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Thermally Conductive Polymer Compounds for Injection Moulding: Synergetic Effect of Hexagonal Boron Nitride and Talc

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Abstract

The aim of the research was to investigate and maximize the thermal conductivity of the polymer compounds with low filler content (<30 vol%). The study focused on the effect of the matrix material, the filler type, the processing method and the interaction of the fillers. It was concluded, that the compression moulded samples have higher thermal conductivity than the injection moulded ones due to the segregation effect and the orientation of the anisotropic fillers. Furthermore thermal conductivity can be improved by adding fillers with higher thermal conductivity or by combining – so called hybridizing – the fillers. The synergetic behaviour between hexagonal boron nitride and talc was proved.

Keywords:

hybrid filler, thermal conductivity, synergetic effect, thermally conductive polymer, injection moulding

1. INTRODUCTION

The polymers are popular engineering materials because of their superior properties comparing to the metals, such as low density, low cost, chemical resistance, low thermal conductivity and easy processability. The typical thermal conductivity values of polymers are between 0.1 and 0.5 W/mK. In contrast to the insulating properties of polymers, thermally conductive polymer composites get more and more attention in the industry. In electronics the tendency is producing smaller devices, therefore the amount of heat they generate is more and more. It leads the researchers to develop new polymer composite materials which can dissipate the heat form the parts [1-4].

Traditionally the thermal conduction of insulating polymers is enhanced adding highly conductive fillers such as carbon based-, metallic- or ceramic particles. The thermal conductivity coefficient of these polymer composites is determined by several factors. These factors are the filler concentration, the thermal conductivity of the fillers, their particle size and shape, the manufacturing process and the filler matrix interactions. These parameters are also important for modelling and predicting the thermal conductivity of the compounds [2, 5, 6]. To obtain composite materials with appropriate thermal conduction, high filler content is required, although it is resulting in difficult processability. Although the worsen flow properties, the increased thermal conductivity has a significant effect on the cooling of the part thus the cycle time can be decreased while it might have a negative effect on the shrinkage and warpage properties [1-7].

However, when the intrinsic thermal conductivity of the filler is 100 times higher than that of the polymer matrix, there is no remarkable improvement in the thermal conductivities of polymer composites. Measured thermal conductivity values are much lower than those ones estimated by rule of mixture approach. The main factor which limits the property improvement of polymer composites is the poor dispersion and the so called segregation effect [8-10]. The dispersion is a critical issue mainly for the application of polymer composites with nanofillers [11]. On the other hand, the large nanofiller volume fraction may cause problems, such as the agglomeration, the increase of composite melt viscosity and the degradation of mechanical properties. Yang at al. concluded that hybrid filler system with conductive networks is significant for the fabrication of the next generation heat dissipation materials [12, 13].

The thermally conductive polymers are widely investigated by many researchers, but few of them carried out researches about the effect of hybrid fillers. Teng et al. [14] investigated the hybrid effect of multi-walled carbon nanotubes and boron nitride flakes on thermal conductivity of epoxy composite. They found that the hybrid fillers provide significant enhancement of thermal conductivity. 30 vol% boron nitride and 1 vol% functionalized multi-walled carbon nanotubes resulted in 740% increase in thermal conductivity of epoxy resin (1.9 W/mK). Yang and Gu [13] enhanced the thermal conductivity of epoxy resin with functionalized multi-walled carbon nanotube and silane-modified nano-sized silicon carbide as hybrid fillers. It was established that hybrid filler system could provide synergistic effect and also cost reduction, thus the thermal conductivity of epoxy nanocomposites with hybrid filler system is larger than that of epoxy nanocomposites with any single filler system. Yang et al. [12] proved the synergetic effect between the multi-graphene platelets and multiwalled carbon nanotubes in the mechanical properties and thermal conductivity of epoxy composites. The composite material containing 0.9 wt% graphene platelets and 0.1 wt% MWCNT showed 47% grow in thermal conductivity, 14.5% in tensile strength and 22.6% in tensile modulus.

In our work the aim was to analyzing the effect of different parameters on the thermal conduction of conductive composites with low filler content. The maximum filler content was 30 vol% that it can be processed with injection moulding. Three different matrix materials and two different fillers (hexagonal boron nitride and talc) were investigated. Samples were prepared with compression moulding and injection moulding to prove the shear induced orientation and segregation effect caused differences in thermal conductivity. Boron nitride and talc were used as hybrid filler in different mixing ratio. In this research positive hybrid effect was detected and proved between the applied fillers.

2. EXPERIMENTAL

2.1. Materials

In this work the thermoplastic matrix materials were H145 F polypropylene homopolymer (Tiszai Vegyi Kombinát Nyrt., Hungary) (density is 0.9 g/cm^3), K693 polypropylene block copolymer (Tiszai Vegyi Kombinát Nyrt., Hungary) (density is 0.92 g/cm^3) and Schulamid 6 MV 13 polyamide 6 (A. Schulman Hungary Kft., Hungary) (density is 1.13 g/cm^3). The fillers were hexagonal boron nitride grade A 01 powder (BN) (H.C.Starck GmbH, Germany) and talc ($Mg_3Si_4O_{10}(OH)_2$) (Novia Kft., Hungary). The average thermal conductivity of BN is about 60 W/mK, its density is 2.2 g/cm^3 and its maximum particle size is about 5 μm. The average thermal conductivity coefficient of talc is about 10 W/mK, its density is 2.7 g/cm^3 and its average particle size is about 25 µm. Furthermore the surface of fillers was no modified.

2.2. Sample preparation

The proper amount of matrix material and filler was calculated with Equation (1) and Equation (2).

$$m_f = \frac{m_c}{\frac{\varphi_m \cdot \rho_m}{\varphi_f \cdot \rho_f} + 1} \qquad (1)$$

$$m_m = m_c - m_f \qquad (2)$$

where m_c, m_f and m_m [g] are the weight of the composite, the filler and the matrix material, φ_f and φ_m [vol%] are the volume fraction of the filler and matrix material, and finally ρ_f and ρ_m [g/cm^3] are the density of the filler and matrix material. The materials containing 0-30 vol% fillers were compounded with LabTech Scientific extruder and granulated with LabTech pelletizer. Then 80x80x2 mm sized samples were injection moulded with Arburg Allruonder 370S 700-290 injection moulding machine. The main injection moulding parameters are listened in Table 1.

Table 1. Injection moulding parameters

Parameter	Unit	Value
Volume	[cm^3]	49
Injection rate	[cm^3/s]	50
Holding	[bar]	80% of the injection pressure
Clamping force	[tonne]	70
Cooling time	[s]	10
Zone temperatures	[°C]	200; 185; 180; 175; 165
Mould temperature	[°C]	50

2.2. Thermal conductivity measurement

In physics, thermal conductivity (λ) is a material property that indicates its ability to transfer heat from one to another location. In this research the thermal conductivity was measured using the transient hot plate method. The point of the process is to reach a steady state condition, thus simplifying the measurement to a one-dimensional case to use the Fourier’s law (Equation (3)) [15, 16].

$$q(x,t) = -\lambda \cdot \nabla T(x,t) \qquad (3)$$

where q [W] is the transmitted heat flux, λ [W/(mK)] is the thermal conductivity and T [K] is the temperature.

In this research a one-specimen hot-plate apparatus (Figure 1.) was developed for measuring the thermal conductivity of the samples. In contrast to the conventional two-specimen apparatus, the heat flow is oriented in a single direction between the hot and cold plate through the specimen. Furthermore a cold plate, a hot plate and a specimen can be suppressed, thus simplifying the apparatus. According to the Fourier's law (Equation (3)) the thermal conductivity can be determined with Equation (4) in the case of one-specimen hot-plate method [17].

$$\lambda = \frac{P}{S} \cdot \frac{L}{T_2 - T_1} \qquad (4)$$

where P [W] is the electrical power, S [m^2] is the cross section area and L [m] is the thickness of the specimen T_1 [K] is the temperature of the cooled side and T_2 [K] is the temperature of the heated side of the sample.

Figure 1. shows the main components of the measurement system. The main task is to maintain the temperature difference between the cold and hot plate. The base of the cold and hot side were 1-1 85x85x5 mm sized copper plate, which distribute the heat on the surface. Their thermal conductivity is ~380 W/mK, which are two orders of magnitude higher than the samples, thus their heat resistance does not generate remarkable errors. The cold plate of the apparatus was cooled by four 40x40 mm sized Peltier cells, which allow keeping the temperature of the plate more precisely. The upper plate was heated by heating wire, where the generated heat is equal to the electrical power flowing through the wire (dispensing with the losses). To guarantee the temperature uniformity on the hot plate, the wire was fixed onto it in meander shape. The heat resistance between the components was minimized with thermally conductive tapes (3M 8805). The temperature was measured by 2-2 built-in NTC thermistors (Epcos B57045K) inside the heated and the cooled plate. The resistance-temperature calibration for the NTC thermistors was performed with the Steinhart-Hart equation (Equation (5)) [18].

$$\frac{1}{T} = A + B\ln(R) + C(\ln(R))^3 \qquad (5)$$

where R [Ω] is the resistance of the thermistors at given temperatures T [K], A, B and C are the Steinhart-Hart constants. According the calibration the values of Steinhart-Hart constants are listed in Table 2. Minimizing the heat loss, the apparatus was thermally insulated with polystyrene foam, which thermal conductivity is ~ 0.04 W/mK. To decrease the thermal resistance between the samples and the hot-plate apparatus, ceramic powder filled thermal interface silicone grease (T Silox Kft., Hungary) was applied. Finally the accuracy of the apparatus was calibrated with known samples.

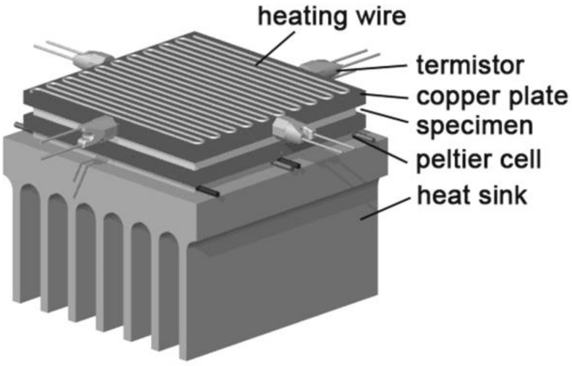

Figure 1. Heat conduction measurement system

Table 2. Steinhart-Hart constants of Epcos B57045K thermistors

Thermistor no.	A	B	C
1st	$2.569\cdot 10^{-3}$	$7.035\cdot 10^{-5}$	$1.838\cdot 10^{-6}$
2nd	$2.378\cdot 10^{-3}$	$6.785\cdot 10^{-6}$	$1.180\cdot 10^{-6}$
3rd	$1.847\cdot 10^{-3}$	$8.564\cdot 10^{-5}$	$9.509\cdot 10^{-7}$
4th	$1.693\cdot 10^{-3}$	$1.239\cdot 10^{-4}$	$6.663\cdot 10^{-7}$

3. RESULTS AND DISCUSSION

Lots of parameters have a significant influence on the thermal conductivity coefficient of the polymer compounds, such as the filler type, the filler volume fraction, the thermal conductivity of the filler and the polymer material, and many others as well. These parameters should be further investigated to know their exact effects on the thermal conductivity.

3.1. Effect of the matrix material on thermal conduction

In this paper firstly the effect of the matrix material on thermal conductivity was investigated. Two different polypropylenes and a polyamide 6 were filled with the same type of talc. As Figure 2. shows, the thermal conductivities of polypropylenes are 0.25 W/mK and 0.32 W/mK, while the thermal conductivity of polyamide is 0.39 W/mK. These differences between the coefficients remain near the same as a function of talc content. Accordingly, compounding the different matrices with 30 vol% talc, the thermal conductivities are 0.59 W/mK using H145 F PP, 0.64 W/mK using K693 PP and 0.86 W/mK using polyamide 6 matrix.

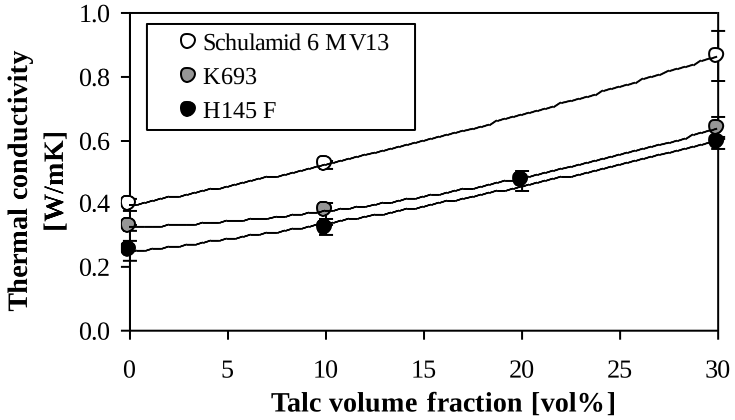

Figure 2. Thermal conductivity of different matrix materials as a function of talc content

3.2. Effect of fillers on thermal conductivity

Secondly the effect of the filler type and the filler content was investigated on the thermal conductivity of polymer matrix. The matrix material was H145 F polypropylene and it was compounded with talc and boron-nitride. The filler content varied between 0 and 30 vol%. Figure 3. shows the effect of the different fillers on the thermal conductivity of compounds. As expected, with the increasing filler content, the thermal conductivity increases. The pure polypropylene has 0.25 W/mK thermal conductivity. The thermal conductivity of the compounds rises slowly at low filler volume fractions because the ceramic particles dispersed smoothly in the polypropylene matrix and has weak interaction between each other. 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 and filled with talc and titanium-dioxide rises slowly. Adding 30 vol% filler, the thermal conductivity coefficient of the compound is 0.6 W/mK with talc and almost doubled, 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 pure PP.

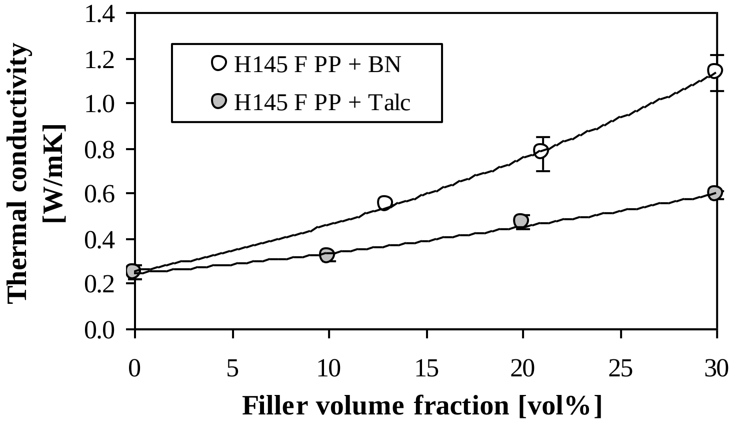

Figure 3. Thermal conductivity of H145 F PP as a function of boron nitride and talc content

3.3. Effect of the moulding process on thermal conduction

Comparing the thermal conductivity of injection moulded and compression moulded samples, a higher thermal conductivity can be observed in the case of compression moulded samples (Figure 4.). There is also a difference in the thermal conduction of the unfilled polypropylene. While the injection moulded part has 0.25 W/mK conductivity coefficient, the compression moulded sample has 0.36 W/mK. It can be explained by the difference in crystallinity and in molecular chain orientation. Adding fillers to the matrix, the difference is increasing as a function of the filler content. In this case the shell-core effect has a significant influence on the thermal conductivity, thus on the surface of the injection moulded samples has an insulating polymer layer. This effect is caused by the segregation effect during the polymer fills the cavity. On the other hand this difference can be caused by the orientation of the fillers, as the thermal conductivity of the particles has anisotropic nature. The plate like and fibrous particles show different thermal properties in different directions. In compression moulded samples the filler particles have random directions, while in the injection moulded samples the orientation is induced by the melt flow. In this way the injection moulded parts has lower thermal conductivity coefficient.

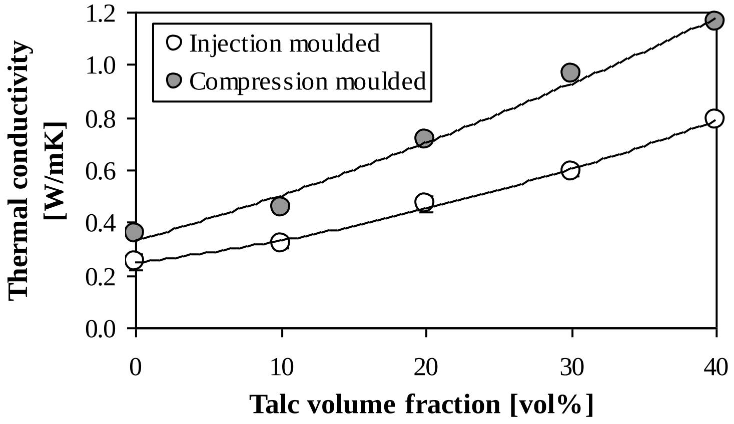

Figure 4. Effect of the moulding process on thermal conductivity of polypropylene/talc composite material as a function of filler content

3.4. Synergetic effect of talc and hexagonal boron-nitride

Proving hybrid effect between boron-nitride and talc, further measurements were performed. In this case the thermal conductivity was measured on three compression moulded specimens. Table 3. contains the notation of the compounds and specimens. The specimens were joined together with thermal interface material to decrease the thermal resistance between them (Figure 5.). First the thermal conductivity of hybrid materials were determined (H1 and H2), using 3-3 specimens joined together in each measurement. Secondly the thermal conductivity of material with single filler was determined (A and B compounds). Thirdly the conductivity of the assembled specimens (Figure 5.) was determined. In one case AAB and in another case ABB single filled specimen composition was tested. Thus the total filler content was 30 vol% in each case and the boron-nitride and talc content was the same as the hybrid material has, but only single filled specimens were used to measure the thermal conductivity.

Table 3. Notation of the compounds

Sign	Compound
A	H145 F PP + 30 vol% talc
B	H145 F PP + 30 vol% BN
H1	H145 F PP + 20 vol% talc + 10 vol% BN (hybrid)
H2	H145 F PP + 10 vol% talc + 20 vol% BN (hybrid)

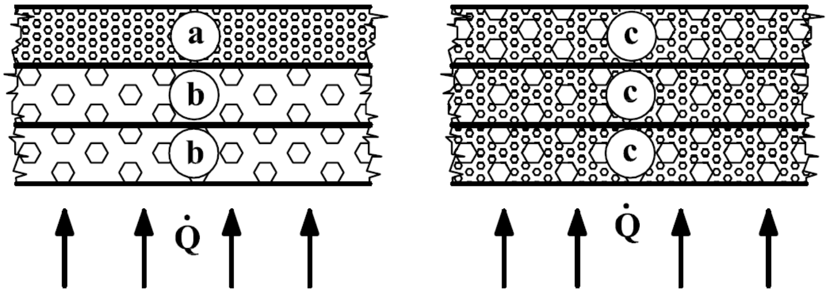

Figure 5. Assemblies for thermal conductivity measurements (a and b - compounds with single fillers (AAB or ABB composition); c - compounds with hybrid fillers (H1 or H2))

As Figure 6. shows using single filled specimens, a linear relationship can be proved between the thermal conductivity of boron-nitride and talc. Thus the thermal conductivity can be easily calculated as a function of the filler content. If hybridizing the talc and boron nitride higher thermal conductivity can be achieved and the relationship between the fillers becomes nonlinear. As it was mentioned, this positive synergetic effect can be explained with the different particle size of BN and talc. In the mixture talc particles formed the main thermally conductive path in the compound, while the smaller BN particles established more contact between the bigger particles to obtain higher thermal conductivity.

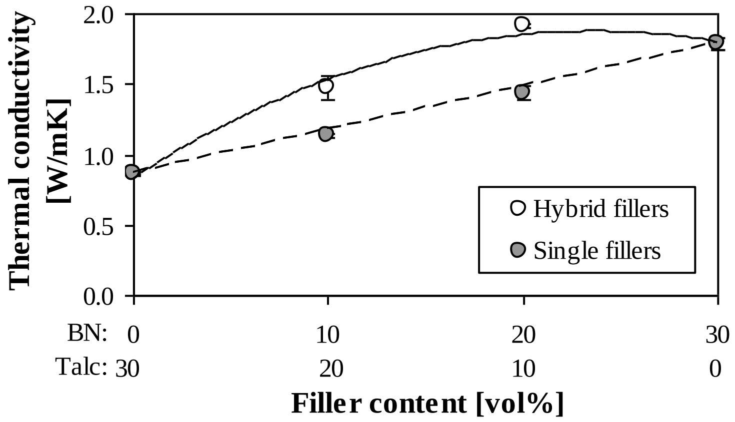

Figure 6. Comparison of the effect of single and hybrid BN/talc fillers on compression moulded samples (notation in Table 3.)

Next the thermal conductivity of the injection moulded and the compression moulded samples were compared to each other, showing the effect of the sample preparation methods on the hybrid filled composite materials. The same compound has been used for both sample prepetition method, thus the filler content was the same. Before compression moulding the samples, the granules were milled to avoid the air traps during the process. The result of the measurement can be seen on Figure 7. At each measured point the thermal conductivity of the compression moulded samples was about 60% higher than the injection moulded ones. It proves that the skin-core effect has a great influence on thermal conductivity. The skin layer has lower filler content, thus it behaves as an isolating layer that decreases the heat transfer.

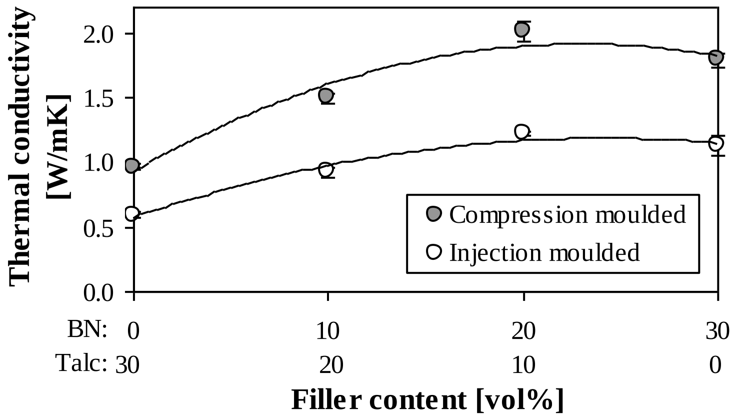

Figure 7. Comparison of the effect of moulding process on BN/talc hybrid filled H145 F PP

4. CONCLUSION

In this paper a comprehensive research was presented about thermally conductive composites containing ceramic fillers. Five different factors were considered: the type of polymer matrix, the type of filler and its volume fraction, the moulding method and finally the interaction of the fillers. We have concluded that changing the matrix material there is no significant increase in the conductivity, because the polymers have low thermal conductivity with ignorable difference between them. As there are major differences between the thermal conductivity of fillers, they have remarkable effect on thermal conductivity. Increasing the filler content, the deviation in the values is increasing as well. Compounding H145 F PP with 30 vol% talc the thermal conductivity coefficient of the composite is 0.6 W/mK and with 30 vol% BN is 1.14 W/mK. The difference is 0.55 W/mK, but lowering the filler content the difference is decreasing, as at 20 vol% filler content it drops to 0.3 W/mK.

The hybrid effect was also studied between talc and boron nitride. Using same amount of total fillers it was proved that the BN and talc filled hybrid composite has almost

10% higher thermal conductivity than that of the composite which contains even BN or talc. At certain filler content varying the ratio of the fillers, the thermal conductivity coefficient shows nonlinear behaviour. Finally it was concluded, that the moulding process influences the thermal conduction. Compression moulded samples always show higher conductivity than injection moulded ones because of the shell-core structure of it. The difference between the shell and the core layer can be explained with the shear induced difference between the orientations of the anisotropic filler particles that can result in an insulating layer on the surface.

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