DEVELOPMENT OF INJECTION MOLDABLE, THERMALLY CONDUCTIVE POLYMER COMPOSITES

PhD thesis

ANDRÁS SUPLICZ
MSc IN MECHANICAL ENGINEERING

SUPERVISOR:
JÓZSEF GÁBOR KOVÁCS, PhD
ASSOCIATE PROFESSOR

2015
ACKNOWLEDGEMENTS

I would like to express my thanks to my supervisor, Dr. József Gábor KOVÁCS for his help and support of my work and his guidance towards a deeper scientific way of thinking. I also would like to say thank to Professor Tibor CZIGÁNY and Dr. Tamás BÁRÁNY, who made me possible to work at the Department of Polymer Engineering. I would like to thank the help and advices of Dr. Tamás TÁBI, Norbert Krisztíán KOVÁCS and Ferenc SZABÓ. I am also grateful to my colleagues and friends at the Department of Polymer Engineering for their significant help and the creative atmosphere. I would also like to express my thanks to my students who helped a lot with my work.

I express my thanks to the Hungarian Scientific Research Fund (OTKA PD105995) for the financial support, to Arburg Hungary Ltd. for the Arburg Allrounder 370S 700-290 injection molding machine, to ANTON Kft. for the injection molds and to HSH Chemie Ltd. for the free graphite sample.

This work is connected to the scientific program of the “Development of quality oriented and harmonized R+D+I strategy and functional model at BME” project. This work is supported by the New Széchenyi Plan (Project ID: TÁMOP-4.2.1/B-09/1/KMR-2010-0002).

The work reported in this thesis has been developed in the framework of the project "Talent care and cultivation in the scientific workshops of BME" project. This project is supported by the grant TÁMOP - 4.2.2.B-10/1-2010-0009.

Last, but not least I would like to express my thanks to my family and friends for their unbroken support of my work.
# Table of Contents

NOTATIONS ........................................................................................................... 5  
ABBREVIATIONS ..................................................................................................... 9  
1. INTRODUCTION ................................................................................................. 11  
2. LITERATURE OVERVIEW .................................................................................... 13  
   2.1. Generalities on thermal conductivity ............................................................. 13  
   2.1.1. Terms of thermal conduction ........................................................................ 13  
   2.1.2. Measuring techniques .................................................................................. 15  
   2.2. Literature survey on thermal conductivity of polymers .................................. 19  
   2.2.1. The effect of temperature ............................................................................ 19  
   2.2.2. The effect of molecular weight ................................................................. 20  
   2.2.3. The effect of morphology ........................................................................... 21  
   2.2.4. Effect of the second component ............................................................... 25  
   2.2.5. Solid fillers for enhanced thermal conductivity ........................................... 26  
   2.3. Modeling methods on thermal conductivity ..................................................... 36  
   2.3.1. Numerical methods .................................................................................... 36  
   2.3.2. Finite element modeling method ................................................................. 41  
   2.4. Summary of the literature, objectives of the dissertation ................................ 44  
3. MATERIALS AND METHODS .............................................................................. 47  
   3.1. Materials .......................................................................................................... 47  
   3.2. Processing methods .......................................................................................... 48  
   3.3. Testing methods ............................................................................................... 50  
4. DEVELOPMENT OF HEAT CONDUCTOMETERS ........................................... 54  
   4.1. Hot plate apparatus ......................................................................................... 54  
   4.2. Linear heat flow apparatus .............................................................................. 56  
5. RESULTS AND DISCUSSIONS ............................................................................ 59  
   5.1. Properties of thermally conductive polymer composites ................................ 59  
   5.1.1. The effect of the matrix ............................................................................... 59  
   5.1.2. The effect of fillers ...................................................................................... 60  
   5.1.3. The effect of the processing method ........................................................... 62  
   5.1.4. Surface modification .................................................................................... 68  
   5.1.5. The hybridization of fillers ......................................................................... 71  
   5.2. Crystallinity of conductive polymer composites ............................................. 75  
   5.2.1. Method of calculation ................................................................................. 76
## Notations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>[-]</td>
<td>data fitting coefficient</td>
</tr>
<tr>
<td>A</td>
<td>[m^2]</td>
<td>surface area</td>
</tr>
<tr>
<td>A_{LN}</td>
<td>[-]</td>
<td>constant of the Lewis and Nielsen model</td>
</tr>
<tr>
<td>a_{r}</td>
<td>[-]</td>
<td>aspect ratio</td>
</tr>
<tr>
<td>A_{SH}</td>
<td>[-]</td>
<td>constant of the Steinhart-Hart equation</td>
</tr>
<tr>
<td>b</td>
<td>[-]</td>
<td>data fitting coefficient</td>
</tr>
<tr>
<td>b_{l}</td>
<td>[-]</td>
<td>Rabinowitsch correction coefficient</td>
</tr>
<tr>
<td>B_{CV}</td>
<td>[-]</td>
<td>first constant of the Cheng-Vachon equation</td>
</tr>
<tr>
<td>B_{LN}</td>
<td>[-]</td>
<td>constant of the Lewis and Nielsen model</td>
</tr>
<tr>
<td>B_{SH}</td>
<td>[-]</td>
<td>constant of the Steinhart-Hart equation</td>
</tr>
<tr>
<td>C</td>
<td>[J/K]</td>
<td>heat capacity</td>
</tr>
<tr>
<td>C_1</td>
<td>[-]</td>
<td>constant in the Agari and Uno model</td>
</tr>
<tr>
<td>c_1</td>
<td>[-]</td>
<td>minimum of the sigmoid function</td>
</tr>
<tr>
<td>C_2</td>
<td>[-]</td>
<td>constant in the Agari and Uno model</td>
</tr>
<tr>
<td>c_2</td>
<td>[-]</td>
<td>range of the sigmoid function</td>
</tr>
<tr>
<td>C_c</td>
<td>[-]</td>
<td>chain formation and orientation factor</td>
</tr>
<tr>
<td>C_{CV}</td>
<td>[-]</td>
<td>second constant of the Cheng-Vachon equation</td>
</tr>
<tr>
<td>C_f</td>
<td>[-]</td>
<td>correction factor for the filler</td>
</tr>
<tr>
<td>C_m</td>
<td>[-]</td>
<td>correction factor for the matrix</td>
</tr>
<tr>
<td>c_p</td>
<td>[J/kgK]</td>
<td>specific isobaric heat capacity</td>
</tr>
<tr>
<td>C_{SH}</td>
<td>[-]</td>
<td>constant of the Steinhart-Hart equation</td>
</tr>
<tr>
<td>D</td>
<td>[-]</td>
<td>calibration constant</td>
</tr>
<tr>
<td>d</td>
<td>[mm]</td>
<td>diameter</td>
</tr>
<tr>
<td>D_p</td>
<td>[mm]</td>
<td>diameter of the piston</td>
</tr>
<tr>
<td>dT</td>
<td>[K]</td>
<td>temperature difference</td>
</tr>
<tr>
<td>dx</td>
<td>[m]</td>
<td>displacement</td>
</tr>
<tr>
<td>E</td>
<td>[GPa]</td>
<td>tensile modulus</td>
</tr>
<tr>
<td>F</td>
<td>[N]</td>
<td>force</td>
</tr>
<tr>
<td>g</td>
<td>[-]</td>
<td>data fitting coefficient</td>
</tr>
<tr>
<td>h</td>
<td>[-]</td>
<td>data fitting coefficient</td>
</tr>
<tr>
<td>K</td>
<td>[-]</td>
<td>Rate constant of Avrami model</td>
</tr>
<tr>
<td>L</td>
<td>[m]</td>
<td>thickness of the specimen</td>
</tr>
<tr>
<td>Symbol</td>
<td>Unit</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td>-------------</td>
</tr>
<tr>
<td>l</td>
<td>[mm]</td>
<td>phonon mean free path</td>
</tr>
<tr>
<td>L_L</td>
<td>[Ω·W/K²]</td>
<td>Lorentz-number</td>
</tr>
<tr>
<td>L_m</td>
<td>[m]</td>
<td>average thickness of specimens</td>
</tr>
<tr>
<td>m</td>
<td>[kg]</td>
<td>mass</td>
</tr>
<tr>
<td>m_c</td>
<td>[kg]</td>
<td>mass of the composite</td>
</tr>
<tr>
<td>m_f</td>
<td>[kg]</td>
<td>mass of the filler</td>
</tr>
<tr>
<td>m_m</td>
<td>[kg]</td>
<td>mass of the matrix</td>
</tr>
<tr>
<td>MVR</td>
<td>[cm³/10 min]</td>
<td>Melt Volume Rate</td>
</tr>
<tr>
<td>n</td>
<td>[-]</td>
<td>Avrami exponent</td>
</tr>
<tr>
<td>n_B</td>
<td>[-]</td>
<td>Bagley correction coefficient</td>
</tr>
<tr>
<td>p</td>
<td>[bar]</td>
<td>pressure</td>
</tr>
<tr>
<td>P</td>
<td>[W]</td>
<td>electrical power</td>
</tr>
<tr>
<td>\dot{q}</td>
<td>[W/m²]</td>
<td>heat flux density</td>
</tr>
<tr>
<td>\dot{Q}</td>
<td>[W]</td>
<td>heat flow</td>
</tr>
<tr>
<td>Q_∞</td>
<td>[J]</td>
<td>heat, generated at infinite time</td>
</tr>
<tr>
<td>Q_t</td>
<td>[J]</td>
<td>heat, generated at a given time</td>
</tr>
<tr>
<td>Q_v</td>
<td>[m³/s]</td>
<td>volumetric flow rate</td>
</tr>
<tr>
<td>RD</td>
<td>[-]</td>
<td>relative density</td>
</tr>
<tr>
<td>RD_0</td>
<td>[-]</td>
<td>relative density at zero pressure</td>
</tr>
<tr>
<td>RD_∞</td>
<td>[-]</td>
<td>relative density at infinite pressure</td>
</tr>
<tr>
<td>R_s</td>
<td>[K/W]</td>
<td>thermal contact resistance</td>
</tr>
<tr>
<td>S</td>
<td>[mW]</td>
<td>gradient of the temperature-logarithmic time function</td>
</tr>
<tr>
<td>T</td>
<td>[K]</td>
<td>temperature</td>
</tr>
<tr>
<td>t</td>
<td>[s]</td>
<td>time</td>
</tr>
<tr>
<td>t_{1/2}</td>
<td>[s]</td>
<td>the half time to reach the maximum temperature</td>
</tr>
<tr>
<td>T_{1-4}</td>
<td>[K]</td>
<td>temperatures extrapolated to the surface</td>
</tr>
<tr>
<td>T_c</td>
<td>[°C]</td>
<td>temperature of isothermal crystallization</td>
</tr>
<tr>
<td>T_e</td>
<td>[K]</td>
<td>ejection temperature</td>
</tr>
<tr>
<td>T_g</td>
<td>[°C]</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>T_{m1-m4}</td>
<td>[K]</td>
<td>measured temperatures</td>
</tr>
<tr>
<td>T_{me}</td>
<td>[K]</td>
<td>melt temperature</td>
</tr>
<tr>
<td>T_{mo}</td>
<td>[K]</td>
<td>mold temperature</td>
</tr>
<tr>
<td>T_{ms}</td>
<td>[K]</td>
<td>temperature of the mold surface</td>
</tr>
</tbody>
</table>
Development of injection moldable, thermally conductive polymer composites

\[ t_p \] [s] periodic time
\[ T_{ps} \] [K] temperature of the polymer surface
\[ u \] [m/s] velocity of phonons
\[ v_{cool} \] [K/s] cooling rate
\[ X \] [%] degree of crystallinity
\[ X_{int} \] [-] interconnectivity of the conducting phase
\[ \Delta H_{cc} \] [J/g] enthalpy of cold crystallization
\[ \Delta H_f \] [J/g] enthalpy of the fully crystalline polymer
\[ \Delta H_m \] [J/g] enthalpy of melting
\[ \Delta P \] [Pa] pressure difference
\[ \Delta T_m \] [K] average temperature difference

\[ \alpha \] [m^2/s] thermal diffusivity
\[ \beta \] [1/K] thermal expansion
\[ \beta_0 \] [1/K] thermal expansion of oriented polymer
\[ \gamma_a \] [1/s] apparent shear rate
\[ \gamma_f \] [1/s] corrected shear rate
\[ \eta \] [Pa s] real viscosity
\[ \eta_a \] [Pa s] apparent viscosity
\[ \lambda \] [W/mK] thermal conductivity
\[ \lambda_{\infty} \] [W/mK] effective thermal conductivity at infinite pressure
\[ \lambda_{f} \] [W/mK] effective thermal conductivity of the filler
\[ \lambda_{m} \] [W/mK] effective thermal conductivity of the matrix
\[ \lambda_l \] [W/mK] thermal conductivity in the direction of orientation
\[ \lambda_{\perp} \] [W/mK] thermal conductivity perpendicular to the orientation
\[ \lambda_0 \] [W/mK] measured thermal conductivity
\[ \lambda_c \] [W/mK] thermal conductivity of the composite
\[ \lambda_f \] [W/mK] thermal conductivity of the filler
\[ \lambda^{HS-} \] [W/mK] lower Hashin-Shtrikman bound
\[ \lambda^{HS+} \] [W/mK] upper Hashin-Shtrikman bound
\[ \lambda_m \] [W/mK] thermal conductivity of the matrix
\[ \lambda_O \] [W/mK] thermal conductivity of oriented polymer
\( \lambda_r \quad [\text{W/mK}] \quad \text{thermal conductivity of reference} \\
\rho \quad [\text{g/cm}^3] \quad \text{density} \\
\rho_a \quad [\text{g/cm}^3] \quad \text{apparent density} \\
\rho_f \quad [\text{g/cm}^3] \quad \text{density of the filler} \\
\rho_m \quad [\text{g/cm}^3] \quad \text{density of the matrix} \\
\rho_{\text{particle}} \quad [\text{g/cm}^3] \quad \text{density of a single particle} \\
\sigma \quad [\text{MPa}] \quad \text{tensile strength} \\
\sigma_e \quad [\Omega \text{m}] \quad \text{electrical conductivity} \\
\tau_a \quad [\text{Pa}] \quad \text{apparent shear tension} \\
\tau_f \quad [\text{Pa}] \quad \text{corrected shear tension} \\
\phi_c \quad [-] \quad \text{percolation threshold} \\
\phi_f \quad [-] \quad \text{filler volume oncentration} \\
\phi_f^\text{max} \quad [-] \quad \text{maximum packing volume fraction of the filler} \\
\phi_m \quad [-] \quad \text{matrix volume concentration} \\
\phi_{\text{max}} \quad [-] \quad \text{theoretically possible filler volume fraction} \)
**ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>Acrylnitril-Butadien-Styrene terpolymer</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminium Oxide</td>
</tr>
<tr>
<td>AlN</td>
<td>Aluminium Nitride</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>BaSO₄</td>
<td>Barium Sulfate</td>
</tr>
<tr>
<td>BeO</td>
<td>Beryllium Oxide</td>
</tr>
<tr>
<td>BN</td>
<td>Boron Nitride</td>
</tr>
<tr>
<td>CBT</td>
<td>Cyclic Butylene Terephthalate oligomer</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EG</td>
<td>Expanded Graphite</td>
</tr>
<tr>
<td>EVA</td>
<td>Ethylene-Vinyl Acetate copolymer</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>Iron Oxide (Magnetite)</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Modeling</td>
</tr>
<tr>
<td>GF</td>
<td>Glass Fiber</td>
</tr>
<tr>
<td>GO</td>
<td>Graphite Oxide</td>
</tr>
<tr>
<td>HDPE</td>
<td>High-Density Polyethylene</td>
</tr>
<tr>
<td>cPP</td>
<td>Polypropylene copolymer</td>
</tr>
<tr>
<td>ICM</td>
<td>Injection-Compression Molding</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low-Density Polyethylene</td>
</tr>
<tr>
<td>LLDPE</td>
<td>Linear Low-Density Polyethylene</td>
</tr>
<tr>
<td>MDSC</td>
<td>Modulated Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>Mg₃(Si₄O₁₀(OH)₂)</td>
<td>Talc</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>NTC</td>
<td>Negative Temperature Coefficient</td>
</tr>
<tr>
<td>PA6</td>
<td>Polyamide 6</td>
</tr>
<tr>
<td>Pb</td>
<td>Lead</td>
</tr>
<tr>
<td>PCB</td>
<td>Printed Circuit Board</td>
</tr>
<tr>
<td>PCM</td>
<td>Phase Change Materials</td>
</tr>
<tr>
<td>Symbol</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>Pd</td>
<td>Palladium</td>
</tr>
<tr>
<td>PLA</td>
<td>Polylactic Acid</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(Methyl Methacrylate)</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly(Vinyl Chloride)</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon Carbide</td>
</tr>
<tr>
<td>Sn</td>
<td>Tin</td>
</tr>
<tr>
<td>SrFe$<em>{12}$O$</em>{19}$</td>
<td>Strontium Ferrite</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>TC</td>
<td>Thermal Conductivity</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Titanium Dioxide</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>Ultra-High-Molecular-Weight Polyethylene</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zinc Oxide</td>
</tr>
</tbody>
</table>
Development of injection moldable, thermally conductive polymer composites

1. Introduction

Polymers are popular engineering materials because of their relatively low density, low cost, good chemical resistance, low thermal conductivity and ease of processability compared to other materials. In the last few decades there has been an increasing demand for polymer-based structural materials to replace or complete metallic parts. So far the goal of researches has been to improve the mechanical properties of synthetic polymers to approach the strength of steel. The basis of these developments was the application of fiber-like reinforcements. On the other hand, metals do not only have better mechanical performances but also have higher thermal conductivity than polymers. There is a great demand for structural materials which are good thermal conductors but also good electrical insulators. Such materials are required in electronics, where good heat dissipation is vitally important to extend the lifespan of the devices, while electrical insulation is essential to eliminate the short circuit failures and other errors [1-4].

In the past few years developments in technology have resulted in smaller devices with higher performance (sensors, controlling units, transformers, amplifiers, integrated circuits and so on). As a result of this development heat dissipation in electronics, especially microelectronics, has an ever-increasing importance. Besides heat dissipation has a great influence on lifespan. It is well-known that the reliability of devices is exponentially dependent on their operating temperature, therefore a small increase in the operating temperature (about 10-15°C) can halve their lifespan. Generally, metallic parts are used as heat sinks to dissipate heat, but metal parts are heavier, often more costly and more difficult to process than plastic parts. Polymers normally have good insulating properties, but thermally conductive polymer composites are receiving more and more attention in the industry. These special materials have a potential in the cooling of electric and mechatronic devices. Conventionally, the cooling of mechatronic parts is done with extruded or cast metal heat sinks. To guarantee the electric insulation between the electric circuit and the heat sink, a heat conductive plastic film is applied as a barrier. However, these polymer films make the assembly process complicated and decrease the efficiency of heat transport. Thus the effectiveness of the metal heat sink also decreases. Accordingly, by eliminating the polymer barrier, thermally conductive and electrically insulating polymer composites can be innovative new materials in device development. Although in electronic packaging injection
moldable thermally conductive polymers are considered a novelty but more and more engineers apply them as an alternative solution [4-7].

It is well-known that polymer materials are good thermal insulators as their thermal conductivity varies between 0.1 and 0.5 W/mK. Traditionally, conductive polymer composites are obtained by the dispersion of conductive fillers in an insulating polymer matrix. These fillers are mainly graphite, carbon black and carbon fibers, ceramic or metal particles. If the dielectric behavior of the composite is an important requirement, thermally conductive but electrically non-conductive particles should be applied. Ceramic fillers, such as boron nitride, aluminum oxide, aluminum nitride, silica, talc and many others can be used in such cases. The fillers can significantly influence the thermal behavior of polymers. Furthermore, thermal properties depend on several other factors: filler concentration, the ratio between the properties of the components, the size, the shape and the orientation of the filler particles, the manufacturing process and filler-matrix interactions. To obtain composite materials with the appropriate thermal conductivity, high filler content is usually required, although this will increase processing difficulties. Although flow properties is reduced in this case, thermal conductivity is increased significantly, which leads to more rapid cooling of the part and thus a reduction of polymer molding cycle times [1, 2, 5, 8, 9].

The main goal of this dissertation is to develop new polymer-based composite materials of high thermal conductivity. A further important aspect is good electrical insulation behavior so that they can be used directly as electronic packaging without a thermal barrier material. It is important to extend the use of these materials so that they can replace conventionally used ceramic and metal cooling units, whose production is costly compared to the production of polymer composites. On the other hand, the modeling and prediction of the thermal conductivity of these special materials is important to tailor their properties to the needs of users. To do this, several problems have to be solved. One of these problems is that highly filled polymer composites have to be processed with conventional industrial processing machines (injection molding machine, extruder etc.). A further important task is to map the thermal and mechanical properties of the composites and their dependency on the properties of the fillers. Furthermore, it is important to know the exact properties of the raw materials so that more precise parameters can be used to develop the mathematical model to predict the thermal conductivity of composites. To achieve this, not only conventional mechanical, thermal and morphological examinations were performed but self developed measurement devices and methods were applied.
2. Literature overview

In this chapter the literature of thermally conductive composites are overviewed. At first, the terms and measurement methods of thermal conductivity are discussed, then the thermal conductivity of polymers and polymer composites are introduced. Finally the mathematical and simulation models for thermal conductivity estimation of polymer composites are overviewed.

2.1. Generalities on thermal conductivity

In this chapter the basics of the thermal conduction and the measurement techniques are presented.

2.1.1. Terms of thermal conduction

Heat conduction is a form of energy transfer, when the energy flows from particles with high temperature to particles with low temperature. It means that there is an interaction between the particles, but their movement can be neglected and is disorganized. Heat flows in the direction of temperature decrease. According to Fourier’s law (Equation (1)), in a homogenous substance heat flow is proportional to the temperature difference across the thickness and the heat transfer area, but it is inversely proportional to the thickness which is normal to the direction of the heat flow (Figure 1). This is an empirical law, which is based on observation:

\[
\dot{Q} = -\lambda \cdot A \cdot \frac{dT}{dx},
\]

where \(\dot{Q} \ [\text{W}]\) is the heat flow, \(A \ [\text{m}^2]\) is the heat transfer area, \(\lambda \ [\text{W/mK}]\) is the thermal conductivity coefficient and \(dT/dx \ [\text{K/m}]\) is the temperature gradient [10, 11].

\[\text{Figure 1. The interpretation of Fourier’s law [12]}\]
The thermal conductivity coefficient (Equation (2)) in Fourier’s law is a physical property of the substance and shows the ability of the material to conduct heat:

\[
\lambda = -\frac{\dot{q}}{dT},
\]

where \( \dot{q} \) [W/m²] is the heat flux density (the proportion of the heat flux and its area). The value of this coefficient depends on the structure of the material and its thermodynamic conditions. The calculation and measurement of thermal conductivity are difficult processes [10-12].

The mechanism of heat transfer significantly differs in different materials. In gases the energy is transferred primarily by the diffusive motion of the molecules and their collisions. In dielectric solids and liquids heat is conducted by the thermal vibration of the atoms and molecules. According to Einstein’s assumption, in solids each atom is considered an oscillator in harmonic motion. Each atom has the same amplitude and the interaction between them is negligible. In this case each atom can be regarded as an elementary oscillator. Deby extended this theory and considered the interactions of oscillations. This led to the theory of the phonon. The phonon is an elementary vibrational energy that arises from oscillating atoms within a crystal. The crystal lattice is the medium which contains the energy packets. According to this theory, thermal conductivity can be expressed in the form of Equation (3):

\[
\lambda = \frac{1}{3}C \cdot u \cdot l,
\]

where \( C \) [J/K] is the phonon heat capacity for a unit volume (\( C = \rho \cdot c_p \)), \( u \) [m/s] is the velocity of the phonon and \( l \) [m] is the mean free path of the phonon. The mean free path is the distance that a particle travels between collisions. Generally, phonon velocity is equal to the velocity of sound [10, 11, 13, 14]. In ideal, perfect crystals there would be no phonon scattering which would result in infinite thermal conductivity. In fact, the structure of polymers is far from the perfect crystals, even in the semicrystalline thermoplastics. Hence the polymers contain defects, which cause phonon scattering. Hence the thermal conductivity of polymers is very low. At temperatures near absolute zero, thermal conductivity is very low. As the temperature increases, the mean free path increases and thermal conductivity also increases and reaches its maximum. A further increase in temperature results in anharmonic atomic vibration, which leads to a decrease in phonon mean free path and consequently a decrease in thermal conductivity [13, 15].
In metals, heat is conducted primarily by mobile electrons and secondly by the phonons. This phenomenon guarantees that metals have good thermal conductivity. In pure metals, the conduction by electrons is dominant. In impure metals or in disordered alloys, the phonon contribution can be comparable with the electronic contribution [16]. Metals that have good electrical conductivity also have good thermal conductivity. At a given temperature, thermal conductivity is proportional to electrical conductivity. This relation can be characterized by the Wiedmann-Franz law (Equation (4)):

\[
\frac{\lambda}{\sigma_e} = L_L \cdot T ,
\]

where \(\lambda\) [W/mK] is the thermal conductivity coefficient, \(\sigma_e\) [Ωm] is the electrical conductivity, \(T\) [K] is the temperature and \(L_L\) is the Lorentz number, whose theoretical value (2.44·10^8 [ΩW/K^2]) is independent of the temperature and is the same for all metals in which free electrons cause the primary energy transfer [10, 11, 17].

2.1.2. Measuring techniques

**Guarded hot plate method**

The standardized guarded hot plate method [18, 19] is one of the most common measurement methods of thermal conductivity for materials of low thermal conductivity (\(\lambda<1\) W/mK). This method is used mainly for construction materials and thermal insulators of buildings. The measurement results are precise enough, at room temperature the uncertainty is about 2%, but at higher temperatures it can be higher, about 5-10% [20].

The calculation of thermal conductivity is based on Fourier’s law (1). The following parameters are needed for the calculation: sample thickness; the heat flux through the sample; the area perpendicular to the heat flux; and the temperature difference between the two sides of the specimen. The temperature difference can be generated with an electrical heating unit, thus the heat flux can be calculated from the electrical power (the product of the voltage and the current). The temperatures are usually registered with thermocouples in a thermal stationary condition. From these data thermal conductivity can be easily calculated [20].

There are two commonly used measurement methods. One is the “two-specimen apparatus” (Figure 2/a), where two specimens are put on each side of a heating unit symmetrically. To minimize heat loss on the sides, the hot plate is surrounded by a separated guard with an independent heating unit. The second variation is the “one-specimen apparatus” (Figure 2/b). In this case only one cold plate and one specimen are required. These units are
replaced by a second heating unit as a back guard, thus the heat will be oriented in the direction of the sample [20].

![Diagram of two and one specimen hot plate apparatus](image)

**Figure 2. Concept of the two-specimen (a) and one-specimen (b) hot plate apparatus [20]**

After measurement thermal conductivity can be calculated with Equation (5) for the one-specimen apparatus and Equation (6) for the two-specimen apparatus:

$$\lambda = \frac{P}{A} \cdot \frac{L}{T_2 - T_1}, \quad (5)$$

$$\lambda = \frac{P}{A} \cdot \frac{L_{m}/2}{\Delta T_m}, \quad (6)$$

where $P$ [W] is the electrical power, $A$ [m²] is the area of the specimen, $L$ [m] is the thickness, $L_m$ [m] is the average thickness of the two specimens, $T_2$ [K] and $T_1$ [K] are the temperature of the hot and cold side of the specimen and $\Delta T_m$ [K] is the temperature difference between the hot and cold side in the two-specimen apparatus. With the changing of temperature $T_2$, thermal conductivity at different temperatures can be calculated. The disadvantage of the method is that it is rather time-consuming, thus it takes a long time to measure the temperature dependency of thermal conductivity [20].

**Hot wire method**

The theory of the hot-wire method was invented in 1888 by Schleirmacher but it was first used in practice in 1949. With this method van der Held and van Drunen measured the thermal conductivity of liquids [21]. Nowadays it is mainly used with thermal insulators. The method is based on measuring the temperature difference which is generated in the specimen by a linear heat source. It is assumed that the heat source generates permanent and uniform heat. Thermal conductivity can be calculated from the temperature change in a known time period. With this method materials whose thermal conductivity is under 2 W/mK can be investigated, but with some special modifications this upper limit can be extended to 25 W/mK. From the measured values thermal conductivity can be calculated with Equation (7):
Development of injection moldable, thermally conductive polymer composites

\[ \dot{\lambda} = \frac{Q}{4 \cdot \pi \cdot \ln \left( \frac{t_2}{t_1} \right)} = \frac{Q}{4 \cdot \pi \cdot S}, \]  

(7)

where \( Q \) [W] is the heat flow (electric power), \( t_1 \) and \( t_2 \) [s] are given times during measurement, \( T_1 \) and \( T_2 \) [K] are the measured temperatures at \( t_1 \) and \( t_2 \) respectively and \( S \) [mK] is the gradient of the linear section in the temperature-logarithmic time function. The general layout of the apparatus is shown in Figure 3. According to standards [22, 23], the size of the specimen is 230x114x76 mm. Measurement requires two specimens and the place for the thermocouples and the heating wire should be machined on one of them. It is essential to make good thermal contact between the samples and the heating unit. Measurement should start in an isothermal condition. The disadvantage of the method is that large samples are necessary. The advantage is that the boundary conditions can be kept easily and it can be used at higher temperatures too [20, 24].

![Figure 3. Concept of the hot wire apparatus [24]](image)

**Flash method**

The flash method [25, 26] is used to determine the thermal diffusivity of different materials. The basic idea of the measurement method was developed by Parker et al. [27] in 1961. During measurement one side of a flat and thin sample is heated with a heat pulse, while on the other side temperature is registered as a function of time (Figure 4). Thermal diffusivity can be calculated with the Parker equation (Equation (8)):

\[ \alpha = 1.38 \frac{L^2}{t_{1/2}}, \]  

(8)

where \( \alpha \) [m²/s] is thermal diffusivity, \( L \) [m] is sample thickness and \( t_{1/2} \) [s] is the half time to reach the maximum temperature. Thermal conductivity can be calculated with the following equation (Equation (9)):

\[ \lambda = \alpha \cdot \rho \cdot c_p, \]  

(9)
where $\lambda$ [W/mK] is the thermal conductivity, $\alpha$ [m$^2$/s] is the thermal diffusivity, $\rho$ [kg/m$^3$] is the density and $c_p$ [J/kg·K] is the isobar specific heat of the sample [28].

The advantage of the method is that only a small sample is required (diameter: 12 mm, thickness: 1-2 mm). Furthermore, measurement only takes a short time (only a few seconds) and the temperature range can be very wide. The main disadvantage is that the equipment is more expensive than transient measurement units and for porous and inhomogeneous materials further special methods are needed to get the correct material properties [20, 27].

**Modulated Differential Scanning Calorimetry (MDSC)**

This method was developed by Marcus and Blaine [30, 31]. It is based on a modulated differential scanning calorimetric measurement (MDSC) (Figure 5), which can be performed on a conventional DSC machine without any modification. The measurement range is between 0.1-1.5 W/mK. MDSC is the patent [32] of TA Instruments, where the test specimen is exposed to a linear heating method which has a superimposed sinusoidal oscillation (temperature modulation), resulting in a cyclic heating profile.
In contrast to steady state methods, modulated heat flow establishes a dynamic equilibrium in the test specimen. It means that the measurement of thermal conductivity can be performed by applying a cyclic temperature program to only one side of the test specimen. First, calibration has to be performed on a known reference: the measurement of specific heat on a thin sample and apparent specific heat measurement on a thick sample. After the measurements thermal conductivity can be calculated with Equation (10) for a sample of general shape and with Equation (11) for a cylindrical sample:

\[
\lambda_{\text{v}} = \frac{2 \cdot \pi \cdot c_p}{\rho \cdot A^2 \cdot t_p},
\]

\[
\lambda_{\text{v}} = \frac{8 \cdot L \cdot c_p}{\rho \cdot m \cdot d^2 \cdot t_p},
\]

where \(\lambda\) [W/mK] is the thermal conductivity, \(C\) [mJ/K] is the apparent heat capacity, \(c_p\) [J/gK] is the specific heat, \(\rho\) [g/cm\(^3\)] is the density, \(A\) [mm\(^2\)] is the cross section, \(L\) [mm] is the length, \(m\) [mg] is the mass, \(d\) [mm] is the diameter of the sample and \(t_p\) [s] is the periodic time. To get the correct results, a calibration constant has to be applied (Equation (12)):

\[
D = \sqrt{\lambda_{\text{v}} \cdot \lambda_r} - \lambda_r,
\]

where \(\lambda_r\) [W/mK] is the thermal conductivity of the reference, \(\lambda_0\) [W/mK] is the measured thermal conductivity and \(D\) [W/mK] is the calibration constant. The value for \(D\) is typically 0.014 W/mK for a 6.35 mm diameter sample. Using factor \(D\), the thermal conductivity of the sample can be calculated with Equation (13):

\[
\lambda = \frac{\lambda_{\text{v}} - 2 \cdot D + \sqrt{\lambda_{\text{v}}^2 - 4 \cdot D \cdot \lambda_{\text{v}}}}{2}.
\]

### 2.2. Literature survey on thermal conductivity of polymers

The thermal conductivity of the polymers depends on many factors, such as chemical composition, bond strength, side group molecular weight, structure type, molecular density distribution, structural defects, processing parameters, temperature, and several other parameters [1, 33]. In this chapter the effects of these factors are presented.

#### 2.2.1. The effect of temperature

The thermal conductivity of a polymer depends on its temperature (Figure 6). In the case of amorphous polymers temperature dependence can be divided into three groups, which
are based on the interchain interactions. The first is when there is a well-defined thermal conductivity maximum near the glass transition temperature (Figure 6/a/I.). This is typical in polymers that contain strong bonds, heavier chain segments and long branches (such as PVC). In the second group there is a wide plateau near the glass transition temperature with only a small increase or decrease (Figure 6/a/II.). Some amorphous polystyrenes show this behavior. In the third group thermal conductivity changes almost linearly as a function of temperature, but at the glass transition temperature the gradient changes (Figure 6/a/III.). It is typical for polymers which have weak interchain interactions, lighter chain segments, and short and fewer branch chains (such as ABS). In the case of semi-crystalline polymers, thermal conductivity reaches its maximum value at about 100 K (Figure 6/b), which is shifted toward higher conductivities and lower temperatures when crystallinity is increased [34, 35].

\[ \text{Figure 6. Temperature dependent thermal conductivity: a, amorphous polymers; b, semi-crystalline polymers [36]} \]

2.2.2. The effect of molecular weight

The effect of molecular weight on thermal conductivity was investigated first by Ueberreiter et al. [37], on different polystyrenes having different molecular weights. It was shown that in the whole temperature range the higher molecular weight polymer has higher thermal conductivity. The explanation was that energy could be transmitted more easily along the molecules and chains, than between them. Using this theory Hansen and Ho [38] developed a model, which shows that thermal conductivity increases proportionally to the square root of the weight averaged molecular weight at low molecular weights and become independent of the molecular weight at high molecular weights. Polystyrene was used to prove the theory. It was also pointed out that the linear extent of the molecules also has an effect on thermal conductivity. It means that if a linear and a branched homolog polymer of equal molecular weight are considered, the linear polymer always have the higher thermal
Development of injection moldable, thermally conductive polymer composites

cconductivity. It was also shown that molecular weight has a remarkable effect on the thermal conductivity of the polyethylene melt, but in solid state it has no effect.

Polymers are often mixed with low molecular weight plasticizers, which change thermal and mechanical properties. Several researchers have shown that plasticizers can decrease thermal conductivity [39, 40].

2.2.3. The effect of morphology

Molecular orientation

During stretching the polymer, its molecules and chains are oriented, which can result in an anisotropic structure. This structural anisotropy can be shown by the anisotropy in macroscale properties. Orientation causes anisotropic thermal conductivity, which should also not be neglected. Much research has been carried out on the thermal conductivity of stretched polymers [41-48] which investigated conductivity in the direction of the orientation, and perpendicular to the orientation. Different changes were shown in different polymers, but in all cases conductivity increased in the direction of the orientation, and decreased perpendicular to the stretch. On the basis of this phenomenon, a model was developed that describes the relationship between the anisotropic thermal conductivity of polymers and the thermal conductivity of unoriented polymers (Equation (14)):

\[
\frac{1}{\lambda_{||}} + \frac{2}{\lambda_{\perp}} = \frac{3}{\lambda},
\]

where \( \lambda \) [W/mK] is the thermal conductivity of the unoriented polymer, \( \lambda_{||} \) [W/mK] is the thermal conductivity of the polymer parallel to the orientation and \( \lambda_{\perp} \) [W/mK] is the thermal conductivity of the polymer perpendicular to the orientation. The correctness of the equation was proved for several amorphous polymers. A further relationship was developed between the thermal conductivity and thermal expansion of polymers (Equation (15)), and it was proved for some materials (Figure 7):

\[
\frac{\lambda}{\lambda_{o}} = \left(0.8 \cdot \frac{\beta_{o}}{\beta}\right) + 0.2,
\]

where \( \lambda_{o}, \lambda \) [W/mK] are the thermal conductivity of oriented and unoriented polymers and \( \beta_{o}, \beta \) [1/K] are the thermal expansion of oriented and unoriented polymers. Hansen and Ho [38] also developed a model (Equation (16)) which calculates the effect of orientation on thermal conductivity.
András SUPLICZ

\[
\frac{\lambda}{\lambda_\perp} = \sqrt{\frac{\lambda_{\parallel}}{\lambda}}.
\] (16)

Figure 7. The relationship between thermal conductivity and thermal expansion [43]

To investigate the effect of orientation, Sheng et al. [49] produced high-quality ultra-drawn polyethylene nanofibers with a diameter of 50-500 nm and a length of 10 mm. The fibers were drawn from UHMWPE gel with a sharp tungsten tip (diameter: 100 nm) and a tipless atomic force microscope. After drying, the fibers were mechanically stretched. The molecular orientation during the manufacturing of the fiber and the TEM image of the final fiber can be seen in Figure 8.

A measurement unit was developed to evaluate thermal conductivity. One end of the polymer fiber was fixed to the tipless AFM cantilever and the other end was attached to a micro-thermocouple, which is mounted on the tip of a steel needle. The amount of heat was adjusted through the needle. If the power of the laser and the temperature are varied and the geometrical sizes are known, thermal conductivity can be easily calculated. If the stretch is increased, the thermal conductivity of the nanofiber also increases and can reach up to 104 W/mK.
Crystallinity

In contrast to amorphous polymers, semicrystalline polymers have a more ordered structure, which results in higher thermal conductivity. Due to the denser structure, there is smaller resistance to intermolecular heat transfer and to the phonon diffusion. It means that thermal conductivity also depends on the crystal fraction of polymers. The thermal conductivity of polymers is typically 0.1-0.5 W/mK. Amorphous materials are in the lower range (PMMA~0.21; PS~0.14; PVC~0.19 W/mK) and semicrystalline polymers are in the upper range (LDPE~0.3; PA6~0.25; HDPE~0.44 W/mK). If crystallinity increases, thermal conductivity also increases [1, 33]. In the Appendix there are listed the thermal conductivities of some polymers (Chapter 9, Table 13).

Processing induced morphology

The properties of composite materials are determined mainly by their macrostructure (form, size, concentration, dispersion and orientation of the reinforcement). The macrostructure can be modified with the correct choice of filler type and processing parameters. In injection molded particle filled polymer products the distribution of particles is inhomogeneous in the cross-section and also along the flow path. This phenomenon is called the segregation of fillers and reinforcements. Orientation is also typical for fillers and reinforcements. During the mold filling phase, the reinforcements orient themselves in the direction of melt flow as a result of the high shear rate. Hence the particles are parallel to the direction of flow in a thin shell layer but in the core they are generally perpendicular to this direction. This structure can be influenced with injection molding technological parameters, and the geometry of the cavity and gating system [50-52]. Segregation has been analyzed by many researchers (Hegler and Mennig [50, 51], Papathanasiou and Ogadhoh [53, 54] and Kovács [55]) and the followings were stated:

- The concentration of filler and reinforcement increases in the direction of the core. In the direction of melt flow transversal inhomogeneity decreases.
- Filler concentration gradually increases away from the gate, it reaches the nominal values at about half the length of flow.
- At a low length/diameter ratio (aspect ratio), with larger particle sizes and at higher filler concentration segregation is more intense.
- At a greater flow length the distribution of the fillers and reinforcements in the polymer matrix will be more inhomogeneous.
Amesöder et al. [56] investigated the direction dependent thermal conductivity of 30 vol% graphite filled PA6. The samples were produced with injection molding. The thermal conductivity of the composite was 1.8 W/mK through the thickness, 6.8 W/mK in the direction of the flow and 4.4 W/mK in the cross-flow direction. It shows that orientation has a significant influence on thermal conductivity.

Michaeli and Pfefferkorn [57] investigated the segregation-induced properties of filled polymers through electrical conductivity. As this property is in close connection with thermal conductivity, the effect should be the same. The authors used copper fiber and a low melting point alloy as filler and reinforcement. They showed that electrical conductivity increased when the thickness of the sample was increased and conductivity depends less on flow length Figure 9.

![Figure 9. The electrical conductivity as a function of sample thickness and flow path [57]](image)

The properties of the composites depend not only on the composition of the material but on technological parameters as well. It was proved that surface conductivity remains nearly the same independently of value of the processing parameters. On the contrary, through-thickness conductivity is significantly influenced by the melt and mold temperature and the injection rate. With longer filling time (lower injection rate) the sheared zone can be decreased, hence conductivity can be increased. By changing the viscosity of the matrix material electrical conductivity can also be influenced. The higher the viscosity of the matrix material is, the more oriented the fillers are. Furthermore, the greater the difference between the temperature of the melt and the mold is, the higher the orientation in the layers near to the surface is.

Michaeli and Pfefferkorn [57] analyzed the effect of injection molding parameters on the properties of highly filled composites. From the molding tests it could be concluded that high metal content significantly influenced the rheological properties of the matrix. At low filler concentration the flow pattern during the filling phase is parabolic. At high filler content the flow shows a different pattern (Figure 10), which can be explained by the high shear and
increased viscosity. Besides this, the reason for this behavior is not only the enhanced melt viscosity of the composite, but also the high thermal conductivity of the material which can cause a local premature freeze-off. Hence the achievable flow length would be shorter using conventional technologies. It was also shown with a spiral mold that the flow length of conductive composites can be increased by increasing mold temperature.

Amesöder et al. [56] also investigated the flow pattern of conductive composites. They pointed out that if a higher flow rate is used during injection molding, the filling will be more even. They also stated that this effect can be caused by the local premature freeze-off of composites.

### 2.2.4. Effect of the second component

**Gases**

The general name of two-component polymer-based materials where the first component is the polymer matrix and the second component is gas is polymer foams. The geometry of the foam cells may be closed or open. Open-cell foams are generally soft and flexible and are used for seating, bedding, acoustical insulation and many other purposes. Closed-cell foams are generally rigid, and suitable for thermal insulation. The matrix of plastic foams is usually polyurethane, polystyrene, polyolefin or PVC. Plastic foams can be produced in a very wide range of density from 0.003 g/cm$^3$ to the neat polymer’s density. Foaming can be carried out by mechanical, chemical or physical means. The thermal conductivity of the foam is determined by four factors: heat conduction through the solid component, conduction through the gas component, convection through the cell and radiation through the cell walls and the voids. The thermal conductivity of foams is influenced by many factors: density, cell size, moisture content, type of gas in the cells and many others.
Generally, the thermal conductivity of plastic foams which are used for thermal insulation is under 0.05 W/mK [58, 59].

**Liquids**

There are two ways to fill liquid in a polymer matrix. The first is when a low melting point alloy is added to the polymer. In this case the filler is in liquid state only during processing. The second method is phase-change materials (PCM). PCMs are used for passive heat storage and temperature control through the absorption of large amounts of energy as latent heat at a constant phase transition temperature. Paraffin waxes belong to the most promising PCMs [60-62].

**Solids**

Conductive polymer composites are most commonly obtained by mixing conductive fillers into an insulating polymer matrix. These fillers are mainly carbon fibers or graphite, carbon black, ceramic or metal particles. The measured thermal properties of a type of particle depend on several factors, such as purity, crystal structure, particle size and also the measurement method. Fibers and flakes display an anisotropic behavior as their thermal conductivity is much higher along their main axis or parallel to the surface of the plate, than perpendicular to these directions. It is also evident that if filler content is increased, thermal conductivity also increases, although the flowability of the polymer melt decreases. Thus processing methods set a limit to filler content and the achievable thermal conductivity [8, 9]. In the Appendix there are listed the thermal conductivities of some typical filler (Chapter 9, Table 13 and Table 14).

### 2.2.5. Solid fillers for enhanced thermal conductivity

**Carbon-based fillers**

The best-known carbon-based fillers are graphite, carbon fiber and carbon black. They combine good thermal conductivity and low density. Graphite is usually used as conductive filler because of its superior thermal conductivity (~200-400 W/mK), low price and good dispersability. Carbon black is the aggregate of graphite microcrystals. Its particle size is about 10-500 nm and has quite a large surface area (25-150 m²/g). Carbon black is good for electrical conductivity enhancement rather than thermal conductivity enhancement [1].

Graphene is the structural base of graphite, carbon nanotubes (CNT) and fullerenes (Figure 11). Graphene is a single-atom thick layer of graphite with hexagonally structured
Development of injection moldable, thermally conductive polymer composites

It was discovered in 1940 but it was only in 2004 that it was produced by Geim and his colleagues [64, 65]. This material has several superior properties. Its electrical conductivity is 7200 S/m, and it shows very high thermal conductivity (as high as 5300 W/mK). Graphene is also the strongest material, its tensile modulus is about 1 TPa and its tensile strength is about 130 GPa. These superior properties make it an ideal reinforcement in polymer composites. In the last few years several methods have been developed to produce graphene. These can be divided in four main groups. The first group contains the various chemical methods, such as the CVD process (Chemical Vapor Deposition) and epitaxial growth. Epitaxial growth means the growing of a thin layer on the surface of a crystal so that the layer has the same structure as the underlying crystal. The second group is the micromechanical exfoliation of graphite. With this method Kun and co-workers also prepared graphene [66, 67]. The third group is epitaxial growth on electrically insulating substrates like silicon carbide. Finally, graphene can be produced with chemical processes, like the chemical reduction of graphite oxide (GO), liquid-phase exfoliation of graphite in organic solvents and the thermal reduction of graphite oxide [66-69].

![Image of graphene, graphite, carbon nanotube, and fullerene](image)

**Figure 11.** The structure of graphene (a), graphite (b), a carbon nanotube (c) and a fullerene (d) [68]

In the last few years the application of graphene nanoparticles and carbon nanotubes has received much attention and thus generated new possibilities for the development of polymer composites. The new composites developed show significantly enhanced properties even when only a small amount of nanofiller is used. Many researches are carried out on graphene or carbon nanotube-filled polymers. In most cases epoxy [70], poly(methyl methacrylate) [71, 72], polypropylene [73], high density polyethylene [74] and polyamide [75] were used as matrix material. The biggest difficulty in the preparation of the composite is to produce the even distribution of the filler in the matrix. In the last few decades several techniques have been developed for the homogeneous dispersion of nanoparticles, such as in-situ polymerization [1, 68, 69], solution mixing [1, 68, 69, 76-78] and melt mixing [1, 68, 69, 79].
Xie et al. made an overview on the possibilities of dispersing CNTs in polymer matrices. It was stated that the key issue is to enhance the thermal conductivity of polymer composites is to control aggregation in polymeric matrices to obtain an interconnecting network suitable for heat transfer. To achieve perfect dispersion, the particles are isolated from each other, which lead to low thermal conduction.

Carbon-based nanoparticles, such as graphene and CNT have excellent thermal properties, hence these fillers are often combined to increase the thermal conductivity and the thermal stability of molded parts, and also decrease their shrinkage. CNT has almost the same thermal conductivity as graphene, but graphene shows lower interface thermal resistance thanks to its two-dimensional geometry. Thus graphene is more efficient in the modification of material properties than CNT. Nanoparticles with a large specific surface area increase the extent of interfacial area between the polymer and particles in the nanocomposites, which results in inefficient heat transfer. Interfacial thermal resistance between polymer and CNT was determined in the order of $10^{-8}$ m$^2$K/W. The source of interface thermal resistance can be the scattering of phonons on the contact surface, the imperfect physical contact between particle and matrix or the different thermal expansion coefficients of matrix and particles [69, 81-83].

**Metal fillers**

With metal fillers both the thermal conductivity and electric conductivity of composite materials can be improved. Metals have high density, thus adding a high amount of fillers to the polymer significantly increases the density of the composite. This way the biggest advantage of polymers, their lightness, disappears. For the enhancement of thermal conductivity aluminum, silver, copper, brass and nickel powder are usually used in the literature. The thermal conductivity of metal-filled polymer composites largely depends on filler content, the TC, size and shape of the fillers and their dispersion in the matrix.

Boudenne et al. [84] investigated the effect of particle size of copper implemented into a polypropylene matrix. The composites were prepared by melt mixing and the samples by compression molding. Besides the size effect, specific heat, electrical conductivity and crystallinity as a function of filler content were investigated. The particle size of the powder was 30 (Cu$_a$) and 200 $\mu$m (Cu$_b$). It was highlighted that smaller particles resulted in higher heat transport ability of the composite (Figure 12).
Molefi et al. [85] also investigated the effect of particle size in the case of copper powder-filled low-density polyethylene. The average particle size of the copper powder was 50 nm in one case and 38 \(\mu\)m in another case. The samples were also prepared by melt mixing and compression molding. It was concluded that thermal conductivity increased as Cu content was increased, but there was little difference between the thermal conductivities of micro- and nanoparticle-filled composites.

Kumlutas and Tavman [86] prepared tin powder-filled (\(\lambda=64\) W/mK) HDPE (\(\lambda=0.55\) W/mK) composites by dry mixing and compression molding. Thermal conductivity was measured with the hot-wire method at different temperatures (Figure 13). It was found that in accordance with the literature, above the glass transition temperature of HDPE (~ -110°C) the thermal conductivity of composites decreased when the temperature was increased. It was also concluded that when 16 vol% tin was filled into the HDPE matrix, thermal conductivity increased to 1.1 W/mK, which is 101% higher than that of unfilled HDPE.
Dey and Tripathi [87] investigated the thermal conductivity of silicon particulate-reinforced high-density polyethylene composites up to 20 vol% filler content. The particle size of silicon powder was 5-10 µm and its thermal conductivity was 140 W/mK. The components of the composite were first dry mixed then compression molded. The measurements showed that the effective thermal conductivity for HDPE containing 20 vol% silicon becomes double (0.85 W/mK) that of unfilled HDPE (0.36 W/mK) (Figure 14). It was also concluded that the thermal conductivity of HDPE-Si composites only show a marginal decrease between room temperature and 80°C.

![Figure 14. The effective thermal conductivity of HDPE/Si composites as a function of Si content [87]](image)

Several researchers have investigated low melting-point alloys used as fillers for polymer composites. During polymer processing (injection molding, extrusion) the alloy melts and remains in the liquid phase until the cooling phase. Therefore the processability of highly filled composites can be improved by the phase change of the alloys. On the other hand, the shape and size of liquid metal can be influenced with the flow properties of the matrix and the processing parameters.

Low melting point alloy powders are generally produced with an automated ultrasonication process [88]. Bormasenko et al. [89] developed a new method to produce low melting metal micropowder in three steps. In the first stage the alloy and polymer matrix was mixed in an extruder, then pelletized. Secondly, from the granulates a thin film was extruded, and finally, the matrix was dissolved. It was shown that the shape of the particles can be influenced by the viscosity of the polymer matrix.

Michaeli and Pfefferkorn [57] introduced a novel polymer-metal hybrid material to further increase the thermal and electrical conductivity of conventionally used conductive polymers, while at the same time improving their processability. The novel composite
Development of injection moldable, thermally conductive polymer composites

contained 15 m% (56 vol%) polyamide 6, 33 m% tin-zinc alloy (melting point: 199°C) and 52 m% copper fiber (length: 0.65 mm; diameter: 35 µm). It was shown that the copper fiber and the low melting point alloy form a three-dimensional network in the injection molded part. Thanks to the fine dispersion of the alloy and the good adhesion between it and the copper fiber, several contact points are developed. The authors only measured electrical conductivity, the thermal conductivity of the hybrid composite was not examined. Electrical conductivity was three orders of magnitude higher when a low melting metal alloy and copper fiber were used together than when only copper fiber was used [90].

Zhang et al. [91] investigated the rheological properties of a low melting alloy-filled (70 m% tin, 30 vol% lead) polystyrene. The melting point of the alloy was 183-188°C, and its particle size was 11 µm. The flowability of the material was investigated with a capillary rheometer. The composite showed a pseudoplastic behaviour and its viscosity obeyed the power law similarly to other filled polymers. The authors showed that below the melting point of the alloy the relative viscosity of the composite first decreases to a minimum value as alloy concentration is increased, then increases as alloy concentration is further increased. The critical volume fraction where relative viscosity starts to increase is equal to the percolation threshold of the composite (Figure 15/a). On the other hand, above the melting point of the alloy the viscosity of the composite decreased as concentration was increased (Figure 15/b).

![Figure 15. The viscosity of tin-lead alloy-filled polystyrene as a function of filler content at 175°C (a) and 190°C (b) [91]](image)

Mrozek et al. [92] investigated the processability of polystyrene filled with nickel powder and a low melting metal (58 m% bismuth, 42 m% tin). At 30 vol% nickel content the material was an unprocessable paste with large void content. It was concluded that in order to increase filler content, a low melting metal alloy needs to be used. In later experiments 20-60 vol% alloy and 10 vol% nickel was filled in the matrix. The nickel particles improved and
maintained the homogeneous dispersion of the alloy. In the absence of nickel powder the eutectic alloy can coalesce into large droplets, which results in decreased conductivity. The authors measured only the electrical conductivity of composites. This statement was not proved for the thermal conductivity.

**Ceramic fillers**

Ceramics have good thermal conductivity, while at the same time they are good electric insulators. As a result, they are the best materials for heat dissipation in the electric industry. In the literature the most investigated ceramic fillers are beryllium oxide (BeO), aluminum nitride (AlN), silicon carbide (SiC), aluminum oxide (Al$_2$O$_3$), talc and boron nitride (BN). The achievable thermal conductivity is influenced mainly by filler concentration, particle size and shape, dispersion and surface treatment.

Lee *et al.* [93] investigated how the efficiency of solar cells can be enhanced by increasing the thermal conductivity of the EVA (ethylene-vinylacetate) layer. A comprehensive study was performed with many different types of filler, such as aluminum oxide, magnesium oxide, zinc oxide, silicon carbide, boron nitride and aluminum nitride. The fillers were surface treated with 1 m% silane. The samples were prepared by two-roll mill and compression molding. The thermal conductivity (Figure 16) and also the electrical resistivity of the composites were measured. The highest thermal conductivity, 2.85 W/mK was obtained with 60 vol% SiC. With 60 vol% ZnO and BN thermal conductivity was lower, 2.26 and 2.08 W/mK respectively, but the composites filled with these fillers showed better electrical insulation.

![Figure 16. Thermal conductivity of the EVA composites [93]](image)

Ishida and Rimdusit [94] prepared a thermally conductive polymer composite by using a polibenzenoxazine matrix and boron nitride as filler (225 µm). The bisphenol-A-metilamin
based polibenzoxazine has very low viscosity, which improves the wetting and dispersion of the filler particles. The monomer and the BN was first dry mixed at room temperature then the specimens were compression molded. In this way a very high, 78.5 vol% filler content was achieved. Thermal conductivity was 32.5 W/mK.

Kemaloglu et al. [95] investigated the effect of micro and nano BN on the thermal, mechanical and morphological properties of silicon rubber. 0, 10, 30 and 50 m% filled composites were prepared with an extruder, then 1 and 3 mm thick samples were compression molded. It was concluded that when BN was added to the matrix, tensile strength decreased in all cases, which means that the interfacial interaction between silicone and BN is poor. It was also stated that larger particle sizes resulted in worse mechanical properties. A similar effect can be seen in the case of elongation at break. The tensile modulus increased with BN content, and nano-sized BN has a more pronounced effect. On the other hand, particle size has the opposite effect on thermal conductivity, and it was found that the aspect ratio of the filler is critical in achieving high thermal conductivity. When 50 m% micro sized BN was added to silicone rubber, the thermal conductivity was more than 2 W/mK.

Zhou [96] prepared thermally conductive linear low-density polyethylene (LLDPE) composite with aluminum nitride (particle size: 8-10 µm; TC: 170 W/mK) as filler. The composite was made on a two-roll mill up to 70 m% filler content and the samples were prepared with compression molding. Zhou also prepared titanate-coated AlN powder. According to Gu et al. [97] the titanate creates a monomolecular layer on the interface of AlN and LLDPE. One end of the titanate coupling agent makes a strong chemical bond with the free protons on the AlN surface, and the van der Waals force links the other end of the coupling agent to the LLDPE chains. The DSC measurements showed that as the AlN content was increased, the crystallinity of the composite decreased. According to Luyt et al. [98], the main reason is that LLDPE has relatively high crystallinity and has no bigger amorphous phase where the crystals could be placed. Hence at low filler content the AlN particles are in the interlaminar layers, which blocks further crystal evolution. At higher filler content there is a change in crystal evolution. Thermogravimetry analysis (TGA) showed that there is a significant increase in the thermal stability of LLDPE with increasing AlN concentration. The explanation can be the higher heat capacity and the high thermal conductivity, which cause an improved heat absorption ability. In this manner LLDPE chains start to degrade at higher temperatures. According to thermal conductivity measurements, at 70 m% (~40 vol%) AlN and titanate modified AlN concentration the thermal conductivity of the composites is 1.25 and 1.39 W/mK, respectively. The temperature dependence of thermal conductivity was also
investigated between 25 and 120°C. It was found that by increasing the temperature, thermal conductivity decreases, which is caused by thermal expansion. As a consequence of thermal expansion the distance between the AlN particles in the LLDPE matrix starts to increase.

Weidenfeller et al. [99] concluded that by the addition of metal and oxide fillers to polymer matrices, the thermal conductivity and heat capacity of polymers can be varied systematically. The polypropylene-based composite samples with various fillers were prepared with injection molding. Magnetite (Fe$_3$O$_4$), barite (BaSO$_4$), talc (Mg$_3$(Si$_4$O$_{10}$(OH)$_2$)), copper, strontium ferrite (SrFe$_{12}$O$_{19}$) and glass fiber were used as fillers between 0 and 50 vol% concentration. The thermal conductivity of the prepared compounds is shown in Figure 17/a. Surprisingly, the thermal conductivity of talc-filled polypropylene is significantly higher than that of copper-filled PP although the TC of copper (~400 W/mK) is much higher than the TC of talc (~10 W/mK). At 30 vol% the thermal conductivity of PP/talc material was 2.5 W/mK, two times higher than that of the PP/Cu composite. This can be explained with the high interconnectivity of the talc particles.

![Figure 17. Thermal conductivity of PP-based composites with different fillers (a) and the interconnectivity of the particles at 30 vol% filler concentration (b) [99]](image)

The interconnectivity ($X_{int}$) was also calculated based on the work of Schilling and Partzsch [100]. The lower ($\lambda^{HS-}$) and upper bound ($\lambda^{HS+}$) of thermal conductivity was derived from the Hashin–Shtrikman model (Equation (17)-(19)):

$$\lambda^{HS-} = \lambda_m \frac{2\lambda_m + \lambda_f - 2\varphi_f (\lambda_m - \lambda_f)}{2\lambda_m + \lambda_f - \varphi_f (\lambda_m - \lambda_f)} , (\lambda_m<\lambda_f) , \quad (17)$$

$$\lambda^{HS+} = \lambda_f \frac{2\lambda_f + \lambda_m - 2\varphi_m (\lambda_f - \lambda_m)}{2\lambda_f + \lambda_m - \varphi_m (\lambda_f - \lambda_m)} , (\lambda_m>\lambda_f) , \quad (18)$$
In the equations $\lambda_m$ and $\lambda_f$ are the thermal conductivity of the matrix and fillers, and $\phi_f$ and $\phi_m$ are the filler and matrix concentration by volume. The results are shown in Figure 17/b. It can be clearly seen that talc and glass fiber form the best interconnected network through the matrix.

Droval et al. [101] investigated the properties of BN, talc, aluminum nitride and aluminum oxide filled polystyrene conductive composites. The fillers were investigated with scanning electron microscope (SEM) and it was found that the BN and talc particles have a plate-like shape, while AlN and Al$_2$O$_3$ particles have a spherical shape. Boron nitride was found to be the most effective filler offering a good compromise between high intrinsic thermal conductivity, a high shape factor and high connectivity. The DSC measurements showed that the glass transition temperature of PS decreases as filler fraction is increased. BN had the most pronounced, at 10 vol% $T_g$ decreased by 15°C. In the case of other fillers this decrease was less than 8°C. The results of thermal conductivity measurements are presented in Figure 18. It can be clearly seen that the thermal conductivity of the PS/BN composite is about twice as high as that of the other composites.

Figure 18. The thermal conductivity of polystyrene-based composites as a function of filler concentration [101]
2.3. Modeling methods on thermal conductivity

In this chapter the most important basic and advanced models used for the prediction of thermal conductivity of composites are introduced. Besides the mathematical models, some authors presented Finite Element Modeling methods to estimate the conductivity of the composites as a function of filler concentration.

2.3.1. Numerical methods

To keep the price of polymer composites as low as possible, it is important that their properties can be tailored to needs. Hence it is important that the composite can be designed using the proper type and ratio of the matrix and fillers [87]. However, not only mechanical, but also thermal properties, such as thermal conductivity should be predictable. The thermal conductivity of composite materials is influenced by several factors, such as filler concentration, particle size and shape, filler dispersion and distribution in the matrix, the thermal conductivity of the components, the contact between the particles and the contact surface resistance between the matrix and the filler [1, 87]. Although numerous empirical, semi-empirical and theoretical models have been developed for the prediction of thermal conductivity of two- or multiphase polymer composites, its reliable and precise prediction still remains a challenge. The three basic models are the rule of mixtures (parallel model), the inverse rule of mixtures (series model) and the geometric mean model. In the rule of mixtures (Equation (20)) it is assumed that the components contribute to the thermal conductivity of the composite proportionally. It generally overestimates the experimental values and provides an upper bound for conductivity. This model assumes the existence of a percolation network of the filler in the matrix and perfect contact between the filler particles. On the other hand, the inverse rule of mixtures (Equation (21)) assumes that there is no contact between the particles, thus it underestimates the experimental values and provides a lower bound for conductivity:

$$\lambda_c = \lambda_f \varphi_f + \lambda_m \varphi_m,$$

(20)

$$\frac{1}{\lambda_c} = \frac{\varphi_f}{\lambda_f} + \frac{\varphi_m}{\lambda_m},$$

(21)

where $\lambda_c$ is the thermal conductivity of the composite, $\lambda_m$ and $\lambda_f$ are the thermal conductivity of the matrix and the filler, and $\varphi_f$ is the filler fraction. The geometric mean model (Equation (22)) is an empirical method for the prediction of the thermal conductivity of
composites. It provides better results than the rule of mixtures and inverse rule of mixtures [1, 102, 103].

$$\lambda_c = \lambda_m^{\phi_f} \cdot \lambda_f^{(1-\phi_f)}.$$  (22)

Besides these basic models, many advanced models have been developed. The most important theoretical equations are the Maxwell [104], Bruggeman [102], Cheng-Vachon [105], Hamilton-Crosser [106] and Meredith-Tobias [107] model. Maxwell (Equation (23)) supposed that spherical filler particles are randomly distributed in the matrix and there is no interaction between them. This model describes the thermal conductivity of composites with a low volume fraction of fillers well, but as filler content is increased, the particles start to develop interactions between each other and form conductive chains [102, 104, 108, 109].

$$\lambda_c = \lambda_m \cdot \frac{[2 \cdot \lambda_m + \lambda_f + 2 \cdot \phi_f \cdot (\lambda_f - \lambda_m)]}{[2 \cdot \lambda_m + \lambda_f - \phi_f \cdot (\lambda_f - \lambda_m)]}.$$  (23)

Bruggeman developed another theoretical model. This implicit relation (Equation (24)) also supposes that the spherical, non-interacting particles are homogeneously dispersed in the continuous matrix [87, 102, 108, 109].

$$1 - \phi_f = \frac{(\lambda_f - \lambda_c) \cdot (\lambda_m - \lambda_c)^{1/3}}{\lambda_f - \lambda_m}.$$  (24)

Cheng and Vachon [105] developed another theoretical model (Equation (25) and (26)) for two-phase composite materials. This equation assumes that the discontinuous phase has a parabolic distribution in the continuous matrix. The parabolic distribution constants ($B_{cv}$ and $C_{cv}$) were introduced and related to the volume fraction of the filler [102, 105, 110, 111].

$$\frac{1}{\lambda_c} = \frac{1}{\sqrt{C_{cv} (\lambda_m - \lambda_f) \cdot (\lambda_m + B_{cv} (\lambda_f - \lambda_m)}} \cdot \ln \frac{\lambda_m + B_{cv} (\lambda_f - \lambda_m)}{\lambda_m + B_{cv} (\lambda_f - \lambda_m)} + \frac{2 \cdot \sqrt{C_{cv} (\lambda_m - \lambda_f)}}{B_{cv} / 2 \cdot \sqrt{C_{cv} (\lambda_m - \lambda_f)}} + 1 - B_{cv}, \quad (25)$$

$$B_{cv} = \sqrt{\frac{3 \cdot \phi_f}{2}}, \quad C_{cv} = -4 \cdot \sqrt{\frac{2}{3 \cdot \phi_f}}.$$  (26)

On the other hand, there are numerous empirical and semi-empirical models that contain experimental factors for thermal conductivity and for the volume fraction of the components. Agari and Uno [112] and Lewis and Nielsen [113] developed such models, for example. These models also show good correlation with the experiments up to 30 vol% filler content. Only the Lewis-Nielsen model gives better fit above 30 vol%, thanks to the introduction of the maximum volume fraction of fillers in the equation [1, 102].
The Agari and Uno [112] model is based on the generalization of series and parallel conduction models. It assumes that the particles form conductive chains through the matrix. Accordingly, the thermal conductivity of two-phase composites can be written according to Equation (27):

$$\log \lambda_c = \varphi_f \cdot C_2 \cdot \log \lambda_f + (1 - \varphi_f) \cdot \log(C_1 \cdot \lambda_m),$$  

(27)

where $\lambda_c$, $\lambda_f$, and $\lambda_m$ are the thermal conductivity of the composite, the filler and the matrix, $\varphi_f$ is the filler volume fraction and $C_1$, $C_2$ are experimental constants. $C_1$ is dedicated to the effect of filler particles on the secondary structure of the polymer matrix (crystallinity, crystal size) and $C_2$ shows the conductive chain formation ability of the particles. Lewis and Nielsen [114] reported a semi-empirical model, which was developed on the basis of the Halpin-Tsai [115] equation. In this model the effect of particle shape, the orientation of the particles and the packing of the fillers are included (Equation (28) and (29)):

$$\lambda_c = \lambda_m \left[1 + A_{LN} B_{LN} \varphi_f \right],$$  

(28)

$$B_{LN} = \frac{(\lambda_f / \lambda_m) - 1}{(\lambda_f / \lambda_m) + A_{LN}}, \; \psi = 1 + \left(\frac{1 - \varphi_m}{\varphi_m^2}\right) \cdot \varphi_f,$$

(29)

where $\lambda_c$, $\lambda_f$, and $\lambda_m$ are the thermal conductivity of the composite, the filler and the matrix, $\varphi_f$ is the filler volume fraction, $A_{LN}$ is a constant that depends on the shape and orientation of the particles and $\varphi_m$ is the maximum packing fraction of the filler. The values of $A_{LN}$ and $\varphi_m$ were determined for several filler types and orientation and can be found in tables. As an example, for spherical particles, $A_{LN} = 1.5$ and $\varphi_m = 0.637$ and for randomly packed irregularly shaped particles $A_{LN} = 3$ and $\varphi_m = 0.637$.

From the literature survey it is obvious that the exact prediction of thermal conductivity for highly filled composites still poses difficulties. The theoretical models often underestimate the results and can be used only up to 30 vol% filler content [108, 109, 111, 116, 117]. The semi-empirical models give better correlation with the experiments, but they need more experimental parameters.

Kumlutas and Tavman [86] compared the thermal conductivity of HDPE/tin composites to the results from some mathematical models. They found that all the models used are in good agreement with the measured values at low filler content, except the Cheng-Vachon model. At higher filler fractions (>10 vol%) the particles form conductive chains and the gradient of the curves start to increase more rapidly. This range can be described with the Cheng-Vachon and Agari-Uno models (Figure 19).
Droval et al. [101] analyzed the thermal conductivity of more ceramic-filled (BN, Al₂O₃, AlN, talc) PS composites and compared it to the predicted values from theoretical, empirical and semi-empirical models. They stated that the Cheng-Vachon, Lewis-Nielsen and Agari-Uno model have a good correlation with the experiments and the Maxwell model can be used only at low filler fractions (Figure 20).

The authors also calculated the interconnectivity coefficient of the fillers (Equation 19) in the composites based on the work of Weidenfeller et al. [99]. They found that in a PS matrix talc particles have the best interconnectivity, BN and Al₂O₃ have the same effect, and AlN has the worse interconnectivity factor (Figure 21).
Dey and Tripathi [87] used several mathematical models to predict the filler concentration dependent thermal conductivity of HDPE/Si composites between 0 and 20 vol% Si fractions. The Agari-Uno and Lewis-Nielsen models seem to correlate best with the experiments. The experimental and modeled results can be seen in Figure 22/a and the calculation error of the models in Figure 22/b.

$$\lambda(\varphi_f; a_r) = \lambda_0 \left[ \varphi_f - \varphi_p(a_r) \right]^{\gamma_r(a_r)}, \quad (30)$$
where $\lambda$ is thermal conductivity, $\lambda_t$ is a factor that takes into consideration the thermal conductivity of nanotubes and their contacts with each other, $\varphi_f$ [vol%] is filler concentration, $\varphi_p$ [vol%] is the percolation threshold, $a_r$ is the aspect ratio of fillers and $t_\lambda$ is a factor that characterizes the conductive chain. The value of $\lambda_t$ is between 64 and 137 W/mK according to the experiments. Haggenmueller et al. [119] investigated the percolation model on HDPE/SWCNT nanocomposites. It was stated that the percolation model has a good correlation with the experiments up to 20 vol% (Figure 22).

![Figure 23. Comparison of the experimental values (dots) and percolation model (line) for HDPE/SWCNT nanocomposites [119]](image)

**2.3.2. Finite element modeling method**

In addition to the mathematical models, numerous studies exist on the finite element modeling (FEM) of composites and the calculation of their effective thermal and mechanical properties. In cases when a problem cannot be solved analytically, FEM and simulation can be effective methods. A considerable obstacle to the use of this method can be complicated material arrangement, proper mesh generation and computational cost [120].

Kumlutas and Tavman [86] numerically modeled the thermal conductivity of polymer composites. The models of particle-filled composites are cubes in a cube and spheres in a cube lattice array (Figure 24). The ANSYS finite-element program was used for the calculations. The results were compared to the experimental results of tin particle (0-16 vol%) filled HDPE. It was found that up to 10 vol% tin the numerical model estimated thermal conductivity well. Above 10 vol% the model underestimates the experiments.
Mortazavi et al. [121] investigated and numerically simulated the thermal conductivity of an expanded graphite-filled (EG) polylactic acid (PLA) composite. In the simulation model the filler particles are randomly distributed in the matrix (Figure 25). The analyses were carried out with the ABAQUS simulation software. It was found that the simulation results are in good agreement with the experiment, although filler content was varied only between 0 and 6.75 wt%.

Li et al. [122] developed a three-dimensional computational model using the finite element method based on continuum mechanics. With the proposed model they evaluated the thermal behavior of randomly distributed SWCNT/polyolefin and SWCNT/epoxy composites. The 3D model was generated with a program developed in-house, and the 3D tetrahedral elements were generated with the ANSYS software (Figure 26). To reduce the computational costs, some simplifications were made regarding the shape, aspect ratio and properties of SWCNTs. The authors analyzed the effects of interfacial thermal resistance, volume fraction, thermal conductivity and the diameter of SWCNTs on the thermal
conductivity of the composite. It was found that the model can be applied up to 10 vol\%. Above 10 vol\% the error of prediction can be explained with the simplification of the model and with the agglomeration of particles.

![Figure 26. Model for three-dimensional randomly distributed SWCNT in a polymer matrix (a) and the discretized model with tetrahedral elements (b) [122]](image)

Nayak et al. [123] constructed a three-dimensional spheres-in-cube lattice array model to simulate the structure of epoxy/pinewood dust composite materials for filler concentrations between 6 to 36 vol\%. In the model the thermal conductivity of composites were numerically analyzed with ANSYS and compared to experimental values and to other theoretical and experimental models. It was concluded that the FEM analysis is more accurate than the rule of mixture or the Maxwell model.
2.4. Summary of the literature, objectives of the dissertation

The aim of the literature survey was to show the possibilities of application and development of thermally conductive polymers. At the beginning the theory and physics of thermal conductivity and its measurement methods were reviewed. Next, methods to improve thermal conductivity were surveyed, such as the effect of molecular orientation, crystallinity, processing methods and additives. According to the literature, the best method is the use of fillers. Hence the three main groups of fillers (metallic, ceramic and carbon-based fillers) were analyzed. It was also concluded that fillers can significantly influence the flow properties of polymers. Moreover, a segregation effect can develop during the production of the parts, which can influence the thermal and mechanical properties of the composites.

The thermal conductivity of polymers can be modified in many ways. If the crystallinity of the polymers is increased, thermal conductivity also increases. This statement can prove that fact that amorphous polymers have lower thermal conductivity than semi-crystalline polymers. Research shows that the molecular weight also has a significant influence; polymers with higher molecular mass also have higher thermal conductivity. The orientation of the polymer chains can improve conductivity as well, but the material will be anisotropic. Thermal conductivity increases in the direction of the orientation and decreases perpendicular to that. These methods only have a slight effect on thermal conductivity. The best results can be obtained with the use of solid fillers, which was proved by many researchers. Metallic and carbon-based fillers are the best for this purpose, but the composite will also be an electrical conductor. As the goal of this research is to produce dielectric polymer composites of high thermal conductivity, these fillers can be applied up to the percolation threshold. In contrast, ceramic fillers have better properties, such as good thermal conductivity, low density and good electrical insulating properties.

In the literature, many different results can be found for the same type of fillers or matrices. These differences can be attributed to the different measuring methods or different processing methods. Many different measuring techniques exist, such as the hot plate, hot-wire, laser flash methods and others, and these methods work on different principles. Accordingly, the results may be different but the different measurement principles cannot explain the huge deviations. To analyze the effect of different processing methods and processing parameters is essential to understand their effect on filler distribution within the matrix. Hence the segregation effect could not be neglected. Segregation can be through the
Development of injection moldable, thermally conductive polymer composites

thickness (shell-core effect) and along the flow length. Segregation can decrease the thermal conductivity of the part and cause inhomogeneity regarding the thermal and mechanical properties. Therefore this effect should be investigated.

In most articles the authors only used a single filler to produce conductive compounds. Generally these fillers were copper, carbon black, graphite, carbon nanotubes, silicon dioxide, talc, aluminum nitride and boron nitride. Only a few articles investigated polymer composites with a hybrid filler system. In these papers at least one of the fillers is an electrical conductor, such as carbon black or graphite. So far I have not found any articles applying only dielectric fillers to utilize the advantages of the hybrid effect between different fillers.

It is important that the thermal conductivity of polymer composites should be tailored to requirements. As was shown earlier, the thermal conductivity of composite materials is influenced by several factors, which should be taken into account. Although numerous empirical, semi-empirical and theoretical models have been developed for the prediction of the thermal conductivity of two- or multiphase polymer composites, its reliable and precise prediction still remains a challenge. From the literature survey it is obvious that the exact prediction of thermal conductivity for highly filled composites still poses difficulties. The theoretical models often underestimate the results and can be used only up to 30 vol% filler content. The semi-empirical models give better correlation with the experiments, but they need more experimental parameters.

Improving thermal conductivity with solid fillers can cause difficulties in material processing. The viscosity of the polymer increases drastically as filler concentration is increased. Generally, in the literature conductive polymer composites with a thermoplastic matrix were prepared with internal mixing and compression molding, or simply a low viscosity thermosetting matrix was used. These techniques are too slow for mass production and can compromise design freedom. On top of that, only a few articles were published on the injection molding of thermally conductive polymers, therefore this is a new area to investigate.

Also, only a few articles can be found on the thermal properties of highly filled polymers and so there is not much information on the influence of fillers on the glass transition temperature and the crystallinity of thermally conductive polymers.
Based on the literature survey, I have set out the following objectives of this PhD dissertation:

1. The development and investigation of a novel thermally conductive polymer, which is an electrical insulator.

2. The investigation of the effects of different parameters (matrix, filler, processing technology, etc.) on the effective thermal conductivity of polymer composites.

3. The development of a polymer composite with a dielectric hybrid filler system to enhance effective thermal conductivity with the same amount of filler.

4. The investigation of the thermal properties and crystallinity of conductive polymers, influenced by the injection molding process.

5. The improvement of processability of highly filled polymers.

6. The development of a model to predict the thermal conductivity of composites as a function of filler concentration.
3. Materials and methods

In this chapter the selected materials, their processing methods and the testing methods are introduced.

3.1. Materials

In my research composites were prepared with the use of different matrices and fillers. The names, manufacturers and abbreviations (used in my research) of the applied materials are presented in Table 1 and Table 2. Talc, boron nitride and graphite have plate like shape which show anisotropic behaviors (Figure 27/a, b, d). The titanium dioxide has spherical shape (Figure 27/c). The matrices can be processed directly, only polyamide 6 and polylactic acid need to be dried at 80°C for 4 hours.

<table>
<thead>
<tr>
<th>Name</th>
<th>Trade name</th>
<th>Manufacturer</th>
<th>Abbreviation in the dissertation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene homopolymer</td>
<td>Tipplen H 145 F</td>
<td>Tisza Chemical Group Public Limited Company</td>
<td>PP</td>
</tr>
<tr>
<td>Polypropylene copolymer</td>
<td>Tipplen K 693</td>
<td>Tisza Chemical Group Public Limited Company</td>
<td>cPP</td>
</tr>
<tr>
<td>Polyamide 6</td>
<td>Schulamid 6 MV 13</td>
<td>A. Schulman, Inc.</td>
<td>PA6</td>
</tr>
<tr>
<td>Polylactic acid</td>
<td>PLA AI-1001</td>
<td>Shenzhen eSUN Industrial Co., Ltd.</td>
<td>PLA</td>
</tr>
</tbody>
</table>

Table 1. Matrix polymers used in the experiments

<table>
<thead>
<tr>
<th>Name</th>
<th>Trade name</th>
<th>Manufacturer</th>
<th>Particle size (D50)</th>
<th>Abbreviation in the dissertation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talc</td>
<td>Talc Powder 325 mesh coating grade</td>
<td>QualChem Zrt.</td>
<td>24.4 μm</td>
<td>talc</td>
</tr>
<tr>
<td>Boron nitride</td>
<td>HeBoFil 482</td>
<td>Henze BNP GmbH</td>
<td>3-5 μm</td>
<td>BN</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>Titanium dioxide KTR 600</td>
<td>QualChem Zrt.</td>
<td>n.a.</td>
<td>TiO₂</td>
</tr>
<tr>
<td>Graphite</td>
<td>Timrex C-Therm 011</td>
<td>Timcal Ltd.</td>
<td>n.a. (soft granules)</td>
<td>Graphite</td>
</tr>
</tbody>
</table>

Table 2. Fillers used in the experiments

The melt flow of the polypropylene homopolymer matrix was enhanced with CBT 100 cyclic butylene terephthalate oligomer (CBT). The CBT was purchased from Cyclics Europe GmbH (Germany). Cyclic butylene terephthalate is the cyclic form of polybutylene terephthalate (PBT), which can enhance the melt flow performance of the matrix material, while at the same time it does not influence mechanical properties. In addition, CBT 100 can improve filler dispersion during the process.
Figure 27. Scanning electron microscopic pictures of talc (a), boron nitride (b), titanium dioxide (c) and graphite powder (d)

For the surface treatment of boron nitride silane coupling agent was used. The Geniosil GF 56 vinyltriethoxysilane coupling agent was purchased from Wacker Chemie AG (Germany). The surface treatment method is detailed in Chapter 5.1.4.

For the thermal conductivity measurements to decrease the thermal contact resistance between the samples and the measurement unit, ceramic powder filled thermal interface silicone grease was applied. The conductive grease was purchased from T-Silox Kft., (Hungary).

3.2. Processing methods

Compounding methods

The components of the composites were compounded with two different methods. In the first case the composites were prepared with a Brabender Plastograph internal mixer. The components were mixed at 230°C for 20 minutes at a rotational speed of 25 1/min to achieve the desired homogeneity. In the second case the materials were compounded with a Labtech
Development of injection moldable, thermally conductive polymer composites

Scientific LTE 26-44 twin screw extruder (L/D ratio is 44; D=26 mm) at 230°C (zone temperatures from 230°C to 210°C) at a rotational speed of 30 l/min. Not only the composites but the unfilled matrices were also processed with these technologies to have the same thermal history. The proper amounts of matrix and filler materials were calculated with Equation (31) and (32):

\[
m_f = \frac{m_c}{\phi_m \cdot \rho_m + 1}, \quad \phi_f \cdot \rho_f
\]

\[
m_m = m_c - m_f
\]

where \(m_c\), \(m_f\) and \(m_m\) [g] are the mass of the composite, the filler and the matrix material, \(\phi_f\) and \(\phi_m\) [vol%] are the volume fraction of the filler and the matrix material, and finally \(\rho_f\) and \(\rho_m\) [g/cm\(^3\)] are the density of the filler and the matrix material.

**The preparation of samples**

From the compounds 2 mm thick plate-like samples were compression molded and injection molded. Compression molding was performed with a Collin Teach-Line Platen Press 200E machine at 230°C for 15 minutes, where average cooling speed was 15°C/min. The injection molded samples were produced with an Arburg Allrounder Advance 370S 700-290 machine. The main technological parameters can be seen in Table 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>PP/cPP</th>
<th>PA6</th>
<th>PLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>[cm(^3)]</td>
<td>49</td>
<td>49</td>
<td>49</td>
</tr>
<tr>
<td>Injection rate</td>
<td>[cm(^3)/s]</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Holding</td>
<td>[bar]</td>
<td>80% of injection pressure</td>
<td>80% of injection pressure</td>
<td>80% of injection pressure</td>
</tr>
<tr>
<td>Clamping force</td>
<td>[kN]</td>
<td>700</td>
<td>700</td>
<td>700</td>
</tr>
<tr>
<td>Residual cooling time</td>
<td>[s]</td>
<td>10</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Zone temperatures</td>
<td>[°C]</td>
<td>200; 195; 190; 185; 180</td>
<td>230; 225; 220; 215; 210</td>
<td>210; 195; 190; 185; 180</td>
</tr>
<tr>
<td>Mold temperature</td>
<td>[°C]</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

**Table 3. Injection molding parameters**

Injection-compression molding technology was also applied to produce samples. During the process first the polymer melt was injected into the partially open mold. In the second step the mold was closed. This clamping forced the melt to fill completely the cavity and acts as holding pressure (Figure 28). The injection-compression molded samples were produced with an Arburg Allrounder Advance 370S 700-290 injection molding machine. The main molding parameters can be seen in Table 4.
Figure 28. Scheme of injection-compression molding [124]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injected volume</td>
<td>[cm$^3$]</td>
<td>56</td>
</tr>
<tr>
<td>Injection rate</td>
<td>[cm$^3$/s]</td>
<td>50</td>
</tr>
<tr>
<td>Compression stroke</td>
<td>[mm]</td>
<td>1.5</td>
</tr>
<tr>
<td>Compression force</td>
<td>[kN]</td>
<td>700</td>
</tr>
<tr>
<td>Compression speed</td>
<td>[mm/s]</td>
<td>25</td>
</tr>
<tr>
<td>Residual cooling time</td>
<td>[s]</td>
<td>10</td>
</tr>
<tr>
<td>Zone temperatures</td>
<td>[°C]</td>
<td>200; 195; 190; 185; 180</td>
</tr>
<tr>
<td>Mold temperature</td>
<td>[°C]</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 4. Injection molding parameters

3.3. Testing methods

The samples for thermal, mechanical and morphological investigation were cut from the 2 mm thick plates with a water jet cutting machine. On these specimens mechanical, thermal and morphological analyses were performed. The details of the testing methods are presented in this section.

Mechanical tests

Tensile testing

The tensile tests were carried out according to the recommendation of the ISO 527-1:2012 standard [125] with a Zwick Z020 universal testing machine. The type of the standard specimen was 5A (length: 75 mm, width: 4 mm, thickness: 2 mm, grips length: 50 mm). The testing speed was 2 mm/min. The tests were performed at room temperature (25°C). From the force-displacement curves the tensile strength ($\sigma$ [MPa]) and tensile modulus ($E$ [MPa]) of the samples were calculated. The tensile strength was determined from the maximum developed force. The tensile modulus was calculated between 0.0005 and 0.0025 strain. The tensile properties were determined from five measurements in each case.
**Charpy impact testing**

The Charpy tests were carried out according to the recommendation of the ISO 179-2:1997 standard [126] with a Ceast Resil Impactor Junior machine. For the tests unnotched specimens with a 2x6 mm cross-section were used with a 40 mm span distance. The tests were performed at room temperature with a 2 J pendulum. From the absorbed energy the Charpy impact strength ($a_{cU}$ [kJ/m²]) could be calculated. The impact properties were determined from ten measurements in each case.

**Thermal analysis**

**Thermal conductivity**

The thermal conductivity of the composite samples was measured with two different methods: the hot plate (applied for the measurements in Chapter 5.1-5.3) and the linear heat flow method (applied for the measurements in Chapter 5.4). Apparatuses were developed for the measurements; they are presented in Chapter 4.

**DSC analysis**

A DSC Q2000 (TA Instruments) differential scanning calorimeter was used to analyze the specific heat, crystallization temperature and crystallinity of the samples. 3-5 mg samples were cut off from the center of the injection molded plates and placed into pans. The measurements consisted of three phases: heating to 225°C from 25°C, cooling back to 25°C and heating to 225°C again. The first heating is used to measure the effect of the injection molding process, as in the next two phases crystals are created and melted during a controlled process (at a heating and cooling rate of 10°C/min). The degree of crystallinity ($X$) was determined from the exothermic and the endothermic peaks with Equation (33), which takes into account the filler fraction of the compound [127]:

$$X = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f \cdot (1 - \phi)},$$

(33)

where $\Delta H_m$ is the enthalpy of melting, $\Delta H_{cc}$ is the enthalpy of cold crystallization, $\Delta H_f$ is the melting enthalpy of a theoretically fully crystalline polymer and $\phi$ is the mass fraction of the filler. For the calculations the $\Delta H_f$ is 165 J/g [128] and 93 J/g [129] at the case of polypropylene homopolymer and polylactic acid respectively.
Microscopy

The fracture surface of the samples was analyzed with a Jeol JSM 6380LA Scanning Electron Microscope. The samples were first coated with an Au/Pd alloy with a Jeol JFC-1200 fine coater apparatus to avoid electric charging.

Segregation investigation

To determine filler distribution in the injection molded samples, they were cut into 16 identical parts, as can be seen in Figure 29. Next, the density of the samples was measured based on Archimedes' principle.

![Figure 29. Sample preparation for the investigation of segregation](image)

Knowing the density of the matrix, the filler and the composite, the filler and matrix concentration can be calculated according to the Equations (34) and (35):

\[
\varphi_f = \frac{\rho_c - \rho_m}{\rho_f - \rho_m} \cdot 100, \tag{34}
\]

\[
\varphi_m = 100 - \varphi_f, \tag{35}
\]

Flow properties

Melt volume rate measurements

To characterize the flow properties of the materials, the melt volume rate (MVR) was determined according to the ISO 1133-1:2013 [130] standard at 230°C, with a load of 2.16 kg using CEAST Modular Melt Flow (7027.000) apparatus. In each case 6 measurements were performed. The measurement procedure consists of the following steps: 60 seconds preheating; compacting with 375 N to the position of 75 mm; compacting with the standard (2.16 kg) weight; and performing a measurement at 40, 30 and 20 mm.
Viscosity measurement

The viscosity of the CBT modified polypropylene was measured with an Instron capillary rheometer, installed on a Zwick Z050 tensile-testing machine. Measurements were made at four different temperatures: 190, 200, 220 and 240°C, with three capillaries of different length (Table 5) and at seven different crosshead speeds: 5, 10, 20, 50, 100, 200 and 500 mm/min. The details of the calculations and corrections are presented in Chapter 5.3.

Table 5. Sizes of the capillaries used for the viscosity measurements

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Sizes of the capillaries</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diameter [mm]</td>
</tr>
<tr>
<td>1</td>
<td>1.23</td>
</tr>
<tr>
<td>2</td>
<td>1.20</td>
</tr>
<tr>
<td>3</td>
<td>1.20</td>
</tr>
</tbody>
</table>
4. Development of heat conductometers

To measure the thermal conductivity of the composite samples, two different thermal conductometers were developed, a hot plate and a linear heat flow apparatus. In this section the basic theory and layout of these units are presented.

4.1. Hot plate apparatus

In this research a single-specimen hot plate apparatus was developed. In contrast to the conventional two-specimen apparatus, heat flows in a single direction between the hot plate and the cold plate through the specimen. Furthermore, in this arrangement a cold plate, a hot plate and a specimen can be omitted, thus the apparatus is simpler. Figure 30 shows the main components of the designed measurement system.

![Main components of the hot plate apparatus](image)

The main task is to maintain the temperature difference between the cold and the hot plates. The thermal conductivity of the applied copper plates is ~380 W/mK, which is two orders of magnitude higher than that of the samples, thus their heat resistance does not generate a significant error. The cold plate of the apparatus was cooled by four 40x40 mm sized Peltier cells, which facilitated keeping the temperature of the plate more precisely. The upper plate was heated by a heating wire, where the generated heat is equal to the electrical energy flowing through the wire (with losses ignored). To provide uniform heating of the hot plate, the heating wire was meander-shaped. The heat resistance between the components was decreased with thermally conductive tape (3M 8805). The temperature was measured with two built-in NTC thermistors (Epcos B57045K) inside both the heated and the cooled plate.
The resistance-temperature calibration for the NTC thermistors was performed with the Steinhart-Hart equation (Equation (36)) [131]:

\[
\frac{1}{T} = A_{SH} + B_{SH} \ln(R) + C_{SH} (\ln(R))^3,
\]

where \( R [\Omega] \) is the resistance of the thermistors at given temperatures \( T [K] \), and \( A_{SH}, B_{SH} \) and \( C_{SH} \) are the Steinhart-Hart constants. Table 6 contains the values of the Steinhart-Hart constants obtained by calibration. The whole measurement system was controlled with a programmed microcontroller (ATMEGA64). The scheme of the thermal conductometer control system can be seen in Figure 31.

<table>
<thead>
<tr>
<th>Thermistor no.</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.569·10^{-3}</td>
<td>7.035·10^{-5}</td>
<td>1.838·10^{-6}</td>
</tr>
<tr>
<td>2</td>
<td>2.378·10^{-3}</td>
<td>6.785·10^{-6}</td>
<td>1.180·10^{-6}</td>
</tr>
<tr>
<td>3</td>
<td>1.847·10^{-3}</td>
<td>8.564·10^{-5}</td>
<td>9.509·10^{-7}</td>
</tr>
<tr>
<td>4</td>
<td>1.693·10^{-3}</td>
<td>1.239·10^{-4}</td>
<td>6.663·10^{-7}</td>
</tr>
</tbody>
</table>

Table 6. Steinhart-Hart constants of the thermistors

To reduce heat loss, the apparatus was thermally insulated with polystyrene foam, whose thermal conductivity is \( \sim 0.04 \) W/mK. To decrease the thermal resistance between the samples and the hot plate apparatus, thermal interface silicone grease was applied. To control the input parameters for the measurement, such as heating power, the temperature of the cold plate and the size of the specimen, a computer program was written. Using the input and output parameters the program can also calculate thermal conductivity. Finally the apparatus was calibrated with samples of known conductivity.

Figure 31. Scheme of the thermal conductometer control system
4.2. Linear heat flow apparatus

A further thermal conductivity meter was designed and built, based on the Comparative Longitudinal Heat Flow method [132, 133]. In this method the unknown sample is compressed between the known reference samples and a heat flux passes through the measurement unit as a temperature difference is created between the two sides of the unit. The thermal conductivities of the sample and the reference sample are inversely proportional to their thermal gradients. The apparatus developed (Figure 32) contains two C10 steel (55 W/mK) cylinders with a diameter of 30 mm; and a length of 30 mm. A specimen of a diameter of 30 mm and a thickness of 10 mm is placed between the steel cylinders. On the contact surface thermal grease was applied to decrease heat resistance. 3 thermocouples were inserted in each cylinder to detect temperature: one 3 mm below the top, one in the middle and one 3 mm above the bottom (T\textsubscript{m1}-T\textsubscript{m6}/Figure 32). The temperatures were registered with an Ahlborn Almemo 8990-6-V5 data acquisition module with a resolution of 0.1°C. The apparatus was clamped and the temperature difference maintained with a hot press (Collin Teach-Line Platen Press 200E), and the assembled unit was insulated with polyurethane foam to minimize heat loss. When the steady state is reached, the temperature slope is linear along the reference sample and the specimen thickness. Surface temperatures (T\textsubscript{1}-T\textsubscript{4}/Figure 32) can be calculated by extrapolation from the measured temperatures.

![Figure 32. Longitudinal heat flow measurement unit and its measurement principle](image)

As the thermal conductivity of steel and the temperature difference between the surfaces are known, the heat flux of the hot and cold sides can be calculated with Fourier’s law. From the average of the heat fluxes the thermal conductivity coefficient of the sample (λ\textsubscript{c}) can be calculated with Equation (37):

\[
\lambda_{c} = \frac{1}{\frac{1}{\lambda} + \frac{1}{\lambda_r}}
\]
\[
\lambda_c = \lambda_r \frac{A_r}{A_c} \frac{1}{\sum_{i=1}^{n} \frac{\Delta T_i}{x_i}},
\]

where \(\lambda_r\) is the thermal conductivity and \(A_r\) is the cross-section of the reference steel cylinder, \(x_i\) is the distance between the sensors, \(\Delta T_i\) is the temperature differences measured by the sensors, \(A_c\) and \(x_c\) are the cross-section and the thickness of the sample, and \(\Delta T_c\) is the temperature drop on the sample. The temperature difference between the hot and cold sides was 30°C. The cold side was 50°C and the hot side was 80°C, meaning that the average temperature was 65°C. This big difference in temperature was necessary to achieve a more precise result, because the thermal conductivity of the reference sample is significantly higher than the thermal conductivity of the sample.

The linearity of the temperature slope in the steel references was also tested with three temperature sensors in each one. The results (Figure 33) prove that the two slopes are almost linear. As the figures show, the graph of the linear regression is close to the measured points and the coefficients of determination (R²) are very high (~0.99). Furthermore, the slopes of the fitted curves are close to each other (0.21 and 0.25) thus the temperature slopes are nearly parallel, and there is a minimal heat loss on the system.

With the new instrument the thermal conductivity (TC) of four different samples were measured and compared to the results of the hot plate method (Figure 34). The methods show nearly the same results, the values are within the standard deviation of the measurements. On
the other hand, the two-sample t-test also shows that means of the two measurements are equal, if a statistical significance of 0.05 is applied.

Figure 34. Comparison of the results of thermal conductivity methods (Linear heat flow unit with steel references and the hot plate method)
5. Results and discussions

In this chapter the results of my researches are introduced and discussed.

5.1. Properties of thermally conductive polymer composites

A number of parameters have a significant influence on the thermal conductivity coefficient of polymer compounds, including filler material, filler volume fraction, the thermal conductivity of the filler and the polymer material etc. These parameters should be investigated further to determine their exact effect on thermal conductivity.

5.1.1. The effect of the matrix

Firstly the effect of the matrix material on thermal conductivity was investigated. Two different polypropylenes, a polyamide 6 and a polylactic acid were filled with the same type of talc. The compounds were prepared with extrusion and the samples were produces with injection molding technology. As Figure 35 shows, the thermal conductivities of polypropylene homopolymer and polypropylene copolymer are 0.25 W/mK and 0.32 W/mK respectively, while the thermal conductivity of polylactic acid and polyamide is 0.31 W/mK and 0.39 W/mK, respectively. The differences between the coefficients measured as a function of talc content remain nearly the same up to the investigated 30 vol%. The differences are caused by the differences in the thermal conductivity of the matrices and the different adhesion between the filler and polymer. Accordingly, when the different matrices are compounded with 30 vol% talc, the thermal conductivities are 0.59 W/mK when a polypropylene homopolymer is used, 0.64 W/mK when a polypropylene copolymer is used, 0.79 W/mK when a PLA matrix is used and 0.86 W/mK when a PA6 is used.

![Figure 35. The thermal conductivity of different matrices as a function of filler content](image-url)
5.1.2. The effect of fillers

Secondly, the effect of filler material and filler content on the thermal conductivity of the polymer matrix was investigated on injection molded samples. The matrix material was polypropylene homopolymer and it was compounded with talc, boron nitride and titanium dioxide. The filler content was varied between 0 and 30 vol%. Figure 36 shows the effect of the different fillers on the thermal conductivity of the PP compounds. As it was expected, thermal conductivity increases with filler content. Pure polypropylene has a thermal conductivity of 0.25 W/mK. The thermal conductivity of the compounds rises slowly at low filler volume fractions because the ceramic particles are dispersed evenly in the polypropylene matrix and there is only little or no interaction between them. There are significant differences between the thermal conductivities of the compounds at high filler loading. The thermal conductivity coefficient of the composites filled with BN rises rapidly but that of the samples filled with talc and titanium dioxide rises slowly. With 30 vol% filler, the thermal conductivity coefficient of the compound is 0.6 W/mK with talc and almost double that amount, 1.14 W/mK with boron nitride. The thermal conductivity of the compound containing 30 vol% BN is more than four times higher than that of the pure PP.

![Figure 36. Thermal conductivity of PP homopolymer as a function of filler type and concentration](image)

To characterize the changes in the mechanical properties of the compounds, quasistatic and dynamic tests were performed. The results of the tensile test (as a quasistatic test) can be seen in Figure 37 and Figure 38. In comparison to the unfilled polypropylene, particle filled compounds have significantly smaller tensile strength. This might be due to the fact that there is poor adhesion between the fillers and matrix. It can be improved with surface treatment of the fillers.
Development of injection moldable, thermally conductive polymer composites

The tensile modulus shows a reverse tendency (Figure 38). When fillers were added to the polypropylene, the modulus increased. While the unfilled H145 F PP has a tensile modulus of 2.1 GPa, the composites have a significantly higher (4-6 GPa) tensile modulus. It means that the particles as a filler raise the stiffness of the compound.

As the typical loads of polymer parts have dynamic characteristics, Charpy tests were performed. The results are shown in Figure 39. As can be seen, the unfilled polypropylene has an impact strength of 72 kJ/m$^2$. When 10 vol% talc is added to the matrix, a significant drop can be observed, as the impact strength decreases to one-third of the impact strength of the unfilled polypropylene. As filler content is increased, impact strength shows a decreasing tendency. This drop is much more remarkable than the drop in tensile strength. At 30 vol% filler content all the materials have the same impact strength, which is only 8 kJ/m$^2$. 

![Figure 37. Tensile strength of PP homopolymer-based composites as a function of filler type and concentration](image)

![Figure 38. Tensile modulus of PP homopolymer-based composites as a function of filler type and concentration](image)

![Figure 39. Charpy impact strength of PP homopolymer-based composites as a function of filler type and concentration](image)
5.1.3. The effect of the processing method

*Compression molding vs. injection molding*

When the thermal conductivity of injection molded and compression molded samples are compared, it can be seen that compression molded samples have higher thermal conductivity (Figure 40). Using a polypropylene homopolymer matrix, and boron nitride and talc as filler, the thermal conductivity of injection molded samples are 16-39% and 30-39% lower than that of compression molded samples with 10-30 vol% filler concentration. Furthermore, it can be seen that as filler concentration increases, the difference increases too. There is also a difference in the thermal conduction of unfilled polypropylene. While the injection molded sample has a conductivity coefficient of 0.25 W/mK, the compression molded sample has a conductivity coefficient of 0.36 W/mK. This can be explained by the difference in crystallinity and molecular chain orientation. When fillers are added to the matrix, the differences in thermal conductivity increase as a function of filler content. Next to the effect of the crystallinity and the molecular chain orientation of the matrix, the shell-core effect of the fillers may have also a significant influence on thermal conductivity – there is an insulating polymer layer on the surface of the injection molded samples. This effect is caused by the segregation effect when the polymer fills the cavity. On the other hand, this difference could also be caused by the orientation of the filler particles, as the thermal conductivity of the particles has an anisotropic nature. Plate-like and fibrous particles show different thermal properties in different directions. In compression molded samples the filler particles have random orientations, while in the injection molded samples the orientation is determined by the melt flow. This way injection molded parts have a lower thermal conductivity coefficient.
This phenomenon was proved by SEM analysis. Figure 41 shows the SEM micrographs of the fracture surface of shell and core layers of a 2 mm thick injection molded BN filled polypropylene sample. In the shell layer highly oriented particles can be observed, which is caused by the flow and high shear rate during the filling of the cavity. On the other hand, unoriented particles can be observed in the core. The core layer is very thin, about 200-300 µm thick. One of the reasons may be the high thermal conductivity of the composite; hence the frozen layer is thick and rapidly grows while the cavity is being filled.

Figure 42 shows the SEM images of the shell and core layers of a 2 mm thick compression molded BN filled polypropylene sample. In contrast to the injection molded specimens, both in the shell and in the core layer a random orientation of BN particles can be observed.
Therefore more particles are oriented in the through-thickness direction, and higher thermal conductivity can be achieved. In the injection molded samples the highly oriented shell decreases the achievable through-thickness thermal conductivity.

![SEM micrographs of a compression molded 10 vol% BN filled PP sample](image)

A further comparison was performed between the compounding methods: extrusion and internal mixing. It was found that compounding methods have no significant effect on thermal conductivity. On the other hand, extrusion is more productive, therefore it is a better technology to use when filler content is relatively low (under 50 vol%).

**Injection-compression molding**

In the previous experiments it was pointed out that the processing method influences the orientation of the filler particles, hence the achievable effective thermal conductivity of composites. The injection-compression molding (ICM) was applied, which is the combination of the injection molding and compression molding, thus it could result in higher thermal conductivity. The thermal conductivity of the injection-compression molded samples was compared to the previously presented results from the other processing methods. Figure 43 shows that the specimens produced by the newly applied method have about 20% higher thermal conductivity at 20 and 30 vol% BN concentration than the injection molded samples, but still have lower TC than compression molded samples. This method can provide a good solution to increase the achievable TC, and keep the cycle time as low as possible.
Development of injection moldable, thermally conductive polymer composites

Figure 43. Thermal conductivity of injection-compression molded PP/BN composites

The fracture surface of the ICM samples was analyzed with SEM. The rate of the shell and core layers and the filler orientation was observed. In the shell the particles are perpendicular to the direction of heat flow and in the core the particles are near parallel to the heat flow. Because of the anisotropic nature of the BN particles, the higher the core/shell rate in the sample, the higher its effective TC is. Figure 44 shows that the injection molded samples have very thin core layer and the injection-compression molded ones have thicker core, more than 600 µm.

Figure 44. SEM micrographs of injection molded (a) and injection-compression molded (b) 30 vol% BN filled PP samples

In the shell of ICM samples more unoriented sections can be observed which can further increase the TC (Figure 45/a). Furthermore at the end of the flow path, which is filled during the compression phase of ICM technology, the BN particles are oriented nearly parallel to the through-thickness direction and only very thin shell layer can be observed (Figure 45/b). Hence the particles have ideal orientation regarding to the heat dissipation, but it results in different TC at the gate and at the end of the flow path.
András SUPILCZ

Figure 45. SEM micrographs of injection-compression molded 30 vol% BN filled PP samples: oriented and unoriented parts of shell layer (a) and filler orientation at the end of the flow path (b)

Segregation of fillers

To analyze the filler distribution along the flow path in injection molded samples, the segregation of the talc and boron nitride was measured at different filler concentrations. As the results show (Figure 46), actual filler concentration is in good agreement with nominal concentration, and there is no significant segregation of talc and BN particles along the flow path. It means that thermal conductivity and consequently the mechanical properties are uniform along the flow length.

Figure 46. Talc (a) and boron nitride (b) concentration along the flow path in the polypropylene matrix

Static and dynamic mixers for injection molding

Different mixing elements (static and dynamic mixers) were also tested to show their efficiency concerning homogenous mixing and thermal conductivity enhancement during
Development of injection moldable, thermally conductive polymer composites

injection molding. First of all a 30 vol% filler content masterbatch was prepared with a twin screw extruder, then injection molded samples were made with 5, 10 and 20 vol% BN and also with talc by dilution with polypropylene. Two 22 mm inner diameter Stamixco static mixers were used with 5 (SM5) and 8 (SM8) mixing elements. The dynamic mixer was used with two different parameter setups. The first run was performed at a low screw rotation speed (15 l/min) and low back pressure (20 bar) (DM_1) and the second run at higher rotation speed (35 l/min) and higher back pressure (60 bar) (DM_2). Reference samples were also injection molded without mixing elements (SM0). Figure 47 shows the effect of different mixers on the thermal conductivity of BN and talc filled polypropylene. It can be stated that changing the number of static mixing elements cause no significant change in thermal conductivity. On the other hand, the use of dynamic mixers results in only a minor enhancement of thermal conductivity. The increase is less than 0.1 W/mK in the case of talc-filled and less than 0.17 W/mK in the case of BN-filled composites. Hence it can be stated that neither static nor dynamic mixers have a remarkable effect on thermal conductivity and the homogeneous distribution of aggregates.

To further analyze the effect of mixing elements, mechanical tests were also performed. As Figure 48 and Figure 49 show, there are also no significant differences in mechanical properties between the composites prepared with a different number of static mixing elements. On the other hand, dynamic mixing at a low screw rotation speed and low back pressure caused a decrease in both tensile strength and tensile modulus. The difference is minor compared to the other setups, but it can mean that the aggregates are not broken up and

![Figure 47. Effect of different mixing elements on thermal conductivity of talc (a) and boron nitride (b) filled polypropylene composites (SM=static mixer; DM=dynamic mixer)]
homogenized properly, which leads to impaired mechanical properties and an increase in thermal conductivity.

![Graph](image1)

**Figure 48.** Tensile strength of BN (a) and talc (b) filled PP composites injection molded with different mixing elements (SM=static mixer; DM=dynamic mixer)

![Graph](image2)

**Figure 49.** Tensile modulus of BN (a) and talc (b) filled PP composites injection molded with different mixing elements (SM=static mixer; DM=dynamic mixer)

### 5.1.4. Surface modification

The most effective way to improve the thermal conductivity of composites is increasing filler concentration. This method increases the apparent viscosity of the material and it could cause problems during processing. Surface treatment could be an alternative method to improve the thermal conductivity of the composites at given filler content. The surface of BN is very inert and it leads to poor interfacial adhesion between the particles and the polymer. It is well-known that a coupling agent can improve the phase interfacial bonding strength between filler and matrix, which enhances thermal conductivity as well as
mechanical properties. Thus a good contact between the phases is critical to the efficiency of heat flow. Thermal conductivity is very sensitive to interface defects because the thermal contact resistance between the filler and matrix leads to a phonon-scattering effect.

Three different surface treatment methods were applied on boron nitride powder based on the works of Xu and Chung [134], Zhou et al. [135] and Kim et al. [136]. The three methods were the followings:

1st method (M1): a silane/distilled water solution was prepared with 2.4 m% silane concentration with reference to the amount of BN. First BN was added to the solution and stirred at room temperature for 30 minutes, then stirred at 80°C for 1 hour. The mixture was dried out at 90°C in a drying chamber for 4 hours.

2nd method (M2): 2.4 m% silane (with reference to the amount of BN) was added to the 95/5 m% distilled water/ethanol solution adjusted to pH 4.5 with diluted hydrochloric acid. Boron nitride powder was added to the solution and stirred at room temperature for 30 minutes, then stirred at 80°C for 1 hour. The mixture was dried out at 90°C in a drying chamber for 4 hours.

3rd method (M3): boron nitride powder was treated with a 5M NaOH (20 g/100 ml) solution for 5 hours at 80°C, and then the powder was rinsed and washed three times with distilled water to reach the neutral pH. Next the silane treatment was performed according to the 2nd method.

BN particles have a plate-like shape. Its basal plane is molecularly smooth and has no surface functional groups available for chemical bonding. On the other hand, its edge planes have hydroxyl and amino functional groups. These functional groups allow the BN to chemically bond with other molecules. This is the reason why in the third method it was treated with a NaOH solution, to attach more hydroxide ions onto the surfaces.

PP based composites were prepared from untreated and the surface treated BN powder with an internal mixer at 30 vol% filler content. The samples were produced with compression molding. For reference samples unfilled PP was used. The thermal conductivity of the composites (Figure 50) was determined with the hot plate apparatus. PP has a thermal conductivity of 0.36 W/mK and the thermal conductivity of PP filled with untreated BN is 1.92 W/mK, which is a 433% increase. The results show that the best method of the three is the third surface treatment method; with it a thermal conductivity of more than 2.5 W/mK can be achieved. It presents close to 700% increase compared to neat PP.
Figure 50. Thermal conductivity of the 30 vol% BN filled compounds with different surface treatments
(UT=untreated; M1–M3=1\textsuperscript{st} method–3\textsuperscript{rd} method)

The mechanical properties of the composites were also analyzed. According to the results (Figure 51), it can be stated that the filled polypropylene has higher stiffness than the unfilled PP. All surface treatment methods increased mechanical properties, both tensile strength and modulus. The best mechanical properties can be obtained with the 1\textsuperscript{st} and the 2\textsuperscript{nd} method. It also proves that the silane coupling agent increased the interfacial adhesion between the PP and the BN.

Table 7 lists the DSC results. The calculated crystallinity shows that silane surface treatment does not modify the crystallinity of the composites. The untreated PP/BN composite has a crystal fraction of 64.7% and after surface modification, the matrices have a 63-64% crystal fraction. When these results are compared to the crystallinity of neat PP, a 5% increment can be observed in all cases, which shows the nucleating efficiency of BN.
Furthermore, a shift can be observed in melting and crystallization temperature. Melting temperature decreased by 4°C due to the increased thermal conductivity. Crystallization temperature increased about by 10°C, which also proves the nucleating efficiency of the filler. These results are also presented in the Appendix (Chapter 9, Figure 89 and Figure 90).

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting temperature [°C]</th>
<th>Crystallization temperature [°C]</th>
<th>Enthalpy of fusion [J/g]</th>
<th>Crystallinity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>162.95</td>
<td>123.56</td>
<td>96.49</td>
<td>58.48</td>
</tr>
<tr>
<td>PP+BN (UT)</td>
<td>159.12</td>
<td>133.36</td>
<td>53.38</td>
<td>64.70</td>
</tr>
<tr>
<td>PP+BN (M1)</td>
<td>158.37</td>
<td>134.01</td>
<td>52.03</td>
<td>63.07</td>
</tr>
<tr>
<td>PP+BN (M2)</td>
<td>159.44</td>
<td>138.30</td>
<td>52.16</td>
<td>63.22</td>
</tr>
<tr>
<td>PP+BN (M3)</td>
<td>156.30</td>
<td>130.72</td>
<td>52.72</td>
<td>63.90</td>
</tr>
</tbody>
</table>

Table 7. DSC measurement results of the PP/BN compounds (UT=untreated; M1–M3=1st method–3rd method)

5.1.5. The hybridization of fillers

To show the hybrid effect between boron nitride and talc, further measurements were performed. In this case the thermal conductivity of three compression molded specimens was measured. Table 8 contains the notation of the compounds and specimens. The specimens had a thermal interface material between them, which reduced thermal resistance (Figure 52). First the thermal conductivity of hybrid materials were determined (H1 and H2), using three specimens joined together in each measurement. Secondly, the thermal conductivity of materials with a single filler was determined (compounds A and B). Thirdly, the conductivity of the specimens joined together (Figure 52) was determined. A system made up of specimens filled with a single filler was also tested, first with specimen arrangement AAB then with ABB. Total filler content was 30 vol% in each case and the boron nitride and talc content was the same as in the case of the hybrid material, but only specimens with a single filler were used for the measurement of thermal conductivity.

<table>
<thead>
<tr>
<th>Sign</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>H145 F PP + 30 vol% talc</td>
</tr>
<tr>
<td>B</td>
<td>H145 F PP + 30 vol% BN</td>
</tr>
<tr>
<td>H1</td>
<td>H145 F PP + 20 vol% talc + 10 vol% BN (hybrid)</td>
</tr>
<tr>
<td>H2</td>
<td>H145 F PP + 10 vol% talc + 20 vol% BN (hybrid)</td>
</tr>
</tbody>
</table>

Table 8. Notation of the single and hybrid composites
As Figure 53 shows, in the case of specimens containing a single filler, a linear relationship can be observed between the thermal conductivity of boron nitride and talc filled specimens. Thus thermal conductivity can be easily calculated as a function of filler content. If talc and boron nitride are hybridized, a higher thermal conductivity can be achieved and the relationship between the fillers becomes nonlinear. As was mentioned, this positive synergetic effect can be explained with the different particle size of BN and talc and the fragmentation of talc particles. In the compound the talc particles formed the main thermally conductive path in the compound, while the smaller BN particles established more contact between the larger particles to obtain higher thermal conductivity.

Next, the thermal conductivity of the injection molded and the compression molded samples were compared to each other, which showed the effect of the sample preparation methods on hybrid filled composite materials. The same compound was used for both sample preparation methods, thus filler content was the same. Before compression molding the samples, the granules were milled to avoid air traps during the process. The measurement
results can be seen in Figure 54. At each measurement point the thermal conductivity of the compression molded samples was about 60% higher than that of the injection molded ones. It proves that the skin-core effect has great influence on thermal conductivity. The skin layer has lower filler content, thus it behaves as an isolating layer, which decreases heat transfer.

![Thermal conductivity graph]

**Figure 54. Comparison of the effect of molding process on BN/Talc hybrid filled H145 F PP**

To characterize the changes in mechanical properties of the compounds, quasistatic and dynamic tests were performed. The results of the tensile test (as a quasistatic test) can be seen in Figure 55 and Figure 56. Compared to unfilled polypropylene, particle-filled compounds have significantly lower tensile strength. The tensile strength of unfilled PP (31.9 MPa) decreased by 6-10 MPa when 30 vol% filler was added.

![Tensile strength bar graph]

**Figure 55. The tensile strength of the compounds**

The tensile modulus shows a reverse tendency (Figure 56). When fillers are added to the polypropylene, the modulus increased significantly. While the unfilled PP has a tensile modulus of 2.1 GPa, the PP/10 vol% BN 20 vol% talc compound has a tensile modulus three times higher (6 GPa). It means that the particles as reinforcement increase the stiffness of the
compound. It was also found that BN has a better reinforcing effect than talc. Filling 30 vol% talc into the matrix increased the modulus by 2.8 GPa. When the same amount of BN was used, the modulus increased by 3.7 GPa. With hybrid fillers a higher modulus can be achieved. It means that a synergetic effect exists between talc and BN.

![Figure 56. Tensile modulus of the compounds](image1.png)

As the typical loads of polymer parts have dynamic characteristics, Charpy impact tests were also performed. The results of the measurements can be seen in Figure 57. The unfilled polypropylene has an impact strength of 72 kJ/m². When 30 vol% talc is added to the matrix, a significant drop can be observed, as impact strength lowered to one-tenth of that of unfilled polypropylene. This drop is far more remarkable than the drop in tensile strength. The most brittle of the compounds is polypropylene containing 20 vol% BN and 10 vol% talc. Its impact strength is only 3.6 kJ/m². The results show that in contrast to tensile modulus, hybrid materials have a negative synergetic behavior concerning impact strength.

![Figure 57. Impact strength of single filled and hybrid materials](image2.png)
With the Melt Volume Rate (MVR) measurement the compounds can be characterized regarding the processability. The MVR values of the single and hybrid filled compounds is shown on Figure 58. The melt volume rate of the unfilled polypropylene is 44 cm$^3$/10 min. Filling 30 vol% talc into the matrix, the MVR decrease to 11.8 cm$^3$/10 min and at the case of 30 vol% boron-nitride this value is only 2.5 cm$^3$/10 min. Boron-nitride and talc as hybrid filler has a negative hybrid effect to the viscosity. The compound, containing 20 vol% BN and 10 vol% talc has lower MVR value (1.65 cm$^3$/10 min) than that of the 30 vol% boron-nitride filled PP.

![Figure 58. Melt volume rate of single filled and hybrid materials](image)

### 5.2. Crystallinity of conductive polymer composites

Many papers have investigated the influence of filler fraction on thermal conductivity and mechanical properties, but few of them have examined crystallinity, thermal parameters, cooling behavior and their relationship. One of the most important physical parameters of semi-crystalline polymers is their degree of crystallinity, as it determines their mechanical properties. The modulus of elasticity, yield stress and impact resistance increase gradually with crystallinity. Crystallinity and crystalline morphology are critical parameters during injection molding because they are strongly influenced by processing conditions, including molding temperature, cooling rate, holding time and temperature. There is a correlation between cooling rate and crystallinity. The degree of crystallinity is proportional to the cooling rate, and it can be determined by DSC measurements. Furthermore, the fillers added to increase thermal conductivity can work as an effective nucleating agent. Thus they can increase the number of crystal nuclei. In this chapter the effects of different ceramic fillers on the cooling rate and thermal properties of polypropylene-based compounds are examined.
5.2.1. Method of calculation

The temperature distribution in the specimen can be described with the heat diffusion equation (Equation (38)) [10]. This differential equation was solved numerically with a finite difference equation (explicit difference method) (Equation (39)). This numerical method describes the cooling process in the substance using a one-dimension model without an inner heat source [137].

\[
\frac{1}{\alpha} \frac{\partial T}{\partial t} = \nabla^2 T + \frac{\dot{q}}{\lambda}. \tag{38}
\]

\[
\frac{T(x,t + \Delta t) - T(x,t)}{\Delta t} = \alpha \cdot \frac{T(x + \Delta x,t) + T(x - \Delta x,t) - 2T(x,t)}{\Delta x^2}, \tag{39}
\]

where \(T\) is the temperature, \(x\) and \(t\) indicate the position and time, \(\Delta x\) and \(\Delta t\) are the distance and time step in the calculation, and \(\alpha\) is the thermal diffusivity. Thermal diffusivity was calculated as the proportion of thermal conductivity and the product of density and specific heat capacity (Equation (40)). Using temperature-dependent values in the equations, more accurate results can be achieved.

\[
\alpha(T) = \frac{\lambda(T)}{\rho \cdot c_p(T)}, \tag{40}
\]

where \(\rho\) is density, \(c_p\) is specific heat capacity and \(\lambda\) is thermal conductivity.

In an actual process the polymer shrinks and warps during cooling, therefore thermal contact resistance \((R_s)\) varies during the cycle. Several studies have examined thermal contact resistance between the polymer and the metal surface, in which the mean value of resistance is \(5 \cdot 10^{-4} \text{ m}^2\text{K/W}\) [138, 139]. Contact resistance induces a temperature difference between the polymer \((T_{ps})\) and the surface of the mold \((T_{ms})\). Equation (41) gives the temperature field which is the input data of the explicit difference method.

\[
T_{ps}(t) = R_s \cdot q(t) + T_{ms}. \tag{41}
\]

The heat flux \((q)\) was calculated from the temperature drop \((\Delta T)\) in the substance between two discrete points \((\Delta x)\) (Equation (42)), according to Fourier’s law. This heat also flows through the air gap between the surface of the mold and the polymer.

\[
q(t) = \lambda \cdot \frac{\Delta T}{\Delta x}. \tag{42}
\]

The cooling rate of the sample was calculated from the temperature field, which was obtained from the explicit difference method. The derivation of the time-temperature curves at discrete distances from the surface gives the cooling rate \((v_{cool})\) as a function of time and distance (Equation (43)).
Development of injection moldable, thermally conductive polymer composites

\[ v_{\text{cool}}(x,t) = \frac{\partial T(x,t)}{\partial t}. \]  

(43)

The cooling time required to reach the ejection temperature was determined with three different methods: simulation; the explicit difference method and an empirical formula (Equation (44)) [140]. The simulations were performed with the Moldflow injection molding simulation software.

\[ t_{\text{cool}} = \frac{s^2}{\pi \cdot \alpha} \cdot \ln \left( \frac{4}{\pi} \cdot \frac{T_{\text{me}} - T_{\text{mo}}}{T_e - T_{\text{mo}}} \right), \]  

(44)

where \( s \) is the thickness of the sample, \( T_{\text{me}} \) is the melt temperature, \( T_{\text{mo}} \) is the temperature of the mold and \( T_e \) is the ejection temperature.

5.2.2. Cooling rate in the sample

The three stages of specific heat measurement (heat-cool-heat) are plotted in Table 9. Only unfilled PP shows a significant difference between the first and the second heating, which is about 500 J/kgK. In the case of the filled materials there is no considerable difference between the two measurements. In the neat PP the first heating phase refers to the injection molding process, and the second heating to the behavior caused by controlled cooling. In the filled PP this effect is not significant as there are no changes in the fillers at this low temperature range, therefore the high filler content leads the process. On the other hand, there are significant differences between the values measured in the heating and the cooling phase. The specific heat measured during the cooling phase has to be used for calculations, as Equation (39) describes a cooling process.

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific heat [J/kgK] (25-225°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st heating</td>
</tr>
<tr>
<td>H145 F</td>
<td>1460-1930</td>
</tr>
<tr>
<td>H145 F + 30 vol% talc</td>
<td>1390-2030</td>
</tr>
<tr>
<td>H145 F + 30 vol% BN</td>
<td>1390-2030</td>
</tr>
<tr>
<td>H145 F + 30 vol% TiO₂</td>
<td>1960-2045</td>
</tr>
</tbody>
</table>

Table 9. Specific heat of the compounds

The cooling gradients were determined as a function of the time and positions across the thickness using the explicit difference method. In accordance with the injection molding tests, a melt temperature of 200°C and a mold temperature of 40°C were used in the calculations. Specific heat and, as a result, calculated heat diffusivity varied as a function of temperature. The temperature was uniform throughout the whole specimen at the initial
calculation step, then it started to cool down to 40°C. The cooling gradients (Figure 59) show that unfilled PP has the lowest cooling rate. When 30 vol% of filler is used, cooling time can be shortened significantly. The maximum ejection temperature of polypropylene is about 100-110°C. It means that if the temperature is lowered below this value, the polymeric parts are hard enough to be removed from the mold without any damage [141]. With 30 vol% of TiO$_2$ the cooling time to reach ejection temperature decreased by 35%, with talc it decreased by 50% and in the case of BN by more than 70%.

The time to reach ejection temperature in the cross-section is shown in Figure 60. From the cooling gradients the cooling rates can be calculated. Figure 61 shows the average cooling rate of the material between the injection temperature (200°C) and the ejection temperature (100°C) as a function of position across the thickness. On the surface a very high cooling rate can be observed, but it decreases rapidly towards the center. In the middle of the PP sample the average cooling rate is 22.6°C/s. With 30 vol% of talc the cooling rate is 45.8°C/s, with TiO$_2$ it is 57.1°C/s and with BN it increases to 75°C/s. These significant differences in the cooling rates can be explained with the differences in thermal conductivity (Figure 62). Moreover, there is a strong linear correlation between the cooling rate and thermal conductivity.
Development of injection moldable, thermally conductive polymer composites

Figure 60. The time to reach ejection temperature in the cross-section

Figure 61. The average cooling rate between the injection and ejection temperatures

Figure 62. The relationship between the cooling rate and the thermal conductivity of the compounds

The explicit difference method was compared to other cooling time calculation methods (empirical calculation and Moldflow simulation). The explicit difference method shows good agreement with the Moldflow simulation, especially in higher thermal conductivity ranges (Figure 63). The empirical method gives a lower estimation of the real processes, because this equation uses an average thermal diffusivity value and approximates the gradient with a logarithmical curve.
5.2.3. Crystallinity

The thermal characterization of the compounds was performed with a DSC apparatus. The compounds had crystallization peaks. As Figure 64 and Table 10 show, there is a remarkable shift in the crystallization peaks. The biggest difference is about 13°C when 30 vol% of BN is used. It means that the crystals can be created at a higher temperature, and the polymer material has a longer time for crystallization.
In the DSC measurements, the thermal history of the materials was erased during the first heating, then the crystals were created and melted under controlled circumstances with a slow cooling and heating rate. This method is widely used when a small amount of filler is added to the polymer matrix. This way the effect of the fillers on crystallinity can be compared. On the other hand, in a real process such as injection molding, the cooling rate is more than 15°C/s, thus the polymers have less time for crystallization. The higher the cooling rate, the lower crystallinity will be. Process-induced crystallinity can be obtained from the first heating scan of DSC measurements.

The results of the crystallinity measurements are shown in Figure 65. It can be seen that the degree of crystallinity increased with the addition of fillers when the heating and cooling rate was 10°C/min (the second heating and the first cooling). Titanium dioxide increased the crystallinity of PP from 63% to 71%. BN or talc only increased it to 65-66%. Among the three filler types, the best nucleating agent is the BN, because the PP/BN composite shows the highest crystallization temperature. Injection molding-induced crystallinity was determined from the first heating phase. It is noticeable that crystallinity is 5-15% lower than after recrystallization. With 30 vol% boron nitride crystallinity is only 64.2%, which is lower than in the case of unfilled polypropylene (68.1%). This drop can be explained by the higher thermal conductivity of the composite. While the unfilled polypropylene cooled slowly in the mold after injection, the 30 vol% boron nitride filler increased thermal conductivity and also the cooling rate. Due to the higher cooling rate, lower crystallinity can be obtained. It means that the nucleating effect of the boron nitride was not enough to compensate for the effect of thermal conductivity.

![Figure 65. Crystallinity of the compounds in the first and second heating phase](image)

The crystallinity of talc and BN filled compounds were investigated as a function of filler content and the thermal conductivity of the composite. Up to 30 vol% talc
(\(\lambda=0.58\) W/mK) crystallinity increased monotonously, which shows a good nucleating agent behavior. On the other hand, when boron nitride is added to the PP matrix, first crystallinity increases, then above a threshold it decreases. This limit value is 10 vol\%, where the thermal conductivity of the compound is 0.55 W/mK. Above 10 vol\% BN fraction, the high thermal conductivity results in faster cooling during injection molding, thus crystallinity decreases (Figure 66).

![Figure 66. The crystallinity of PP compounds as a function of talc (0, 10, 20 and 30 vol\%) and BN (0, 4.4, 12.1, 20 and 30 vol\%) content](image)

To prove this phenomenon, further investigation was performed with polylactic acid (PLA) matrix composites. PLA has low crystallinity even at a very low cooling rate (without using nucleating agents). During processing, when the cooling rate is much higher, the material can remain amorphous. Nucleating agents, like talc or boron nitride can enhance the crystalline ratio of PLA significantly, and the effect of the thermal conductivity of the compounds can be analyzed and compared.

According to the measurements on the injection molded samples, the unfilled PLA has a thermal conductivity of 0.31 W/mK (Figure 67).

![Figure 67. The thermal conductivity of talc and BN filled injection molded PLA samples](image)
When a filler was added to the matrix, TC changed significantly. With 30 vol% BN, thermal conductivity increased by 365% (1.44 W/mK) and with 30 vol% talc it increased by 155% (0.79 W/mK).

As Figure 68 shows talc-filled PLA has a well-determined crystallization peak. The curves indicate that talc is a good nucleating agent because there is no cold crystallization during the second heating phase. With BN as filler the crystallization peak is much lower and in the second heating phase cold crystallization can be observed. This phenomenon can have two main reasons. First, BN is not as good a nucleating agent as talc; second, its thermal conductivity is much higher than that of talc, which increases the cooling rate inside the sample during the measurement.

The crystallinity of talc and BN filled PLA was investigated as a function of filler content (Figure 69).
Up to 30 vol% talc ($\lambda = 0.79$ W/mK) crystallinity increased monotonously, which shows a good nucleating agent behavior. On the other hand, when boron nitride is added to PLA, first the crystalline ratio increases then after a threshold it decreases. This limit value is 20 vol%, where the thermal conductivity of the compound is 0.82 W/mK. Above 20 vol% BN fraction, the high thermal conductivity results in faster cooling during injection molding, thus crystallinity decreases. This phenomenon was also detected previously in the case of the PP matrix.

5.2.4. Isothermal crystallization

The isothermal crystallization of an unfilled polypropylene homopolymer and its compounds with boron nitride was analyzed. The isothermal crystallization kinetics of a material at a constant temperature can be described by evaluating its degree of crystalline conversion as a function of time. Relative crystallinity at different crystallization times ($X(t)$) can be calculated with Equation 45 [142]:

$$X(t) = \frac{Q_t}{Q_\infty} = \int_0^t \frac{(dH / dt)dt}{(dH / dt)dt},$$  

where $Q_t$ is the heat generated at time $t$, $Q_\infty$ is the heat generated at infinite time, and $dH/dt$ is the rate of heat production. In order to understand the evolution of crystallinity during isothermal crystallization, the Avrami model was applied to analyze isothermal crystallization kinetics (Equation 46):

$$X(t) = 1 - e^{-K \cdot t^n},$$

where $n$ is the Avrami exponents. The value of $n$ depends on the mechanism of nucleation and the form of crystal growth, while $K$ is a rate constant dedicated to nucleation and growth. Exponent $n$ consists of two terms, one from nucleation (0 or 1) and one from crystallization (1, 2 or 3) (Table 11). If the number of nuclei is constant in time (athermal nucleation), $n$ gives the dimension of crystal growth directly. On the other hand, if the number of nuclei increases in time during crystallization (thermal nucleation), $n$ is equal to the dimension of growth+1 [143].
Development of injection moldable, thermally conductive polymer composites

<table>
<thead>
<tr>
<th>n</th>
<th>Crystal geometry</th>
<th>Nucleation type</th>
</tr>
</thead>
<tbody>
<tr>
<td>3+1</td>
<td>sphere</td>
<td>thermal</td>
</tr>
<tr>
<td>3+0</td>
<td>sphere</td>
<td>athermal</td>
</tr>
<tr>
<td>2+1</td>
<td>disc</td>
<td>thermal</td>
</tr>
<tr>
<td>2+0</td>
<td>disc</td>
<td>athermal</td>
</tr>
<tr>
<td>1+1</td>
<td>rod</td>
<td>thermal</td>
</tr>
<tr>
<td>1+0</td>
<td>rod</td>
<td>athermal</td>
</tr>
</tbody>
</table>

Table 11. Definition of the Avrami exponent $n$ [142, 144]

Using the logarithmic form of the Avrami equation (Equation 47.) and fitting the experimental data, the values of $n$ and $K$ can be determined from the slope and intercept of the plots of $\log[-\ln(1-X(t))]$ versus $\log t$:

$$\log[-\ln(1-X(t))] = \log K + n \cdot \log t.$$  \hspace{1cm} (47)

The isothermal crystallization in the melt of the PP and its compounds was analyzed at four different temperatures ($T_c$: 130, 135, 140 and 145°C) with a DSC apparatus. The samples were heated up to 200°C at 25°C/min and kept at a constant temperature for 5 minutes to eliminate its thermal history. Then it was rapidly cooled down (50°C/min) to the previously determined temperatures and maintained there for 40 minutes. The exothermic curves of heat flow were recorded as a function of time. Figure 70 shows the isotherm crystallization curves of the H145F PP/5 vol% BN compound at four different temperatures. Further results are presented in the Appendix (Chapter 9, Figure 91).

![Figure 70. Isotherm crystallization of polypropylene homopolymer + 5 vol% BN at different crystallization temperature](image)

It was observed that when the crystallization temperature is increased, the exothermal peak becomes broader, which implies that the crystallization rate is reduced. Thus, the induction time of the exotherm increases. Furthermore the position of the crystallization peaks of boron nitride filled PP appeared earlier than that of unfilled PP. The relative amount of crystallization of PP/5 vol% BN compound has been plotted in Figure 71 for different
crystallization temperatures. It was calculated from the exotherms of the DSC measurements. Further results are presented in the Appendix (Chapter 9, Figure 92).

![Graph showing relative crystallinity vs. time for different temperatures](image)

**Figure 71. Relative crystallinity of the polypropylene homopolymer + 5 vol% BN as a function of time at different temperatures**

Half-time of crystallization ($t_{0.5}$) is defined as the time at which the extent of crystallization is 50%. It can be read conveniently from the relative crystallinity–time curves, and is also regarded as a very important crystallization kinetic parameter. Usually $t_{0.5}$ is employed to characterize the rate of crystallization directly. The greater the value of $t_{0.5}$ is, the lower the rate of crystallization is. As Figure 72 shows, the crystallization rate can be increased significantly by adding boron nitride to the PP matrix.

![Graph showing half-time vs. crystallization temperature](image)

**Figure 72. Half time of crystallization of the polypropylene homopolymer and its compounds as a function of crystallization temperature**

For example at 140°C, crystallization is 5 times faster when 5 vol% BN is added to the PP, and 30 times faster when 30 vol% BN is filled into the matrix. It shows that BN is an effective nucleating agent.
Finally, the Avrami constants were determined by plotting the experimental data in the \( \log[-\ln(1-X(t))] \) versus \( \log t \) diagram (Figure 73). (Further results are presented in the Appendix, in Chapter 9 on Figure 93.) \( n \) and \( K \) can be determined from its equation by data fitting. The constants and half time of crystallization values are plotted in Table 12.

![Figure 73. Avrami plots of \( \log[-\ln(1-X(t))] \) versus \( \log t \) for isothermal crystallization of the polypropylene homopolymer + 5 vol% BN at different crystallization temperatures](image)

<table>
<thead>
<tr>
<th>( T_c )</th>
<th>Compound</th>
<th>( n )</th>
<th>( k )</th>
<th>( t_{0.5} )</th>
<th>( T_c )</th>
<th>Compound</th>
<th>( n )</th>
<th>( k )</th>
<th>( t_{0.5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>130°C</td>
<td>PP</td>
<td>2.7</td>
<td>1.41</td>
<td>0.7</td>
<td>130°C</td>
<td>PP</td>
<td>2.7</td>
<td>0.00</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>PP+5BN</td>
<td>1.8</td>
<td>5.25</td>
<td>0.3</td>
<td></td>
<td>PP+5BN</td>
<td>2.1</td>
<td>0.11</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>PP+10BN</td>
<td>1.6</td>
<td>7.94</td>
<td>0.2</td>
<td></td>
<td>PP+10BN</td>
<td>1.9</td>
<td>0.28</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>PP+20BN</td>
<td>1.6</td>
<td>10.96</td>
<td>0.2</td>
<td></td>
<td>PP+20BN</td>
<td>1.8</td>
<td>1.41</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>PP+30BN</td>
<td>1.6</td>
<td>15.14</td>
<td>0.1</td>
<td></td>
<td>PP+30BN</td>
<td>1.6</td>
<td>2.57</td>
<td>0.5</td>
</tr>
<tr>
<td>135°C</td>
<td>PP</td>
<td>2.8</td>
<td>0.02</td>
<td>3.6</td>
<td>140°C</td>
<td>PP</td>
<td>2.2</td>
<td>0.01</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>PP+5BN</td>
<td>1.9</td>
<td>1.02</td>
<td>0.8</td>
<td></td>
<td>PP+5BN</td>
<td>2.1</td>
<td>0.03</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>PP+10BN</td>
<td>1.8</td>
<td>2.14</td>
<td>0.5</td>
<td></td>
<td>PP+10BN</td>
<td>2.0</td>
<td>0.18</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>PP+20BN</td>
<td>1.7</td>
<td>5.89</td>
<td>0.3</td>
<td></td>
<td>PP+20BN</td>
<td>1.8</td>
<td>0.41</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>PP+30BN</td>
<td>1.6</td>
<td>7.76</td>
<td>0.2</td>
<td></td>
<td>PP+30BN</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 12. Avrami constants (\( n \) and \( k \)) and the half time of the crystallization of the compounds

As Table 12 shows, exponent \( n \) of the unfilled PP is about 3, which indicates that the growth of crystals in the melt is probably three-dimensional (spherulite), and the nucleation process is athermal. According to the literature, in the presence of a heterogeneous nucleating agent the crystallization is supposed to be athermal [145]. Accordingly, when the boron nitride fraction is increased, the crystals will be disc-shaped. On the other hand, when the crystallization temperature is increased, exponent \( n \) also increases, thus crystallization and nucleation kinetic change with temperature.
5.3. Improving processability of conductive polymer composites

The processability of highly filled polymeric materials is a key issue in research and in the industry as well. The fillers drastically decrease the flowability of the melt, thus energy consumption increases and throughput decreases. In order to improve the processability of the filled polypropylene, cyclic butylene terephthalate oligomer (CBT) was added to the matrix.

The effect of CBT 100 concentration

First, the effect of CBT content on the properties of the PP matrix was analyzed. 0.5, 1, 3 and 5 vol% of CBT 100 was blended with PP in a twin screw extruder then flat 80x80x2 mm samples were injection molded. As Figure 74 shows, the tensile strength of neat PP is about 30 MPa, and as CBT content is increased, there is only a minor effect, but the results are within the standard deviation of measurements. The same effect can be observed in the tensile modulus (Figure 75). When CBT content is increased, the results are also within the standard deviation of measurements. It can be established that the CBT 100 additive has only a minimal effect on tensile strength and tensile modulus.

![Bar chart showing tensile strength of PP/CBT compounds as a function of CBT content.](image1)

![Bar chart showing tensile modulus of PP/CBT blend as a function of CBT content.](image2)
Thermal conductivity was also measured. The tests were performed with a hot plate apparatus at 55°C. The result shows that the CBT additive does not modify the thermal conductivity of the polypropylene matrix (Figure 76). Further measurements need to be carried out to study the effect of CBT on fillers. As CBT 100 is a good dispersion agent and also a good wetting agent, it can develop better contact between the filler and the polymer, thus reducing contact resistance and enhancing conductivity.

![Figure 76. Thermal conductivity of PP/CBT 100 blend](image)

The results of the melt volume rate measurement show that when the CBT fraction in the blend is increased, MVR also increases (Figure 77). In the 0-5 vol% range the relationship between the CBT fraction and the MVR value is non-linear. By adding 5 vol% CBT 100 to the PP, MVR increased by more than 100%. Up to 3 vol% CBT only a minor change can be observed in the melt flow rate but above 3 vol% it changes drastically.

![Figure 77. Melt Volume Rate of the PP/CBT blend as a function of CBT content](image)
Next, polypropylene/CBT/talc compounds were prepared with extrusion to explore the effect of a solid filler on the PP/CBT blend. Figure 78 shows that the differences between the MVR of PP/CBT blends decrease with increasing talc concentration, as the interaction between the solid particles are more and more pronounced. At 30 vol% talc the difference is minor, only 5-10 cm$^3$/10 min. Above 30 vol% talc CBT has no significant effect.

![Figure 78. Melt Volume Rate of PP/CBT/talc composites](image)

Based on the experiments it can be stated that the CBT 100 oligomer can improve the flow properties of the matrix, while it has no significant effect on mechanical properties. With CBT 100 the flowability of filled polymers can also be improved, up to a certain filler content. Above this concentration the particle-particle interaction blocks the flow of polymers and in this case CBT has no significant effect.

**The effect of shear rate**

The viscosity of the CBT modified polypropylene homopolymer was measured with a capillary rheometer. During the tests the developing forces on the piston of the rheometer were measured at given settings. The viscosity of the material was calculated with the following formulas:

\[
\gamma_a = \frac{4 \cdot Q_v}{\pi \cdot R_c^3}, \quad (48)
\]

\[
\tau_a = \frac{\Delta P \cdot R_c}{2L_c}, \quad (49)
\]

apparent shear rate [1/s]:

apparent shear stress [Pa]:
apparent viscosity [Pa-s]:

\[ \eta_a = \frac{\tau_a}{\gamma_a}, \]  

(50)

where \( Q_v \) is the volumetric flow rate, \( R_c \) and \( L_c \) are the radius and length of the capillary, \( \Delta P \) stands for the pressure difference. \( Q_v \) and \( \Delta P \) can be calculated from the measured forces \( (F) \), the diameter of the piston \( (D_p = 9.525 \text{ mm}) \) and the speed of the cross head \( (v_{crosshead}) \):

\[ Q_v = D_p \cdot v_{crosshead}, \]  

(51)

\[ \Delta P = \frac{F}{(D_p^2 \cdot \pi) / 4}. \]  

(52)

the Bagley correction formula was used to eliminate the inlet pressure loss and the exit pressure loss:

\[ \tau_f = \frac{\Delta P \cdot R_c}{2 \cdot (L_c + R \cdot n_B)}. \]  

(53)

At 3 selected capillaries the pressure differences represented as functions of the \( L_c/R_c \) ratio are a linear graph. The \( n_B \) correction coefficient can be calculated from the axis intercept of this graph (Figure 79). The correction coefficient is also a function of the shear rate, thus correction has to be calculated at each apparent shear rate value.

![Figure 79. The calculation of the \( n_B \) constants of the Bagley correction (PP+5 vol% CBT at 200°C)](image)

As the flow rate profile in the capillaries is not parabolic, the shear rate near the wall was corrected with the Rabinowitsch correction:
\[
\ddot{\gamma}_f = \frac{3 + b_1}{4} \dot{\gamma}_f,
\]
(54)

\[
\dot{\gamma}_f = \frac{d \ln(\dot{\gamma}_f)}{d \ln(\tau_f)}.
\]
(55)

If the \( \tau_f \) value calculated from the Bagley correction and the apparent shear rate are displayed in a log-log plot, a linear graph will be produced. The gradient of this line gives the value of the \( b_1 \) correction coefficient used for the calculation of the real shear rate. The quotient of \( \tau_f \) and \( \dot{\gamma}_f \) represents real viscosity irrespective of capillary geometry:

\[
\eta = \frac{\tau_f}{\dot{\gamma}_f}.
\]
(56)

Figure 80 shows the results of the viscosity measurements at different temperatures. When 1 vol% CBT was added to PP, there was no significant difference compared to neat PP. At 5 vol% CBT content real viscosity decreased significantly, but the difference decreases as shear rate is increased. It shows that CBT is a good sliding agent for PP when a low shear rate processing method is used, such as extrusion.
5.4. Modeling the thermal conductivity

The goal was to establish a mathematical model that can predict the thermal conductivity of composites up to the maximum achievable filler content. In the literature various thermal conductivity values can be found for different fillers. To characterize the thermal conductivity and maximum packing of these fillers, a new methodology was developed.

5.4.1. Development of a new method

A novel thermal conductivity model

A new model, based on the rule of mixtures, was developed to predict the thermal conductivity of particle-filled composites. The relationship between the thermal conductivity and the filler fraction of the composites is non-linear, thus the rule of mixtures gives the upper limit. The following assumptions were made:

- the filler content varies between 0 and the maximum theoretically possible filler fraction ($\phi_{\text{max}}$),
- the thermal conductivity of the composite varies between the TC of the matrix and the bulk TC of the filler,
- the relationship between filler content and thermal conductivity is non-linear.

The rule of mixtures was modified according to these assumptions, yielding Equation (57).

$$\lambda_c = \lambda'_{\text{m}} \cdot \left[1 - \left(\frac{\phi}{\phi_{\text{max}}}\right)^C\right] + \lambda'_{\text{f}} \cdot \left(\frac{\phi}{\phi_{\text{max}}}\right)^C; \quad (0 \leq \phi \leq \phi_{\text{max}}),$$

where $\lambda_c$ is the thermal conductivity of the composite, $\lambda'_{\text{m}}$ and $\lambda'_{\text{f}}$ are the effective thermal conductivities of the matrix and the filler, $\phi$ and $\phi_{\text{max}}$ are actual filler content and the maximum achievable filler content, and $C$ is a constant describing the conductive chain formation capability and shape factor of the material. The model and its dependence on factor $C$ are depicted in Figure 81. The dependence of the matrix and filler thermal conductivity factor on exponent $C$ is plotted in Figure 82.
Thermal conductivity \[ \lambda \] [W/mK] and filler content \[ \phi \] [vol\%] increasing can be determined by direct measurements, or can be calculated from values in the literature with Equation (58) and (59).

\[
\lambda'_{m} = C_{m} \cdot \lambda_{m}, \tag{58}
\]

\[
\lambda'_{f} = C_{f} \cdot \lambda_{f}, \tag{59}
\]

where \( \lambda_{m} \) and \( \lambda_{f} \) are the thermal conductivities of the matrix and the filler from literature. \( C_{m} \) describes the morphology change in the matrix caused by the cooling rate, the processing technology and the nucleating efficiency of the fillers. \( C_{f} \) depends on the orientation of the filler, the number of contacts between the particles and the thermal contact resistance between them.

Maximum filler content

The maximum filler content was determined with the thermal conductivity meter presented in Chapter 4.2. The powders were filled in a wooden frame and pressed with the
Development of injection moldable, thermally conductive polymer composites

steel reference cylinders. The displacement of the press plate was registered as a function of compaction pressure. From the displacement \((l)\), the inner diameter of the frame \((d)\) and the mass of the measured filler \((m)\) apparent density \((\rho_a)\) was calculated (Equation (60)). The Relative Density \((RD)\) of the filler can be determined as a ratio of the apparent density and the real density of the filler (Equation (61)).

\[
\rho_a(p) = \frac{m}{d^2 \cdot \pi \cdot l(p)}, \quad (60)
\]

\[
RD(p) = \frac{\rho_a(p)}{\rho}, \quad (61)
\]

In the next step \(RD\) was plotted as a function of compaction pressure. To determine its limit, a saturation curve was fitted to the measured points. This saturation curve is based on a logistic (sigmoid) curve (Equation (62)). In the equation \(c_1\) is the minimum and \(c_2\) is the range of the sigmoid function. Relative density at zero and infinite pressure can be obtained with the help of these constants, as shown in Equation (63) and (64). Combining Equation (62) with Equation (63) and (64), we get Equation (65), the final form of the saturation curve, where \(a\) and \(b\) [-] are data fitting parameters. By fitting the curve to the measured values, the parameters and the maximum of relative density can be determined.

\[
RD_p = c_1 + \frac{c_2}{1 + e^{-a \cdot p}}, \quad (0 \leq p \leq \infty), \quad (62)
\]

\[
RD_0 = c_1 + \frac{c_2}{2} = \frac{\rho_a(p = 0)}{\rho_{\text{particle}}}, \quad (63)
\]

\[
RD_a = c_1 + c_2, \quad (64)
\]

\[
RD_p = [2 \cdot RD_0 - RD_a] + 2 \cdot \left[\frac{RD_0 - RD_a}{1 + e^{-a \cdot p}}\right], \quad (0 \leq p \leq \infty). \quad (65)
\]

**The thermal conductivity of the filler**

It is crucial to determine the exact bulk thermal conductivity \((TC)\) values of the fillers for the modeling of the conductivity of the composite material. In the literature only approximate values are available; the TC of fillers depends to a great extent on their purity and structure. Moreover, the bulk thermal conductivity of a filler and the thermal conductivity of a single particle are very different, due to the thermal contact resistance between the particles. To determine the effective TC of the filler, the press was heated up to 50 and 80°C
and the temperatures were shown as a function of compacting pressure during the measurement of maximum filler content. Thermal conductivity was calculated from Fourier’s law as a function of pressure. A logistic curve (Equation (66)) was fitted to the measured points to determine the theoretical maximum thermal conductivity of the compacted fillers.

\[ \lambda'(p) = \lambda'_{\infty} \frac{1-e^{-\frac{g}{h} p}}{1+e^{-\frac{g}{h} p}}, \quad (0 \leq p \leq \infty), \]  

where \( \lambda'_{\infty} \) is the thermal conductivity at infinite pressure \( (p) \) and \( g \) and \( h \) [-] are data fitting parameters.

5.4.2. The verification of the new model

The new model and the methodology were verified with three types of fillers: talc, boron nitride and graphite. Therefore, the applicability of the model was proved for a wider range of TC in the case of plate-like particles.

Maximum filler fraction

The maximum filler fractions (relative density limit) of talc, boron nitride and graphite were determined with the method developed (Figure 83). To eliminate the uncertainties originating from the compression and thermal expansion of the reference steel cylinders, a baseline was determined as a function of pressure and the measurements were compensated with it. The measured values show saturation characteristics as compaction pressure is increased. At zero pressure the relative densities of talc, BN and graphite were 28.1%, 8.6% and 6.8%, respectively. The relative density limits for each material \( (RD_{\infty}) \) were determined by data fitting. The fitted curves have good correlation with the measurements, the \( R^2 \) value is over 0.94 in all cases. The relative density limits of talc, boron nitride and graphite powder are 89.9%, 82.2% and 96.2%, respectively.

Figure 83. Relative Density of talc, boron nitride and graphite powders (the dots are the measured points and the dashed lines are the fitted functions)
The effective thermal conductivity of fillers

During the compaction of powders the temperatures of the reference cylinders were also registered. After reaching the steady state condition, the thermal conductivities were determined as a function of compacting pressure (Figure 84).

![Graph showing the thermal conductivity vs. pressure for different fillers.]

Figure 84. Bulk thermal conductivity of the talc, boron nitride and graphite powders (m=measured values, f=fitted values)

The effective thermal conductivities of the talc, boron nitride and graphite powder were determined as 2.24 W/mK, 8.83 W/mK and 20.67 W/mK respectively, based on the fitted sigmoid curves. Although the thermal conductivity of the powders at atmospheric pressure is not zero, a simplification can be used in which the initial points of the sigmoid curves are forced into the origin. It was proved that the uncertainty in the thermal conductivity of the fillers ($\lambda_\infty$) at infinite pressure (Equation (66)) is below 8% when this simplification is used.

The applicability of the model

For this analysis cylindrical samples were compression molded. The measured thermal conductivity of the polypropylene matrix is 0.36 W/mK, which is higher than the 0.11 W/mK [1] value found in the literature. The reason for the difference may be the difference in the preparation of the samples and the measurement method. Hence the correction constant of the matrix is $C_{m,PP}=3.27$. The measured thermal conductivities of the fillers also differ considerably from the values in the literature. The correction constants for the talc, boron nitride and graphite are the following: $C_{f,talc}=0.224$, $C_{f,BN}=0.035$, $C_{f,graphite}=0.052$.

In Figure 85 the measured thermal conductivities for the matrix, the composites and the fillers are represented in a graph and a non-linear relationship can be observed between thermal conductivity and filler volume fraction. With the newly developed conductivity...
model, the thermal conductivity of the composite materials can be described well as a function of filler content; the correlation between the measurements and the model is higher than 0.95. In the models for polypropylene filled with plate-shaped graphite, boron nitride or talc the chain and shape factors were $C=1.4$ in all cases. It proves that the shape of the fillers determines the chain formation capability and contact between the particles.

![Graph showing thermal conductivity vs filler content](image)

**Figure 85. Thermal conductivities of the compounds**
(m=measured values, c=calculated values with the proposed model)

**Comparison to other models**

Figure 86 shows the measured thermal conductivities of polypropylene composites filled with talc, boron nitride and graphite. The measured values were compared to theoretical models developed by Maxwell, Bruggeman, Cheng and Vachon, to the geometric mean model and to our new model. In most cases, the theoretical models underestimate the measured values and as filler content increases, the differences also increase. The models show a good fit only in the case of talc up to 20 vol% and the Maxwell model describes the change of thermal conductivity as a function of talc content well. The geometric mean model gives a better estimation than the other models, but above 40 vol% it overestimates thermal conductivity. Compared to the theoretical models, the newly proposed model gives by far the best fit to the measured values even above 40 vol% of fillers.
Development of injection moldable, thermally conductive polymer composites

Figure 86. Comparison of the new model to other theoretical models in the case of talc, boron nitride or graphite-filled polypropylene
6. Summary

The aim of my dissertation was the development and characterization of new thermally conductive and electrically insulating polymer composites. Polymers normally have good insulating properties, but thermally conductive polymer composites receive more and more attention in industrial applications. The drive to reduce the size of electronic components has resulted in the generation of a larger amount of heat in the same volume. This has led researchers to develop new polymer composite materials which can dissipate more heat. These kinds of polymer composites are utilized mainly in electronics, where it is important to both increase the power and decrease the size of the components at the same time. In some instruments, such as LED lamps or integrated memory chips, fast and efficient heat dissipation is a key issue, because the generated heat can raise the temperature of the device over its thermal stability limit. Over the critical temperature lifespan decreases significantly or the instrument may be damaged.

As a first step of the dissertation, two different thermal conductivity measurement apparatus were built, calibrated and tested, to be able to determine the exact thermal conductivity of the materials (raw materials and composites). The compression molded and injection molded flat specimens were tested with the hot plate apparatus and the compression molded cylindrical samples and the fillers were tested with the linear heat flow system.

First of all I examined the main parameters which have a significant influence on the thermal conductivity of the composites. These main parameters are filler content, filler type, the type of matrix material and processing methods. As matrices polypropylene homopolymer, polypropylene copolymer, polyamide 6 and polylactic acid were applied. As fillers, boron nitride, talc and titanium dioxide were used. It was concluded that filler type and filler content have the greatest influence on thermal conductivity. The different matrices only modified the results by 0.1-0.3 W/mK.

It was also found that the processing method (compression molding and injection molding) also has a great influence on the results. The main reason is that the fillers migrate from the shell of the molded part toward the core during the injection molding process. Furthermore, in the shell anisotropic fillers are oriented in the direction of flow. This effect should be considered during the design of the part and the design of melt flow direction. This phenomenon does not develop during the compression molding, where the fillers are unoriented.
One of the most important and most efficient processing methods in the plastic industry are the injection molding and extrusion. But these processing methods limit filler content in the polymers due to the increase in melt viscosity. Thus achievable thermal conductivity is also limited. Several methods have been developed to increase thermal conductivity limited by the processing method. The first solution is the use of hybrid fillers, where the synergetic effect increases thermal conductivity. One of my goals was to develop a hybrid filler system using talc and boron nitride. With the proper mixture of the components, a significantly higher thermal conductivity was achieved than that predicted by the rule of mixtures. The second solution is the surface treatment of the particles. Several silane-based surface treatment methods were developed for boron nitride. The increment of thermal conductivity was 5-30% depending on the methods, while viscosity decreased. The third solution is to decrease the viscosity of the matrix. It was proved with viscosity measurements that 0.5-5% cyclic butylene terephthalate oligomer can improve the flowability of the composites significantly, while it has no effect on mechanical properties. It can extend the filler content range of processing methods, thus achievable thermal conductivity, too.

In my work several theoretical models for the prediction of thermal conductivity were investigated, and their weaknesses and limits were analyzed. These models were the geometric mean, Maxwell, Bruggeman and Cheng-Vachon models. My research has shown that there is a non-linear relationship between thermal conductivity and filler content. I developed a semi-empirical mathematical model from the rule of mixtures. The correctness of the model was proved with various plate-shaped fillers, which have significantly different thermal conductivities (talc, boron nitride and graphite). It was found that the new model predicts the thermal conductivity of composites more precisely than conventionally used theoretical models. To determine the input parameters of the model, new methodologies were developed and novel measurement systems (developed in our laboratory) were used.

### 6.1. Applicability of the results

In my work several mono and hybrid-filled thermoplastic based composites were developed, which can be easily used in several industrial applications to conduct heat from devices. These composites are electrical insulators; hence they can be applied in the electronic industry as heat sinks. Thanks to the good sliding properties of the applied fillers, these composites can be processed economically with conventional plastic processing machines without damage to the equipment. The positive hybrid effect on thermal conductivity found
between talc and boron nitride can provide further advantageous properties. Talc can lower
the price of the composite, while at the same time it improves thermal conductivity.

The applied maximum filler concentration is determined by the processing method.
With the introduced surface treatment method the thermal conductivity of BN/PP composites
can be increased at a given filler concentration, or the flow properties of the matrix can be
modified with CBT, therefore higher filler concentration can be used. The introduced
mathematical method and developed apparatuses to estimate the thermal conductivity of
composites can facilitate the designing and tailoring of heat conductive plastic heat sinks.

The advantage and applicability of these materials are presented via a case study with
a cooling system for LED lamp (Light Emitted Diode). The parameters were calculated with
finite element simulation. In a conventional arrangement (Figure 87) the LED chips are
soldered onto a printed circuit board (PCB).

![Figure 87. Comparison of the conventionally used arrangement with conductive plastic heat sink (a) and aluminum heat sink (b)]](image)

The board and the LEDs are joined together with conductive grease, as are the board
and the heat sink. In this simulation (SolidWorks 2010) 16 3528 LED diodes are placed on a
40x40 mm glass-reinforced PCB ($\lambda_{PCB}=0.25$ W/mK). The power dissipation of each LED is
about 0.1 W. 3M TCG-2036 conductive grease is put between the elements. The thermal
conductivity of this grease is 2.7 W/mK, and its thermal contact resistance is $1.39 \times 10^{-6}$

m$^2$K/W. In one experiment the heat sink is made by injection molding from the BN/talc filled
PP hybrid composite developed by us ($\lambda=1.22$ W/mK), and in the other experiment it is made
from an aluminum alloy ($\lambda=230$ W/mK) with extrusion. In the calculation the LED side was
insulated as it would be under a glass bulb and the sink side was free. The ambient
temperature was set to 25°C, and the convection coefficient between the heat sink and the
environment was set to 25 W/m$^2$K (free convection). The result of the simulation shows
(Figure 87) that although the thermal conductivity of the aluminum heat sink is two orders of magnitude higher than that of the conductive plastic. The temperature of the LED diodes is only 10°C lower when the aluminum heat sink is used than when the conductive plastic heat sink is used. It means that the low thermal conductivity PCB insulates the cooling system, hence the cooling efficiency of the aluminum heat sink is very low. As the developed thermally conductive plastic is an electrical insulator, the LED chips can be directly mounted onto the surface of the heat sink without generating short circuits. Accordingly, the conductive plastic can function as heat sink and PCB at the same time. In the next simulation this layout was compared to the conventionally used arrangement with an aluminum cooling unit. The results show that if the glass-reinforced PCB is omitted, the temperature of the LED diodes can be lowered by 10°C compared to the conventional arrangement (Figure 88).

![Figure 88. Comparison of the newly designed assembly with conductive plastic heat sink (a) and the conventionally used arrangement with aluminum heat sink (b)](image)

6.2. Further tasks

Although the applied talc and boron nitride has a plate-like shape, they decreased the tensile strength of the composite, hence the specimens are somewhat brittle. In the future it is important to improve the impact properties of these composites. A possible solution can be the application of ceramic fibers in addition to the ceramic particles. The developed model describes the relationship between filler concentration and the thermal conductivity of composites well. Constant $C$ of this model could be determined for other particle shapes (sphere, fiber). The hybrid effect of the different fillers can be also included in the description of the model. To apply the developed materials in the electric industry as heat sink and PCB at the same time, a method should be developed to produce electric circuits on the surface.
7. Theses

Based on the results of this PhD dissertation the following theses have been deduced:

**Thesis 1/a**

I proved that there is significant difference between the effective thermal conductivity of injection molded and compression molded polymer composites containing plate-like fillers. The differences in the orientation of the particles lead to decreased thermal conductivity in injection molded parts. This statement was confirmed by measurements of boron nitride and talc filled polypropylene homopolymer. The thermal conductivity of injection molded samples were 16-39% and 30-39% lower than that of compression molded samples in the 10-30 vol% filler concentration range [147-151].

**Thesis 1/b**

I showed that the injection-compression molded 20-30 vol% boron nitride filled polypropylene homopolymer samples have 20-23% higher through plane thermal conductivity than that of the injection molded samples. The difference can be originated from the proportion of layers with different particle orientation (core and shell layers). While the core layer of the 2 mm thick injection molded samples is only 300-400 µm thick, the core of the injection-compression molded samples is higher than 600 µm. As the particles in the core layer are near parallel to the heat flow direction (through thickness direction), the thickness of the core has a great effect on the achievable effective thermal conductivity. My statements were proved with scanning electron microscopy and thermal conductivity measurements.

**Thesis 2**

I proved that the thermal conductivity of polypropylene/boron nitride composites can be improved with the surface modification of the boron nitride filler and the efficiency can be further improved with sodium hydroxide pretreatment of the filler and increasing the acidity of the silane solution. With sodium hydroxide treatment more hydroxide ions can be attached onto the surfaces of the boron nitride particles for chemical bonding. By increasing the acidity of the silane solution the hydrolysis can be promoted. This statement was proved with measurements on compression molded 30 vol% boron nitride filled polypropylene homopolymer composites, where the improvement of thermal conductivity was 4-30%.
Thesis 3/a

I proved that there is a positive hybrid effect on thermal conductivity between the fillers when the matrix is a polypropylene homopolymer and the fillers are boron nitride and talc. As a result, using a mixture of these two fillers leads to better thermal conductivity than that predicted by the rule of mixtures. At 30 vol% total filler concentration 30-33% higher through plane thermal conductivity can be achieved with the use of boron nitride and talc in the ratio of 1:2 and 2:1 respectively. This effect can be attributed to the difference in particle sizes of fillers [151-154].

Thesis 3/b

I confirmed that the hybrid effect of boron nitride powder and talc does not only affect thermal conductivity but viscosity and quasistatic and dynamic mechanical properties as well. While the hybrid effect decreases flowability and impact strength, it increases tensile strength and modulus, which can be attributed to the different particle sizes [153-155].

Thesis 4

I proved that a filler concentration upper limit exists in the case of boron nitride filled thermally conductive composites with semi-crystalline polymer matrices. Above this filler content the effect of fillers on crystallinity is minimal, the crystal fraction of the semi-crystalline matrix starts to decrease. Because of increased thermal conductivity and intensive cooling crystallinity decreases. I proved this statement for polypropylene homopolymer and polylactic acid matrices with boron nitride and talc fillers. With boron nitride the filler content limit in the case of a PP and PLA matrix was about 10 and 20 vol%, respectively [156, 157].

Thesis 5/a

I worked out new measurement methods to determine the achievable maximum filler concentration in composites and the effective thermal conductivity of fillers. To determine the achievable filler concentration, powders were compressed between two steel reference cylinders and the relative density was determined in the function of the compacting pressure. The maximum filler concentration was calculated from the saturation curve fitted to the measured values:

\[
RD_p = \left[2 \cdot RD_0 - RD_\infty\right] + 2 \cdot \frac{RD_0 - RD_\infty}{1 + e^{-a \cdot p \cdot b}} \cdot \left(0 \leq p \leq \infty\right),
\]

where \(RD_0\) [-] is the relative density without compression, \(RD_\infty\) [-] is the relative density at infinite pressure, \(p\) [bar] is the pressure on the sample and \(a\) and \(b\) [-] are the data fitting
constants. The effective thermal conductivity of the compacted filler was calculated from the saturation curve fitted to the thermal conductivities measured at different pressure:

\[
\lambda'(p) = \lambda'_\infty \frac{1-e^{-g p}}{1+e^{-g p}}, \quad (0 \leq p \leq \infty),
\]

where \( \lambda'_\infty \) [W/mK] is the thermal conductivity at infinite pressure, \( p \) [bar] is the pressure on the sample, \( g \) and \( h \) [-] are data fitting parameters.

**Thesis 5/b**

I worked out a mathematical model to predict the thermal conductivity of polymer composites in function of filler concentration. The relationship is as follows:

\[
\lambda_c = \lambda'_m \cdot \left[1 - \left(\frac{\varphi}{\varphi_{\text{max}}}\right)^C\right] + \lambda'_f \left(\frac{\varphi}{\varphi_{\text{max}}}\right)^C; \quad (0 \leq \varphi \leq \varphi_{\text{max}}),
\]

where \( \lambda_c \) [W/mK] is the thermal conductivity of the composite, \( \lambda'_m \) and \( \lambda'_f \) [W/mK] are the effective thermal conductivities of the matrix and the filler, \( \varphi \) and \( \varphi_{\text{max}} \) [vol\%] are filler content and maximum achievable filler content, and \( C \) [-] is a constant describing the conductive chain formation capability and shape factor of the material. The applicability of the model was proved for boron nitride, talc and graphite-filled composites with a polypropylene homopolymer matrix, where factor \( C \) was 1.4 in all cases.
8. References


Development of injection moldable, thermally conductive polymer composites


9. Appendices

<table>
<thead>
<tr>
<th>Polymeric material</th>
<th>Abbreviation</th>
<th>Thermal conductivity [W/mK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile butadiene styrene</td>
<td>ABS</td>
<td>0.33</td>
</tr>
<tr>
<td>High density polyethylene</td>
<td>HDPE</td>
<td>0.44</td>
</tr>
<tr>
<td>Low density polyethylene</td>
<td>LDPE</td>
<td>0.3</td>
</tr>
<tr>
<td>Poly(butylene terephthalate)</td>
<td>PBT</td>
<td>0.29</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>PET</td>
<td>0.15</td>
</tr>
<tr>
<td>Polyamide 6</td>
<td>PA6</td>
<td>0.25</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>PC</td>
<td>0.2</td>
</tr>
<tr>
<td>Polyetheretherketone</td>
<td>PEEK</td>
<td>0.25</td>
</tr>
<tr>
<td>Polymethylmethacrylate</td>
<td>PMMA</td>
<td>0.21</td>
</tr>
<tr>
<td>Polypheylene sulfide</td>
<td>PPS</td>
<td>0.3</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>PP</td>
<td>0.11</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>PS</td>
<td>0.14</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>PSU</td>
<td>0.22</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>PTFE</td>
<td>0.27</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>PVC</td>
<td>0.19</td>
</tr>
<tr>
<td>Epoxy</td>
<td>-</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Table 13. Thermal conductivity of polymers [1]

<table>
<thead>
<tr>
<th>Filler</th>
<th>Thermal conductivity [W/mK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>204</td>
</tr>
<tr>
<td>Aluminum nitride</td>
<td>200</td>
</tr>
<tr>
<td>Aluminum oxide</td>
<td>20-29</td>
</tr>
<tr>
<td>Beryllium oxide</td>
<td>260</td>
</tr>
<tr>
<td>Boron nitride</td>
<td>250-300 (in plane)</td>
</tr>
<tr>
<td>Carbon black</td>
<td>174</td>
</tr>
<tr>
<td>Carbon fiber (PAN based)</td>
<td>70 (along the main axis)</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>2000-6000 (along the main axis)</td>
</tr>
<tr>
<td>Copper</td>
<td>483</td>
</tr>
<tr>
<td>Glass fiber</td>
<td>1.5</td>
</tr>
<tr>
<td>Graphite</td>
<td>100-400 (in plane)</td>
</tr>
<tr>
<td>Nickel</td>
<td>158</td>
</tr>
<tr>
<td>Talc</td>
<td>10.7 (in plane)</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Table 14. Thermal conductivity of typical fillers [1, 99, 146]
Figure 89. Crystallization peaks of the PP/BN compounds

Figure 90. Crystal melting peaks of the PP/BN compounds
Figure 91. Isotherm crystallization of polypropylene/boron nitride composites at different crystallization temperature
(a, unfilled PP; b, PP+10 vol% BN; c, PP+20 vol% BN; d, PP+30 vol% BN)
Figure 92. Relative crystallinity of polypropylene/boron nitride composites as a function of time at different temperatures
(a, unfilled PP; b, PP+10 vol% BN; c, PP+20 vol% BN; d, PP+30 vol% BN)
Development of injection moldable, thermally conductive polymer composites

Figure 93. Avrami plots of $\log[-\ln(1-X(t))]$ versus $\log t$ for isothermal crystallization of the polypropylene/boron nitride composites at different crystallization temperatures (a, unfilled PP; b, PP+10 vol% BN; c, PP+20 vol% BN; d, PP+30 vol% BN)