Final report on the 2013-2016 Hungarian Scientific Research Fund project named "Development of graphene/ceramic hybrid filled heat conductive polymers"

(OTKA – 105995)

Literature research

In the research period of 2013-2016 our first task was to review the literature of thermally conductive polymers and conductive fillers. It was found, that 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.

Four different thermoplastic matrix materials were involved in the research: Tipplen H145F polypropylene homopolymer (TVK Nyrt., Hungary), Tipplen K693 polypropylene copolymer (TVK Nyrt., Hungary), Schulamid 6 MV 13 polyamide (A. Schulman Hungary Kft., Hungary) and PLA AI-1001 polylactic acid (Shenzhen eSUN Industrial Co., Ltd, China). As model material Tipplen H145F polypropylene was selected, based on its flow behavior and its availability. The selected filler types for thermal conductivity enhancement were as follows: boron-nitride, talc, aluminum oxide, titanium dioxide, grapheme, graphite and multi-wall carbon nanotube. According to the literature research, from the ceramic fillers the boron nitride is the most promising filler for conductive polymers based on its properties.

Thermal conductivity measurement system development

The key issue of the project is the thermal conductivity measurement of the prepared samples. Hence two different thermal conductivity measurement apparatus were developed and built.

First a single-specimen hot plate apparatus was developed to analyze the thermal conductivity of the injection molded specimens. 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. A further thermal conductivity meter was designed and built, based on the Comparative Linear Heat Flow method. 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. This measuring system was used to determine the thermal conductivity of the compression molded samples and the thermal conductivity of the powder samples.

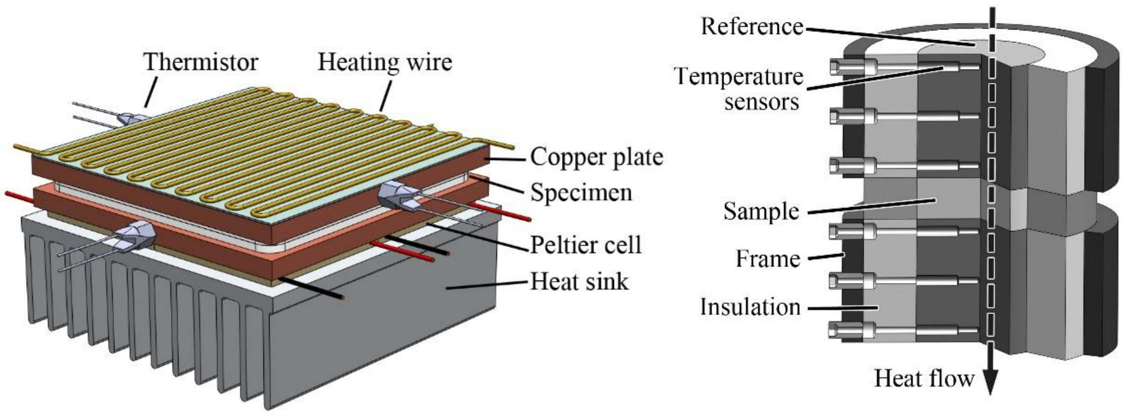


Figure 1. Main components of the hot plate apparatus and the Longitudinal Heat Flow unit

Preliminary tests

First of all, the effects of the components (matrix and fillers) were examined. It was stated that by changing the matrix materials the results can be modified only with about 5%. Next the effect of the filler concentration and filler type was analyzed. 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 negligible interaction between them. There are significant differences between the thermal conductivities of the compounds at high filler loading. It was shown, that the boron nitride increased most significantly the thermal conductivity from 0.25 to 1.2 W/mK.

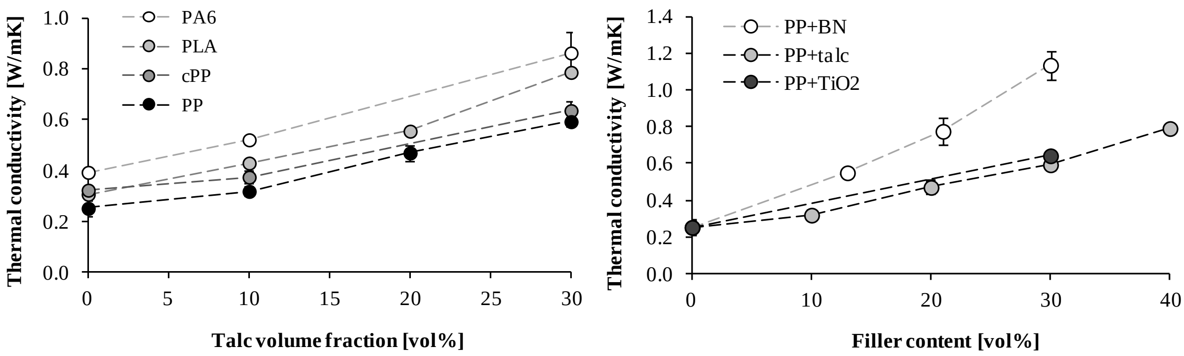


Figure 2. The thermal conductivity of different matrices as a function of filler content (a) and thermal conductivity of PP homopolymer as a function of filler type and concentration (b)

The mechanical properties of the composites were also investigated. The changes in mechanical properties – such as tensile and Charpy impact testing – were caused by different filler types and concentrates. In contrast to the unfilled polypropylene, the particle filled compounds have significant smaller tensile strength. Increasing the filler content, the tensile strength decreases significantly. The tensile modulus shows reverse tendency. As the typical loads of the polymer parts have dynamic characteristic, charpy tests were performed. The unfilled H145 F polypropylene has 72 kJ/m^2 impact strengths. Adding talc to the matrix, a significant drop can be observed, as the impact strength lowered to the one third of the unfilled polypropylene. Increasing filler content, the impact strength shows decreasing tendency. To characterize the processability and compare the flow behavior of the composite materials, their melt volume rate was determined by capillary rheometer. The melt volume flow rate (MVR) value of the unfilled polypropylene is 43 cm^3/10 min. The most significant drop can be observed by using boron-nitride. In this case the melt flow rate was 2.5 cm^3/10 min.

Effect of the processing method

When the effect of the processing methods were compared, compression molding, injection molding and injection-compression molding (ICM) technologies were applied. The ICM technology is the combination of injection molding and compression molding. 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. Thanks to this technology, the filler orientation is favorable for the through-plane thermal conductivity, compared to the conventional injection molding.

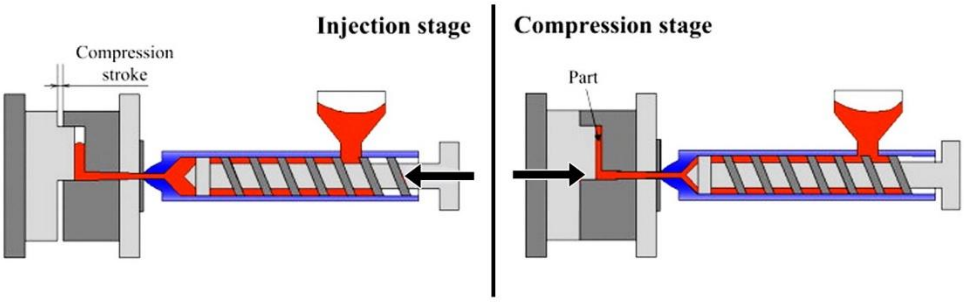


Figure 3. Scheme of injection-compression molding

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. 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. It was observed, that the injection molded samples have very thin core layer and the injection-compression molded ones have thicker core.

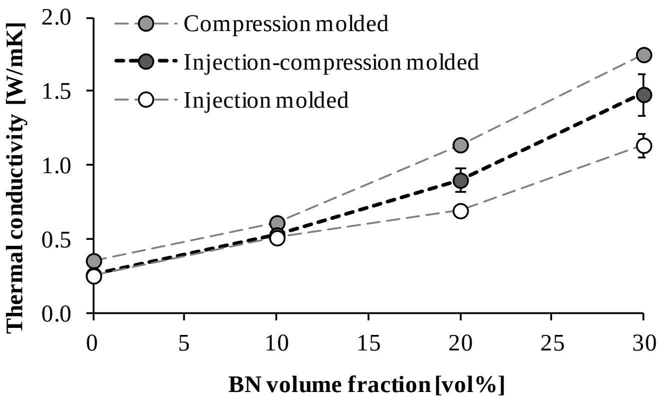
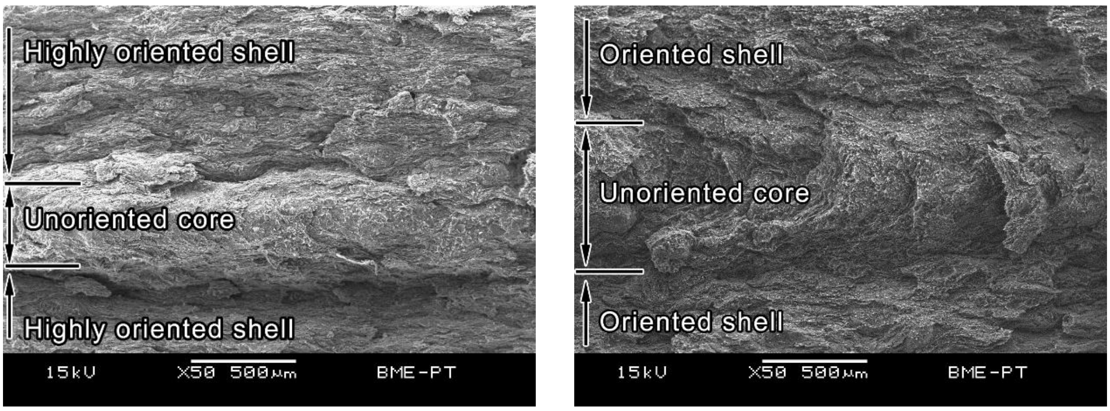


Figure 4. Thermal conductivity of injection-compression molded PP/BN composites



a) b)

Figure 5. SEM micrographs of injection molded (a) and injection-compression molded (b) 30 vol% BN filled PP samples

Design of Experiments (DoE) for hybrid filler system

To analyze the effects of the different fillers on thermal conductivity (TC) of conductive composites and discover their cross effects, the experiment was designed with a data analysis and experimental design software. *Polypropylene homopolymer* (PP) was selected as matrix material and *boron nitride* (BN), *alumina oxide* (Al_2O_3) and *graphene* as filler. 14 different compounds for thermal conductivity measurements were prepared with internal mixer and the samples with compression molding. In the composites the amount of the boron nitride and alumina oxide varied between 0 and 30 vol%, and the amount of the graphene varied between 0 and 5 vol%. After the TC measurement, the single and cross effects were evaluated with the software. First of all the effect of the single fillers were analyzed. It was pointed out that the graphene and the boron nitride have a great effect on the thermal conductivity, while alumina oxide has only minor effect. The thermal conductivity of 30 vol% alumina oxide and boron nitride filled composites is 1.86 W/mK and 1.79 W/mK respectively and its value for 5 vol% graphene filled composite is 1.4 W/mK. By analyzing the cross effect of fillers, the evaluation of the design of experiments shows, that synergetic effect can exist between boron nitride and graphene. Adding 27.5 vol% BN and 2.5 vol% graphene to the polypropylene, the TC was 2.01 W/mK. At the composition of 70 vol% PP 25 vol% BN and 5 vol% graphene the TC was 2.2 W/mK.

Ceramic – ceramic hybrid composite

To show the hybrid effect between boron nitride and talc, further measurements were performed. It was demonstrated, that in the case of specimens containing a single filler (specimen with BN + specimen with talc), 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 rate. If talc and boron nitride are hybridized in one specimen, 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.

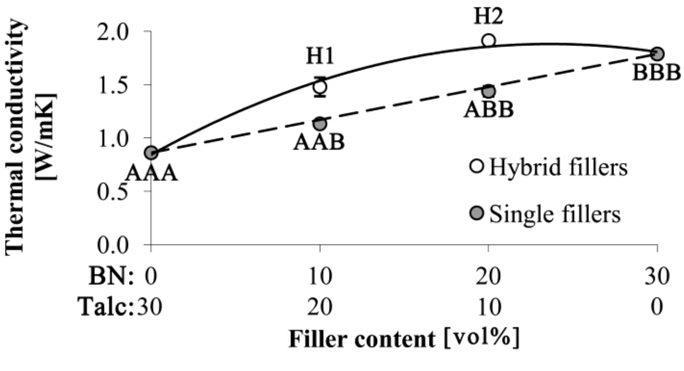


Figure 6. Comparison of the effect of single and hybrid BN/Talc fillers on thermal conductivity of compression molded samples

Next, the thermal conductivity of the injection molded and the compression molded samples were compared to each other. 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. It was 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

Graphene – ceramic hybrid composite

Graphene/ceramic thermally conductive compounds were also prepared. According to the preliminary tests, from the ceramic fillers the boron nitride was selected. Both, single and hybrid filled polypropylene samples were also prepared. Graphene concentration was varied between 0 and 5 vol%, and BN between 0 and 30 vol% in the single filled samples. In hybrid system, constant 20 vol% BN was applied and the grapheme concentration varied between 0 and 5 vol%.

From the thermal conductivity measurements it was shown, that graphene caused only a little improvement, about 60% in thermal conductivity. At 5 vol% graphene content the thermal conductivity of the composite was only about 0.4 W/mK. But the composites with 30 vol% boron-nitride increased it with 300% (~1.1 W/mK). At the case of hybrid composites (when the filler concentration was maximum 25 vol%) the thermal conductivity increased with 380% (~1.2 W/mK) compared to the thermal conductivity of neat PP.

The electrical conductivity of the hybrid composites were also investigated. It was pointed out, that the hybrid system is electrically insulating. It means that the BN particles distributed homogenously the graphene particles in the samples, hence the electrically conductive network could not be formed.

The results of the mechanical tests showed that at small filler concentrations the modulus and strength increased a bit but above 20 vol% both of them decreased. It probably happened because of the poor mixing efficiency. It was confirmed by scanning electron microscopy as the records showed additive agglomerates and the lack of adhesion. With better mixing of components and surface treatment of additives the properties of composites can be improved.

Segregation and distribution of the 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, 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.

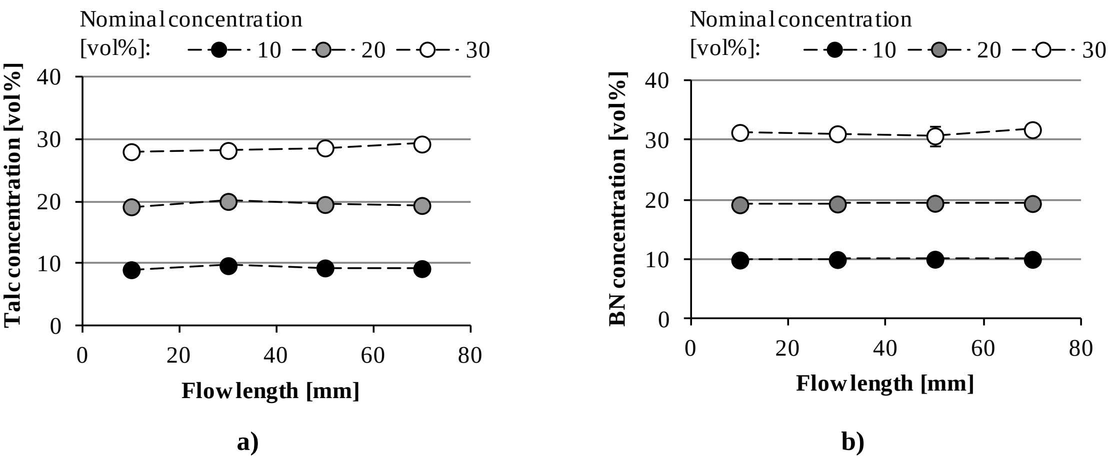


Figure 7. Talc (a) and boron nitride (b) concentration along the flow path in the polypropylene matrix

Different mixing elements (static and dynamic mixers) were also tested to show their efficiency concerning homogenous mixing and thermal conductivity enhancement during 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. It can be stated that changing the number of static mixing elements causes 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.

Mathematical model for thermal conductivity prediction

In this project a new semi-empirical model was proposed to predict the thermal conductivity of two-phase composite materials:

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

where λ_c is the thermal conductivity of the composite, λ'_m and λ'_f are the effective thermal conductivities of the matrix and the filler, φ and φ_{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.

A new methodology was also developed to determine the thermal conductivity of fillers and the theoretical maximum filler content, which were used as the input parameters of the model. In the first step the maximum filler content was determined with a modified linear heat flow thermal conductivity meter (presented previously). The particles were compressed between two steel cylinders, and the relative density of the sample was calculated from the displacement of the cylinders. The relative density was plotted as a function of the compacting pressure and a sigmoid-based saturation curve was fitted to the measurement points to determine the maximum filler content. According to the measurement values and the calculations, the theoretical maximum filler contents for talc, boron-nitride and graphite powder are 89.9%, 85.2% and 96.2% respectively. During compaction thermal conductivity was also shown as a function of compaction pressure. The calculated effective thermal conductivities of talc, boron-nitride and graphite powder are 2.24 W/mK, 8.83 W/mK and 20.67 W/mK respectively.

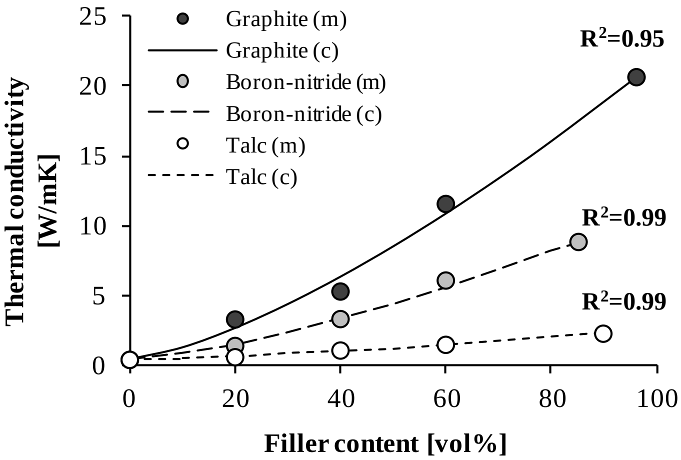


Figure 8. Thermal conductivities of the compounds
(m=measured values, c=calculated values with the proposed model)

To validate the model, composites were prepared by melt mixing and compression molding. The model was validated up to 60 vol% filler fraction. The thermal conductivities obtained from the proposed model were found to be in good agreement with the experimental results up to the investigated filler fraction. The constant in the model, which describes the conductive chain formation capability and shape of the fillers is 1.4 in all investigated cases. The new model was compared to various theoretical models, such as Maxwell, Bruggeman, Cheng and Vachon and the geometric mean model. It was found that in most cases these theoretical models under- or overestimate the results. 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.

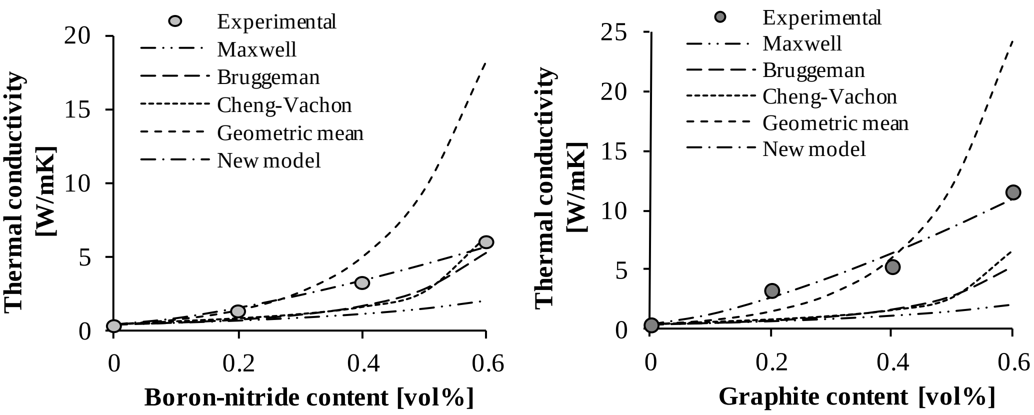


Figure 9. Comparison of the new model to other theoretical models in the case of boron nitride or graphite-filled polypropylene

Utilization of the results

In this project 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. Further hybrid effect was showed between graphene and boron nitride, which composite has superior thermal conductivity.

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 hence an economic processing of polymers can be achieved.