reinforcements have been preferred. Conversely, the introduction of ceramic fillers allowed acting on heat transfer of the neat matrix without compromising the electrical insulation of the starting material [39].

The thermal and electrical behaviour of PP matrix filled with two of copper particles (in micron dimensions), was investigated by Boudenne et al. [40]. Results, compared in terms of fillers size and volume fraction, highlighted the stronger heat transport ability of the formulations including the smaller particles.

A similar study was conducted by Cheewawuttipong et al. [41] by adding into PP two types of boron nitride (BN) with different particle size in micron. The mechanical features (storage and loss modulus) and thermal ones (thermal conductivity, melting and crystallization temperature) were analyzed. They found that the TC increased, according to the BN content and the larger size of the filler.

The application of conductive polymer composites (CPC) in manufacturing a tubular heat exchanger for fluid heating was presented by Glouannec et al. [42]. The materials of the extruded tubes were obtained by blending the insulating thermoplastic polymer (PP) with conductive filler like carbon black (CB) or carbon fibers (CF). The experimental testing showed that the heat conduction of the CPC heat exchanger was improved by a factor of 2 for the filler volume fraction of 25%. For similar applications, Qin et al. [43] realized graphite (GP) enhanced PP hollow fiber heat exchanger. Results showed that the addition of GP fairly improved the crystalline, thermal stability and conductivity of the PP. The overall heat transfer coefficient for a filler content of 15.0 wt% became five times bigger than that of pure PP-based one.

Among the carbonaceous fillers, given the extremely high intrinsic TC, the carbon nanotubes (CNTs) have been also considered [44]. The TC of the PP-based nanocomposites grew up with the CNTs content in particular above 160°C, but the rising trend not seemed to be dramatic as the increase in electric conductivity.

However the advantages of using minerals in many polyolefin applications should not be overlooked. It has been successfully demonstrated that talc, calcium carbonate, and magnetite led to an improvement of the productivity and of physical properties, and to a reduction of costs since a portion of the polymer has been replaced by lower-cost material [45, 46]. Moreover, due to a higher TC of minerals with respect to the matrix, their addition also brought an increase of heat transport in the ultimate compounds. The introduction of calcium carbonate (CaCO_3) nanoparticles in isotactic PP was studied by Vakili et al. [47], verifying the particle effect on crystallization and heat transport behaviour of the ultimate compounds. The TC was increased from pure PP by 64% for the sample containing the highest filler loading (15 phr). The authors stated that their results were better than that obtained with carbon nanofiber (CNF) in the PP matrix [48], for which at 0.08 volume fraction this increase has been almost 45%. Weidenfeller et al. [49] added different micro-size particle of magnetite in various proportions to a standard polypropylene copolymer. The TC increased from 0.22 to 0.93 W/mK for a filler content of 44% in vol. of magnetite, nearly independent of the particle size and distribution; whereas the electrical resistivity decreased more than seven orders of magnitude. Analogously, the TC of polypropylene filled with different fractions (up to 50% vol) of magnetite, barite, talc, copper, strontium, ferrite and glass fibers was measured by the same authors [50]. Despite the highest intrinsic TC of copper, surprisingly, the best result was obtained with talc. Using the model conductivities, according to Schilling and Partzsch, the interconnectivity of the conducting phase has been evaluated. Calculations showed that the interconnectivity for talc was particularly greater than that of copper probably due to the alignment of the talc lamellas in the polymeric resin into the flow direction during injection molding; for copper no contact among particles has been found. The authors concluded that the thermal transport could not be explained solely by the difference in the property of the materials but taking into account also the microstructure.

Fillers	Category	Typical shape	TC (W/mK)
Allumium nitride (AlN)	Ceramics	Roughly spherical	320 [30]
Alluminium oxide (Al ₂ O ₃)	Ceramics	Spherical or platelets	42 [8]
Barium titanate (BaTiO ₃)	Ceramics	Grains	6.2 [8]
Boron nitride (BN)	Ceramics	Hexagonal platelets	3 (through plane) 300 (in plane) [41]
Zinc oxide (ZnO)	Ceramics	Pseudo-spherical	60 [8]
Carbon black (CB)	Carbon-based	Pseudo-spherical	6-174 [39]
Carbon nanotubes (CNTs)	Carbon-based	Cylindrical shells	2000–6000 (on axis) [39]
Carbon fiber (CF)	Carbon-based	Elongated	600 [48]
Graphene (GN)	Carbon-based	Sheets	5000–6000 [39]
Graphite (GP)	Carbon-based	Platelets	100–400 (on plane) [40]
Copper (Cu)	Metals	Pseudo-spherical	389 [40]
Calcium carbonate (CaCO ₃)	Mineral	Pseudo-spherical	4.5 [47]
Magnetite	Minerals	Grains	9.7 [49]
Talc	Minerals	Lamellar	1.76 (through plane) 10.69 (in plane) [50]

Table 2.
TC values of common fillers added into polypropylene.

A list of the used fillers to increase the thermal transport behaviour of PP and their intrinsic TC are given in **Table 2**. These particles are added in the hosting matrix by prevalently melt blending: one among the classical processes for compounding, particularly preferred in an industrial context.

3.2 Critical aspects for optimizing the thermal conduction in composites

According to the rule of mixture (Eq. (6)), each phase contributes to final compounds properties proportionally to its volume fraction:

$$p_c = \sum_{i=0}^n p_i \phi_i \tag{6}$$

where p_c is composite property, p_i is the intrinsic property of each specific constituent and ϕ_i is their volume fraction in a composite system.

However, the experimental evidences confirmed that the values of the TC in the designed composites were lower than those evaluated by applying the simple rule of mixing model and the intrinsic TC of each constituent. This meant that nanoscale unique properties could not be reproduced easily on the macroscale probably for non-continuum effects at filler-polymer interfaces [51].

In fact, besides the filler type and its content, particles shape and size, their orientation and dispersion in polymeric matrix, the adhesion between the filler and the matrix and the thermal properties at the interface symbolized the acting parameters to optimize the desired feature [12].

The interfacial resistance is also known as “*Kapitza Resistance*” from the name of the discoverer that in 1941 found the temperature discontinuity at the interface between metal (copper) and liquid (superfluid helium). It represents a barrier to heat flow at the interface between two phases, due to possible weak contact and differences in the phonon spectra [52]. The thermal contact resistance is attributed

to phonons losses during heat transmission from one medium to another and is qualitatively described by two limiting models: acoustic mismatch model (AMM) and the diffuse mismatch model (DMM), representing the upper bound and lower bound of thermal boundary resistance, respectively. The former assumes that all phonons propagate as a planar wave, so the transmitted energy is related to different acoustic impedances of two materials. Instead, the latter assumes that all phonons, colliding into the interface, are randomly scattered. If the acoustic impedances between materials are very different, the phonons scattering will contribute to further increase the thermal resistance [53].

In addition to Kapitza resistance, in a composite a further resistance to the heat transport, involving the solid-solid interface, i.e., particle-particle interface has to be considered. Two solid bodies, which are apparently in contact, actually touch together only in a few points due to their roughness and geometrical defects. In this case, when heat flows normally from a hotter body to colder one, interstitial spaces between contact points limit the thermal conduction that takes place only between effective connections. The physical consequence is a constriction of flux lines, responsible of the heat resistance best known as “thermal contact resistance” [54].

In many previous works, it has been reported that two essential components for an optimal effect of the reinforcement in a composite are filler dispersion and orientation. A homogeneous filler dispersion in the resin led to a consistent load transfer from the matrix to particle and in the realization of a conductive network for electrical and thermal energy. Furthermore, if the particles were oriented in the direction of applied force or heat, their full potential could be achieved both in terms of load and energy transport. However, an efficient dispersion or/and a perfect alignment of the inorganic filler, particularly for nano-sized, in the matrix represented a real challenge during the process due to van der Waals interactions between individual particles that push to the aggregation and randomly disposition [55]. Yet, in the case of heat transport, the enhancing the filler dispersion not always implied exceptional thermal performance of respective composites, because an increase in the matrix filler interfaces, and consequently in the phonon scattering, could be promoted. In particular for nanocomposites, the large surface area of nano-size particles, by maximizing the touching between particle and polymer, could increase exactly the interfacial resistance. Thus, particles perfectly dispersed in the matrix with a minimized interfacial resistance would not seem anyway the best solution in the perspective of an advantageous heat transport because in this situation the particles would exchange heat only with the matrix and not among themselves. Since the mean phonon free path of the polymer is less than that of the particle, the efficiency of the thermal conduction would not be satisfactorily achieved except by a network of interconnected particles that carry heat among themselves [14].

Additionally, in the composites the conductive pathway can be build also by particle agglomerates if a sufficiently reduced “*mean interparticle distance*” (MID) has realized among them. So, in the case of poor dispersion and low filler loading, the isolated agglomerates resulted not effective as well the dispersed ones. In other words, the thermal network could also be get among the same aggregates that behave like larger-size conductive particles without interfaces by actualizing a sufficiently reduced MID. In this perspective, the aspect ratio of particles became an interesting and important parameter to be considered because bigger was the length of particles, lower could be the filler/matrix interface and scattering of phonons, and greater was the TC value in the final system. Nevertheless, at an equal filler percentage, if on one side the micro-dimension of the particles compared to nano-size could be favorable for reducing the interfaces, on the other side it contributed to an increase in MID [13].

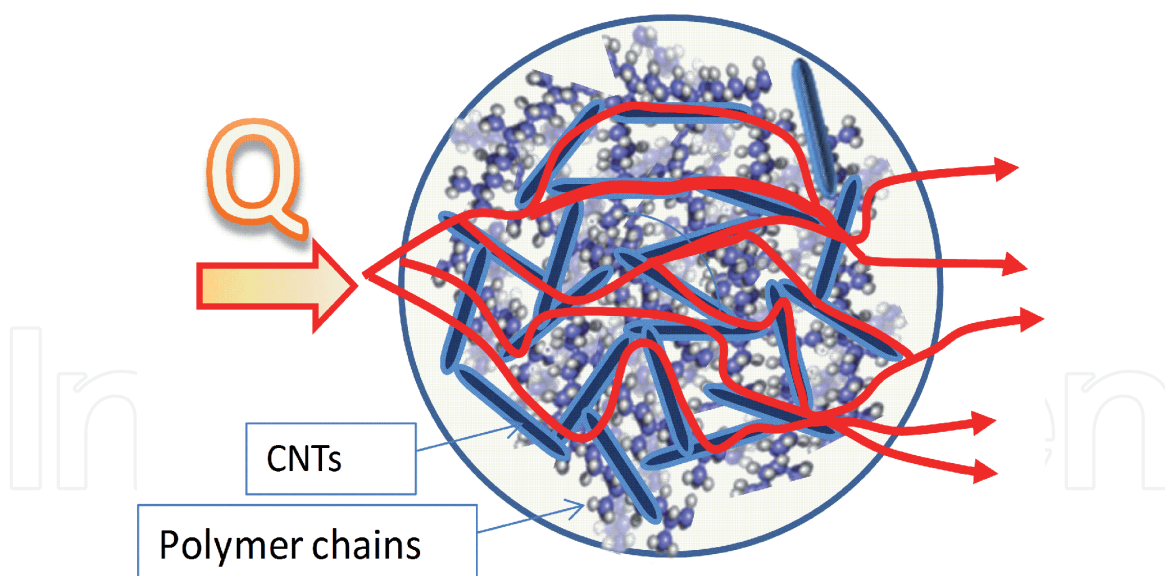


Figure 3.
Schematic of the heat conduction along particles forming a percolated network.

In conclusion, in order to successfully employ the thermal conductive particles in composites for heat management applications, the realization of a conductive pathway through the particles (shown in **Figure 3**) has to be attained through optimal filler dispersion, good interfacial adhesion between filler-matrix and properly contact between particles.

3.3 Effect of functionalization

The functionalization, i.e., the introduction of functional groups on filler surface, obtained by covalent or non-covalent means, is a common approach widely adopted for changing the chemistry of inert inorganic particles. This approach is considered a successful tool for improving the compatibility and wettability between the two phases of the composite system, and affecting positively the dispersion and the interfacial resistance. Although few works are carried out on this way, it is not excluded that between functional groups may arise interactions, stronger than van der Waals forces, which, binding more particles between them, also promote a reduction in the contact resistance.

Patti et al. [56] studied the effect of filler functionalization on dispersion and TC of PP-based composites by adding, in the same resin grade, three different chemically treated surfaces (amino- and carboxyl-functionalized, and pristine one) CNTs. A cubic polynomial trend of the TC as a function of the filler concentration was found, for all three families of nanocomposites. This behaviour was attributed to the occurrence of competitive dispersion/agglomeration phenomena which, affecting the mutual distance among filler aggregates/agglomerates (MID), influenced the formation of thermal paths.

CNTs, aluminum flakes (Al-flakes), and a commercially available Al-CNT powder (embedded CNTs within Al-flakes), were used to prepare PP-based composites. The characterization of these compounds in terms of mechanical and thermal tests indicated that the crystallization and decomposition temperature as well as the TC and tensile modulus of PP/Al-CNT were over than to the PP/CNTs and PP/Al-flakes composites. It was hypothesized that free CNTs, produced during the preparation of PP/Al-CNT systems, played an important role in forming a conductive bridge among Al-CNT particles and in generating synergistic effects [57].

Muratov et al. introduced two different types of surface treated BN into the PP matrix: pristine and covered with silane coupling agent (γ -3-amino-propyl-3-ethoxy-silane-APTES). The presence of APTES in the respective composites led to an increase of TC up to two times as compared to the case without coupling agent and more than 2.5–4 times as compared to pure PP [58].

Thus, if the first method for improving the compatibility filler-matrix is the modification of the filler surface by using functional groups or coupling agents, the other method consists in the modification of the matrix by grafting reactions of different chemical groups. For example, in the case of polyolefins, maleic anhydride is commonly grafted to polypropylene for improving the filler-matrix interface through both physical and chemical interactions, as covalent linkages and hydrogen bonds [59]. Che et al. [60] functionalized the surfaces of micrometric BN with a thin layer of polydopamine coatings (f-BN). Then, maleic anhydride grafted PP (PP-g-MA) was also employed as the compatibilizer in the compounds for helping the covalent bonds with polydopamine. The highest value of the TC was recorded for the prepared mixtures containing the compatibilizer and functionalized filler. On the contrary, the formulations containing pristine BN possessed a higher TC with respect to that prepared with modified one. Probably, the coating of polydopamine layers increased the polarity and hydrophilicity of fillers, which would be less compatible with the non-polar and hydrophobic PP matrix, resulting in voids at the interface and filler aggregation, and inducing a strong interruption of the thermal paths. Szentes et al. [61] utilized novel types of coupling agents (olefin-maleic anhydride copolymer-based) as a compatibilizer in CNTs/PP systems. They found that neither the chemical structure of coupling agent nor the application methods (masterbatch and impregnation) have been conclusive on the heat conduction of prepared compositions.

Although the experimental evidences seem to be lesser and to be explored in greater detail, it should be emphasized that the increasing the compatibility between filler and matrix not always a positive effect on heat transport has been verified. Compatibilized samples sometimes display slightly lower TC with respect to non-compatibilized systems, probably due to a polymeric wrapping around particles that hinders the direct contact among themselves and, as a consequence, the thermal transmission [62]. Patti et al. [63] found that the addition of PP-g-MA significantly reduced the contribution of included CNTs to the ultimate thermal transport properties of the corresponded mixtures, from +42.2 to +19.6% in presence of neat CNTs and from +47.7 to +11.7% for systems containing amino functionalized CNTs.

3.4 Hybrid materials

Nowadays, recent scientific attention has been devoted to hybrid material defined as “a combination of two or more materials in a predetermined geometry and scale, optimally serving a specific engineering purpose”. A hybrid has been conceived as a mixture of two or more raw materials with own intrinsic properties and different shape and size (“A + B + shape + scale”) to enhance or diminish physical, mechanical, thermal and electrical properties, as stiffness or strength, and also to manipulate the percolation limit [64]. In fact, the difference in dimension and geometry allows to maximize the packing density and to favor a greater connection among the various particles. The final properties of hybrids could be a combination between the features of the individual constituents or a result of synergism, intended as a total effect greater than the sum of each component, due to a joint action between fillers, supplied by distinct geometry of shape, aspect ratio as well distribution [65].

King et al. [66] analyzed the effect of single carbonaceous fillers (CB, GP, CNTs) and their combination on the TC of PP in the light of a potential market of fuel cell bipolar plates. The association of these fillers in the matrix appeared always more

effective in improving the tested feature compared to the potential of each single species. In the case of hybrid formulations, the best result was obtained by mixing together the three particles, probably for the formation of linkages among them. In the case of composites including an individual filler, the highest TC value (28 W/mK) was achieved with 80% in wt. of GP and was anyway higher than the desired TC required for bipolar plates (20 W/mK). Krause and Potschke [67] investigated another useful combination of carbon-based fillers (CNTs, CF, graphite nanoplatelets-GNP) in PP by analyzing both the thermal and the electrical conduction of melt blended compounds. Ren et al. [68] obtained the simultaneous enhancement on thermal and mechanical properties of PP composites by adding graphite platelets (GPs) and graphene sheets (GSs). Yao et al. [69] reported the enhancement on the TC and dielectric properties of PP composites due to the synergistic effect of the introduced nano-sized aluminum oxide (Al₂O₃) and micro-sized barium titanate (BaTiO₃). At a maximum of filler content (50% in vol.) the BaTiO₃/PP and Al₂O₃/PP composites exhibited the same increment in TC approximately equal to 100%, while for BaTiO₃/Al₂O₃/PP systems an abnormal heat-conducting properties (of an order of magnitude higher compared

	Materials	TC of PP (W/mK)	Filler content	Filler size	TC measurement method	TC of PP-composites (W/mK)
Boudenne et al. [40]	PP/Cu	0.25	35 vol%	Micron	Periodical method in [72]	2.20
Cheewawuttipong et al. [41]	PP/BN	0.25	30 vol%	Micron	THWM	2.00
Vakili et al. [47]	PP/CaCO ₃	0.21	15 phr	Nano	GHPM	0.36
Frormann et al. [48]	PP/CNF	0.125	8 vol%	Nano	GHPM	0.181
Weidenfeller et al. [49]	PP/magnetite	0.22	44 vol%	Micron	FM	0.93
Weidenfeller et al. [50]	PP/talc	0.27	30 vol%	Micron	FM	2.50
Patti et al. [56]	PP/MWNT	0.09	5 vol%	Nano	HFMM	0.20
HeonKang et al. [57]	PP/Al-CNT	0.20	50 vol%	Micron	FM	0.70
Chen et al. [60]	PP/PP-g-MA/f-BN	0.22	25 wt%	Micron	FM	0.60
King et al. [66]	PP/GP/CB/CNT	0.2	53.2 vol%	Micro-GP Nano-CB Nano CNT	HFMM	5.80
Krause et al. [67]	PP/GNP/CNT	0.26	75 vo%	Nano-CNT Micro-GNP	FM	0.50
Ren et al. [68]	PP/GS/GP	0.28	23 wt%	Nano-GP micron GS	FM	1.72
Yao et al. [69]	PP/Al ₂ O ₃ /BaTiO ₃	0.17	50 vol%.	Sub-micron Al ₂ O ₃ micron BaTiO ₃	THWM	0.90
Cheewawuttipong et al. [70]	PP/VGCF/BN	0.23	53 wt%	Micron BN nano VGCF	THWM	2.90
Russo et al. [71]	PP/CNT/BN	0.09	11.5 vol%	Nano-CNT Micro-n BN	HFMM	0.25

Table 3.
Comparison among TC enhancement in some PP-based formulations due to the effect of different introduced nano-sized and/or micro-sized fillers into the matrix.

to the pristine PP) was recorded. Cheewawuttipong et al. [70] added BN and vapor-grown carbon fiber (VGCF) into the PP resin. They found that by increasing the content, the distance between fillers could be reduced and the development of conductive structure was attained. VGCF/BN hybrids possessed a better heat transport behaviour than of composites incorporating BN single size, since VGCF contributed to generate a conductive bridge by dispersing between BN and PP.

Finally, the development of carbon-based thermally conductive composites with low electrical conductivity was actualized by PP-based ternary formulations, combining CNTs (a thermal and electrical conductive filler) with additional thermally conductive, but electrically insulating, particles (ZnO, CaCO₃, BN, and Talc) having different sizes and shapes [71]. Results showed that, in ternary formulations, an increase of TC was always verified for all kinds of secondary particles, in particular through the union of CNTs with BN. Significant reduction of electrical conductivity was achieved, despite the presence of CNTs, with the addition of smaller secondary species (BN and ZnO), while a further increment of the same feature was obtained with larger ones (CaCO₃ and Talc).

Table 3 shows some values of TC reached in the PP-based composites, according to the filler type, its size and added content.

An effective comparison of reported TC values has not been possible due to differences in the filler loadings in each study. Yet, higher TC measurements were verified in the presence of microparticles, in particular with layered shape (talc); the same results have never been reached by adding nanoparticles. The highest improvement of heat transport in PP was recorded with the introduction of two combined carbonaceous nano- and micro-particles.

4. Conclusion

This review was devoted to summarizing the main literature studies about TC of polypropylene and the recent developments of heat transport ability in PP based compounds.

The TC of polypropylene has been measured in the range approximately between 0.1 and 0.2 W/mK, but different parameters as polymer crystallinity, chain structure and orientation, processing conditions and methods, temperature and pressure have played a positive or negative role on its thermal transport behaviour. In details, for the examined semi-crystalline polymer, starting from room temperature and going up to melting point, an opposite trend of TC have been reported. The TC remained almost the same as the temperature increase until it decreased during melting due to a possible breakup of crystalline regions. On the contrary, opposite results showed a strong increase of TC really at melting point. Finally, below 100 K, a growing tendency of TC against temperature has been verified. The effect of acting pressure on TC of polypropylene seemed to be always positive, probably for the induced stress in a longitudinal direction that led to anisotropy of the tested feature. For the same reason, processes like extrusion, injection molding and foaming, by causing an orientation of the polymeric molecular chains, could determine an increase of TC in the same direction of the inferred one. In the molten state, the TC of polypropylene appeared to be a complex function of molecular weight and chain branching; it continued to increase by pressure but resulted almost unaffected by temperature.

The devices, adopted for measuring the TC of PP and of its composites have been prevalently the Guarded Hot Plate Method and the Heat Flow Meter Method, based on a steady state approach, or the Flash Method and the Transient Hot Wire Method, based on transient approach.

Different efforts have been spent in literature in the improvement the heat conduction of PP, by the addition of inorganic fillers (metallics, carbon-based, ceramics and minerals) in micro- or nano-size, one-, two- or three-dimensional, with a higher thermal transmission compared to the pristine resin. By increasing filler loading, positive but not always satisfactory increases of TC in the respective compounds have been achieved. The size and shape of particles, their orientation and distribution in the polymer, the interfacial interaction between filler and matrix and between filler and filler, have been identified as crucial aspects in the optimization of final heat transport in the polymeric composites. All these factors contributed to realize effective thermally conductive pathways in the composites, actualized among particles with an advanced dispersion, good interfacial adhesion with the pristine material (lower interfacial resistance) and the proper contact among themselves (lower contact resistance).

The filler functionalization (i.e., the introduction of functional group on filler surface) and the addition of compatibilizer in polymer/particles mixtures, have been considered a useful approach for developing the compatibility between the two phases, and consequently for improving the dispersion and the interfacial interaction. Another approach has been the combination of two or more fillers, having different size and shape, to optimize the filler packing and their distribution in the matrix, so to realize and support an effective thermal conductive network.

By comparing data on PP-based compounds, despite the difference in filler loading, the greater efficiency in improving the TC of the matrix seemed to be realized in the case of combined micro- and nano-sized carbonaceous particles in the resin.

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References

- [1] Maddah HA. Polypropylene as a promising plastic: A Review. *American Journal of Polymer Science*. 2016;**6**:1-11. DOI: 10.5923/j.ajps.20160601.01
- [2] Maier C, Calafut T. *Polypropylene, The Definitive User's Guide and Databook*. 1st ed. Norwich: Plastic Design Library; 1998. 452 p. ISBN 9780815518716
- [3] Karian HG. *Handbook of Polypropylene and Polypropylene Composites, Revised and Expanded*. 2nd ed. New York: Marcel Dekker; 2003. 576 p. ISBN 9780203911808
- [4] Tripathi D. *Practical Guide to Polypropylene*. Shrewsbury: Rapra Technology LTD.; 2002. 104 p. ISBN 9781859572825
- [5] Gurses A. *Introduction to Polymer-Clay Nanocomposites*. 1st ed. New York: Pan Stanford; 2016. 360 p. ISBN 9789814613033
- [6] Chen X, Su Y, Reay D, Riffat S. Recent research developments in polymer heat exchangers—A review. *Renewable and Sustainable Energy Reviews*. 2016;**60**:1367-1386. DOI: 10.1016/j.rser.2016.03.024
- [7] Glade H, Moses D, Orth T. Polymer composite heat exchangers. In: Bart HJ, Scholl S, editors. *Innovative Heat Exchangers*. Cham: Springer; 2017. 394 p. DOI: 10.1007/978-3-319-71641-1_2
- [8] Huang X, Jiang P, Tanaka T. A review of dielectric polymer composites with high thermal conductivity. *IEEE Electrical Insulation Magazine*. 2011;**27**:8-16. DOI: 10.1109/MEI.2011.5954064
- [9] Mallik S, Ekere N, Best C, Bhatti R. Investigation of thermal management materials for automotive electronic control units. *Applied Thermal Engineering*. 2010;**31**:355-362. DOI: 10.1016/j.applthermaleng.2010.09.023
- [10] Shojaeefard MH, Azarikhah P, Qasemian A. Experimental investigation of thermal balance and valve cover heat transfer in a small internal combustion engine. *International Journal of Automotive Engineering*. 2017;**7**: 2423-2434. DOI: 10.22068/ijae.7.2.2423
- [11] dos Santos WN, De Sousa JA, Gregorio R. Thermal conductivity behaviour of polymers around glass transition and crystalline melting temperatures. *Polymer Testing*. 2013;**32**:987-994. DOI: 10.1016/j.polymertesting.2013.05.007
- [12] Chen H, Ginzburg VV, Yang J, Yang Y, Liu W, Huang Y, et al. Thermal conductivity of polymer-based composites: Fundamentals and applications. *Progress in Polymer Science*. 2016;**59**:41-85. DOI: 10.1016/j.progpolymsci.2016.03.001
- [13] Burgera N, Laachachi A, Ferriol M, Lutz M, Toniazio V, Ruch D. Review of thermal conductivity in composites: Mechanisms, parameters and theory. *Progress in Polymer Science*. 2016;**61**:1-28. DOI: 10.1016/j.progpolymsci.2016.05.001
- [14] Han Z, Fina A. Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review. *Progress in Polymer Science*. 2011;**36**:914-944. DOI: 10.1016/j.progpolymsci.2010.11.004
- [15] Bird RB, Stewart WE, Lightfoot EN. *Transport Phenomena*. 2nd ed. New York: John Wiley & Sons, Inc; 2002. 914 p. ISBN 0-471-41077-2
- [16] Anderson DR. Thermal conductivity of polymers. *Chemical Reviews*. 1966;**66**:677-690. DOI: 10.1021/cr60244a004

- [17] Ebadi-Dehaghani H, Nazempour M. Thermal conductivity of nanoparticles filled polymers. In: Hashim A, editor. *Smart Nanoparticles Technology*. London: IntechOpen; 2012. 588 p. DOI:10.5772/3384
- [18] Yüксе N. The review of some commonly used methods and techniques to measure the thermal conductivity of insulation materials. In: Almusaed A, Almssad A, editors. *Insulation Materials in Context of Sustainability*. London: IntechOpen; 2016. DOI: 10.5772/64157
- [19] Chapter 16. Determination of Thermal Conductivity [Internet]. 2016. Available from: <http://tpm.fsv.cvut.cz/student/documents/files/BUM1/Chapter16.pdf>
- [20] Gaal PS, Thermitus M-A, Stroe DE. Thermal conductivity measurements using the flash method. *Journal of Thermal Analysis and Calorimetry*. 2004;**78**:185-189. DOI: 10.1023/B:JTAN.0000042166.64587.33
- [21] Rode HM. A transient hot wire thermal conductivity apparatus for fluids. *Journal of Research of the National Bureau of Standards*. 1981;**86**:457-480. DOI: 10.6028/jres.086.020
- [22] Jen C, Fair PG. Determination of thermal conductivity by differential scanning calorimetry. *Thermochimica Acta*. 1979;**34**:267-273. DOI: 10.1016/0040-6031(79)87116-6
- [23] Hu M, Yu D, Wei J. Thermal conductivity determination of small polymer samples by differential scanning calorimetry. *Polymer Testing*. 2007;**26**:333-337. DOI: 10.1016/j.polymertesting.2006.11.003
- [24] Merzlyakov M, Schick C. Thermal conductivity from dynamic response of DSC. *Thermochimica Acta*. 2001;**377**:183-191. DOI: 10.1016/S0040-6031(01)00553-6
- [25] Bashirov AB, Manukyan AM. Thermal conductivity of polymers at various temperatures and pressures. *Polymer Mechanics*. 1974;**10**:484-486. DOI: 10.1007/BF00865620
- [26] Osswald T, Hernandez-Ortiz JP. *Polymer Processing: Modeling and Simulation*. Munich: HANSER; 2006. 606 p. ISBNs 978-1-56990-398-8
- [27] Choy CL, Greig D. The low temperature thermal conductivity of isotropic and oriented polymers. *Journal of Physics C: Solid State Physics*. 1977;**10**:169-179. DOI: 10.1088/0022-3719/10/2/005
- [28] Barucci M, Gottardi E, Olivieri E, Pasca E, Risegari E, Ventura G. Low-temperature thermal properties of polypropylene. *Cryogenics*. 2002;**42**:551-555. DOI: 10.1016/S0011-2275(02)00076-0
- [29] Dawson A, Rides M, Nottay J. The effect of pressure on the thermal conductivity of polymer melts. *Polymer Testing*. 2006;**25**:268-275. DOI: 10.1016/j.polymertesting.2005.10.001
- [30] Andersson P, Sundqvist B. Pressure dependence of the thermal conductivity, thermal diffusivity, and specific heat of some polymers. *Journal of Polymer Science: Polymer Physics Edition*. 1975;**13**:243-251. DOI: 10.1002/pol.1975.180130202
- [31] Eiermann K. Thermal conductivity of high polymers. *Journal of Polymer Science, Polymer Symposia*. 1964;**6**: 157-165. DOI: 10.1002/polc.5070060118
- [32] Dai SC, Tanner RI. Anisotropic thermal conductivity in sheared polypropylene. *Rheologica Acta*. 2006;**45**:228-238. DOI: 10.1007/s00397-005-0012-z
- [33] Antunes M, Realinho V, Velasco JI, Solórzano E, Rodríguez-Pérez M-A, de Saja JA. Thermal conductivity

anisotropy in polypropylene foams prepared by supercritical CO₂ dissolution. *Materials Chemistry and Physics*. 2012;**136**:268-276. DOI: 10.1016/j.matchemphys.2012.07.001

[34] Ramsey JC, Fricke AL, Caskey JA. Thermal conductivity of polymer melts. *Journal of Applied Polymer Science*. 1973;**17**:1597-1605. DOI: 10.1002/app.1973.070170522

[35] Goswami Y. *Principles of Solar Engineering*. 3rd ed. Abingdon: Taylor & Francis Group; 2000. 706 p. ISBN 978-1-4665-6378-0

[36] Maier C, Calafut T. *Polypropylene: The Definitive User's Guide and Databook*. Norwich: William Andrew; 1998. 452 p. ISBN 9780815518716

[37] Guo B, Song Ghalambor A, Chacko J. *Offshore Pipelines*. Amsterdam: Elsevier; 2005 304 p. ISBN 9780080456904

[38] Birley AW. *Plastic Materials: Properties and Applications*. Berlin: Springer Science & Business Media; 2012. 198 p. ISBN 9789401176149

[39] Hussain ARJ, Alahyari AA, Eastman SA, Thibaud-Erkey C, Johnston S, Sobkowicz MJ. Review of polymers for heat exchanger applications: Factors concerning thermal conductivity. *Applied Thermal Engineering*. 2017;**113**:1118-1127. DOI: 10.1016/j.applthermaleng.2016.11.041

[40] Boudenne A, Ibos L, Fois M, Majeste JC, Gehin E. Electrical and thermal behavior of polypropylene filled with copper particles. *Composites: Part A*. 2005;**36**:1545-1554. DOI: 10.1016/j.compositesa.2005.02.005; 10.1016/j.compositesa.2005.02.005

[41] Cheewawuttipong W, Fuoka D, Tanoue S, Uematsu H, Iemoto Y. Thermal and mechanical properties of polypropylene/boron nitride

composites. *Energy Procedia*. 2013;**34**:808-817. DOI: 10.1016/j.egypro.2013.06.817

[42] Glouannec P, Chauvelon P, Feller J-F, Noel H, Ploteau JP. Current passage tubes in conductive polymer composite for fluid heating. *Energy Conversion and Management*. 2008;**49**:493-505. DOI: 10.1016/j.enconman.2007.08.013

[43] Qin Y, Li B, Wang S. Experimental investigation of a novel polymeric heat exchanger using modified polypropylene hollow fibers. *Industrial and Engineering Chemistry Research*. 2012;**51**:882-890. DOI: 10.1021/ie202075a

[44] Kashiwagi T, Grulke E, Hilding J, Groth K, Harris R, Butler K, et al. Thermal and flammability properties of polypropylene/carbon nanotube nanocomposites. *Polymer*. 2004;**45**:4227-4239. DOI: 10.1016/j.polymer.2004.03.088

[45] Roussel MD, Guy AR, Shaw LG, Cara JE. The use of calcium carbonate in polyolefins offers significant improvement in productivity. *Targets*. 2005;**300**:350-355

[46] Markarian J. Mineral Modifiers Take on New Roles. *Plastics, Additives and Compounding* [Internet]. 2004. Available from: <https://www.pharosproject.net/uploads/files/sources/1828/1359649262.pdf>

[47] Vakili MH, Ebadi-Dehaghani H, Haghshenas_Fard M. Crystallization and thermal conductivity of CaCO₃ nanoparticle filled Polypropylene. *Journal of Macromolecular Science Part B*. 2011;**50**:1637-1645. DOI: 10.1080/00222348.2010.543033

[48] Frommann L, Iqbal A, Abdullah SA. Thermo-viscoelastic behavior of PCNF-filled Polypropylene nanocomposites. *Journal of Applied Polymer Science*. 2008;**107**:2695-2703. DOI: 10.1002/app.27349

- [49] Weidenfeller B, Höfer M, Schilling F. Thermal and electrical properties of magnetite filled polymers. *Composites Part A: Applied Science and Manufacturing*. 2002;**33**:1041-1053. DOI: 10.1016/S1359-835X(02)00085-4
- [50] Weidenfeller B, Höfer M, Schilling F. Thermal conductivity, thermal diffusivity, and specific heat capacity of particle filled polypropylene. *Composites Part A: Applied Science and Manufacturing*. 2004;**35**:423-429. DOI: 10.1016/j.compositesa.2003.11.005
- [51] Andrews R, Weisenberger MC. Carbon nanotube polymer composites. *Current Opinion in Solid State and Materials Science*. 2004;**8**:31-37. DOI: 10.1016/j.cossms.2003.10.006
- [52] Pollack GL. Kapitza. Resistance. *Review of Modern Physics*. 1969;**41**: 48-81. DOI: 10.1103/RevModPhys.41.48
- [53] Swartz ET, Pohl RO. Thermal boundary resistance. *Review of Modern Physics*. 1989;**61**:605-668. DOI: 10.1103/RevModPhys.61.605
- [54] Vidal-Sallé E, Marchand A-S. Modelling of the friction thermo-mechanical coupling at the workpiece-tool interface during bulk forming processes. *Tribology Series*. 2003;**43**:349-356. DOI: 10.1016/S0167-8922(03)80062-7
- [55] Hussain F, Hojjati M, Okamoto M, Goiga RE. Review article: Polymer-matrix nanocomposites, processing, manufacturing, and application: An overview. *Journal of Composite Materials*. 2006;**40**:1511-1575. DOI: 10.1177/0021998306067321
- [56] Patti A, Russo P, Acierno D, Acierno S. The effect of filler functionalization on dispersion and thermal conductivity of polypropylene/multi wall carbon nanotubes composites. *Composites Part B Engineering*. 2016;**94**:350-359. DOI: 10.1016/j.compositesb.2016.03.072
- [57] HeonKang CH, Yoon KH, Park Y-B, Lee DY, Jeong SS. Properties of polypropylene composites containing aluminum/multi-walled carbon nanotubes. *Composites Part A: Applied Science and Manufacturing*. 2010;**41**:919-926. DOI: 10.1016/j.compositesa.2010.03.011
- [58] Muratov DS, Kuznetsov DV, Il'inykh IA, Burmistrov IN, Mazov IN. Thermal conductivity of polypropylene composites filled with silane-modified hexagonal BN. *Composites Science and Technology*. 2015;**111**:40-43. DOI: 10.1016/j.compscitech.2015.03.003
- [59] Ezat GS, Kelly AL, Mitchell SC, Youseffi M, Coates PD. Effect of maleic anhydride grafted Polypropylene Compatibilizer on the morphology and properties of Polypropylene/multiwalled carbon nanotube. *Composites*. 2012;**33**:1376-1386. DOI: 10.1002/pc.22264
- [60] Chen L, Xu H-F, He S-J, Yi-Hang D, Yu N-J, Du X-Z, et al. Thermal conductivity performance of Polypropylene composites filled with Polydopamine-functionalized hexagonal boron nitride. *PLoS One*. 2017;**12**:e0170523. DOI: 10.1371/journal.pone.0170523
- [61] Szentes A, Varga CS, Horváth G, Bartha L, Kónya Z, Haspel H, et al. Electrical resistivity and thermal properties of compatibilized multi-walled carbon nanotube/polypropylene composites. *eXPRESS Polymer Letters*. 2012;**6**:494-502. DOI: 10.3144/expresspolymlett.2012.52
- [62] Díez-Pascual AM, Naffakh M, González-Domínguez JM, Ansón AM, Martínez-Rubi Y, Martínez MT, et al. High performance PEEK/carbon nanotube composites compatibilized with polysulfones-II. Mechanical and electrical properties. *Carbon*. 2010;**48**:3500-3511. DOI: 10.1016/j.carbon.2010.05.050

- [63] Patti A, Acierno D, Russo P. Influence of filler dispersion and interfacial resistance on thermal conductivity of Polypropylene/carbon nanotubes systems. AIP Conference Proceedings. 2017;**1914**:030014. DOI: 10.1063/1.5016701
- [64] Ashby MF, Brechet YJM. Designing hybrid materials. Acta Materialia. 2003;**51**:5801-5821. DOI: 10.1016/S1359-6454(03)00441-5
- [65] Szeluga U, Kumanek., Trzebicka B. Synergy in hybrid polymer/nanocarbon composites. A review. Composites: Part A. 2015;**73**:204-231
- [66] King JA, Johnson BA, Via MD, Ciarkowski CJ. Effects of Carbon Fillers in Thermally Conductive Polypropylene Based Resins. Polymer Composites. 2010;**31**:497-506. DOI: 10.1002/pc.20830
- [67] Krause B, Pötschke P. Electrical and TC of polypropylene filled with combinations of carbon fillers. AIP Conference Proceedings. 2016;**1779**:040003. DOI: 10.1063/1.4965494
- [68] Ren Y, Zhang Y, Fang H, Ding T, Li J, Bai S-L. Simultaneous enhancement on thermal and mechanical properties of polypropylene composites filled with graphite platelets and graphene sheets. Composites: Part A. 2018;**112**:57-63. DOI: 10.1016/j.compositesa.2018.05.017
- [69] Yao J, Hu L, Zhou M, You F, Jiang X, Gao L, et al. Synergistic enhancement of thermal conductivity and dielectric properties in Al₂O₃/BaTiO₃/PP composites. Materials. 2018;**11**:1536. DOI: 10.3390/ma11091536
- [70] Cheewawuttipong W, Tanoue S, Uematsu H, Iemoto Y. Thermal conductivity of polypropylene composites with hybrid fillers of boron nitride and vapor-grown carbon fiber. Polymer Composites. 2016;**37**:936-942. DOI: 10.1002/pc.23252
- [71] Russo P, Patti A, Petrarca C, Acierno S. Thermal conductivity and dielectric properties of polypropylene-based hybrid compounds containing multiwalled carbon nanotubes. Journal of Applied Polymer Science. 2018;**135**:46470-46479. DOI: 10.1002/app.46470
- [72] Boudenne A, Ibos L, Gehin E, Candau Y. A simultaneous characterization of thermal conductivity and diffusivity of polymer materials by a periodic method. Journal of Applied Physics. 2004;**37**:132-139. DOI: 10.1088/0022-3727/37/1/022