DEVELOPMENT OF THERMAL CONDUCTIVE HYBRID COMPOSITES

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Abstract

In this work the synergetic effect of boron nitride and talc was investigated on polypropylene based thermally conductive composites. First the effect of single fillers was investigated than the hybrid effect at 30 V% filler content. Talc and boron nitride were compounded with polypropylene up to 40 V% with a twin screw extruder. The samples for thermal measurements were prepared with injection molding. The results show that using 30 V% boron nitride the thermal conductivity of polypropylene was multiplied more than by four, and using 30 V% talc it was multiplied only by two. It was proved that combining talc and boron nitride higher thermal conductivity can be achieved than filling single fillers into the matrix, using the same amount of filler.

1 Introduction

In these days the subject of the researchers is to develop smaller and smaller devices with higher performance. Thanks to this advance the heat dissipation is a critical issue mainly for the electronic devices. The heat dissipation has a great influence on the lifespan of electronic devices. It is well known that the reliability of the devices is exponentially depend on its operating temperature, so a small difference in operating temperatures can halve the lifespan of the devices. Heat produced during the operation of the device is particularly dissipated by thermal conduction. Traditionally this heat is removed from the part by heat sinks [1-6].

Nowadays the polymer based composite materials which have relative high thermal conductivity attract more and more attentions. Thanks to the advantages of polymers (light weight, corrosion resistance, easy processibility) thermally conductive polymer composites offer new possibilities for replacing metal parts in several applications, such as in microelectronics, power electronics, generators, electric motors and many others. It is well known that virgin polymer materials are good thermal insulators as their thermal conductivity varies between 0.1...0.5 W/(m·K). Adding thermally conductive fillers to plastics, for example graphite, carbon black, carbon fibers, ceramic or metal particles; the thermal conductivity of compounds can be increased significantly. Furthermore it should be mention that the thermal properties of these composite materials depend on several factors, first of all on the filler concentration, the ratio between the properties of the components, the sizes and the shapes of the filler particles, the manufacturing process and the filler matrix interactions [4, 5].

Using two or more different fillers in the same composite material provides higher enhancements in thermal conductivity. It is caused by the synergetic effect between the particles. Li et all [8] investigated the enhancement in the conductivity coefficient with different particle sizes. In the composite material the bigger particles formed the main thermally conductive path and the smaller particles establish further contact between the bigger ones to obtain higher thermal conductivity coefficient. Beside the enhanced thermal conductivity the hybrid fillers system can obtain relatively lower cost [9]. Many researchers investigated the synergetic effect of different fillers. In general carbon based nanoparticles (carbon nanotubes, graphene nanoplates...) are one of the components of the hybrid filler. It was established that adding 1...2 wt% nanofiller to a higher amount of other filler can cause significant increase in thermal conductivity of composite materials [9-12].

In this study talc and boron nitride were used as filler for increasing thermal conductivity of polypropylene. Hexagonal boron nitride is a widely used filler thanks to its high thermal conductivity and electrical insulating behavior. Its only drawback is the high price. Talc has lower thermal conductivity but lower cost as well. It is used in polymer compounds to decrease the material price and increase its crystallinity. These fillers were used to prepare polymer based thermally conductive composite materials. In this research the positive interaction between the talc and boron nitride was reported.

2 Materials and testing methods

2.1 Materials

In the experiments the thermoplastic matrix material was H145 F (Tiszai Vegyi Kombinát Nyrt., Hungary) homo-polypropylene, of which density is 0.9 g/cm^3. As filler hexagonal boron nitride and talc was selected without surface treatment. The thermal conductivity coefficient of hexagonal boron-nitride grade A 01 powder (BN) (H.C.Starck GmbH, Germany) is about 60 W/mK, and maximum particle size is 5 μm. The average particle size of talc (Novia Kft., Hungary) ($Mg_3Si_4O_{10}(OH)_2$) is about 25 μm, and its thermal conductivity coefficient is about 10 W/mK. During the measurement of thermal conductivity, the thermal resistance was minimized between the samples and the apparatus with ceramic powder filled thermal interface silicone grease (T Silox Kft., Hungary).

2.2 Sample preparation and measuring methods

The specific gravity of the powders was determined with picnometer. The matrix material and the fillers were compounded with LabTech scientific twin screw extruder at 220°C and 30 rpm. The diameter of the screws is 26 mm, and the L/D relation is 40. For thermal measurements 80x80x2 mm sized samples were injection molded with Arburg Allruonder 370S 700-290 injection molding machine. Table 1. shows the parameters of the injection process. The morphology of the compounds was investigated with JEOL JSM 6380LA scanning electron microscope. The thermal conductivity of the samples was determined according hot plate method at 55°C with the Fourier's law (Equation 1.):

$$q(x,t) = -\lambda \cdot \nabla T(x,t)\,, \tag{1}$$

where q [W] is the transmitted heat flux, λ [W/mK] is the thermal conductivity and T [K] is the temperature [12]. Increasing the measurement reliability, two injection molded specimens were joined together with thermal interface silicon grease thus the measures samples dimension was 80x80x4mm.

Parameter	Unit	Value
Volume	[cm^3]	49
Injection rate	[cm^3/s]	50
Holding pressure	[bar]	80% of the injection pressure
Clamping force	[kN]	700
Cooling time	[s]	10
Zone temperatures of the injection unit	[°C]	200; 185; 180; 175; 165
Mold temperature	[°C]	50

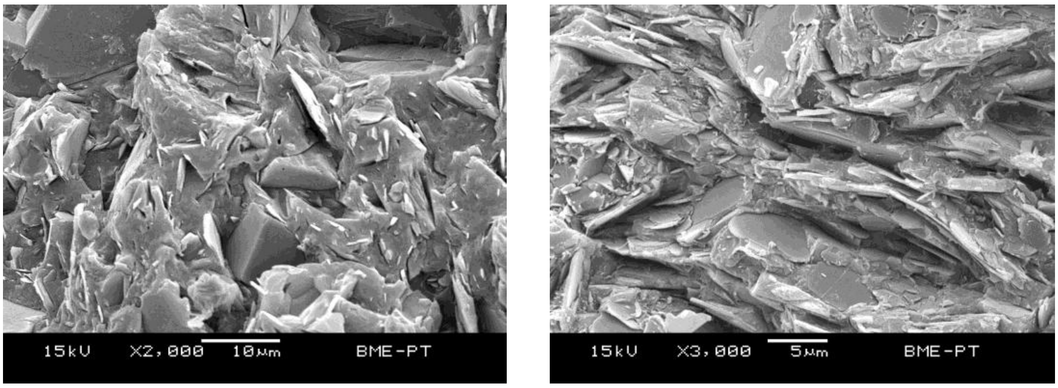
Table 1. Injection molding parameters

3 Results and discussion

3.1 Material characterization

The microstructure of the composite materials was also investigated. Figure 1. shows SEM pictures of the fracture of 30 V% boron nitride and 30 V% talc filled composite. Thanks to the extrusion both of the fillers dispersed uniformly in the matrix material. It can be noticed that the boron nitride and talc particles are well surrounded with polypropylene matrix and the adhesion is high between the components. Furthermore it can be seen that smaller talc particles have plate-like shape with sharp edges and the bigger ones have block shape. On the contrary boron nitride particles have plate-like shape with rounded corners. The advantage of plate-like form is that it has relative high specific surface thus increasing the heat transfer between the filler and matrix.

According the density measurements, the specific density of talc is about 2.7 g/cm^3 and its value of boron nitride is about 2.2 g/cm^3. From these data the proper volume fraction of fillers could be converted into weight fraction.



a, ***b,***

Figure 1. Scanning electron microscopic picture of the talc (a) and boron nitride (b) at 30 V% filler content

3.2 Thermal conductivity of composites with single filler

Figure 2. shows the thermal conductivity coefficients of polypropylene/boron nitride and polypropylene/talc composite materials. According the measurements the matrix material has 0.25 W/mK thermal conductivity coefficients. Increasing the filler content, thermal conductivity increased also. As it was expected, boron nitride has more significant effect on conductivity than talc. At low filler volume fraction the particles can randomly dispersed in the matrix and there is only weak interaction between them. Thus only a minor increase in thermal conductivity can be presented. Increasing the filler content, the particles begin to get

more and more connection and they form more and more conductive path through the matrix material. It means that the change in thermal conductivity is more significant at higher volume fraction of fillers. At 20 V% filler content the BN filled composite has 0.78 W/mK thermal conductivity, while talc filled material has only 0.47 W/mK. Using 30 V% BN, the thermal conductivity of the composite is more than 1.1 W/mK. At 30 V% talc content the conductivity is 0.59 W/mK. It can be seen, that increasing the filler content the difference between the thermal conductivity of composite materials increases further.

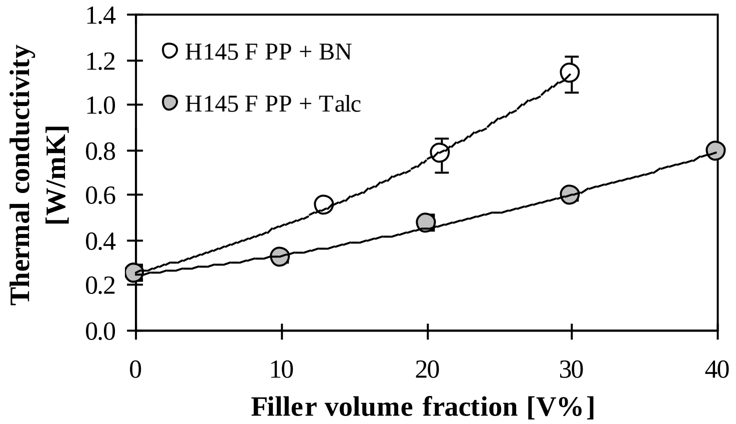


Figure 2. Thermal conductivity of polypropylene/boron nitride and polypropylene/talc composite as a function of filler volume fraction

3.2 Thermal conductivity of hybrid filled composites

The hybrid effect of talc and BN fillers was investigated at 30 V% filler content. The boron-nitride content was 0, 10, 20 and 30 V%, while the talc content was consecutively 30, 20, 10 and 0 V%. Synergetic effect was expected between the fillers, because of their different particle sizes. The compound containing 30 V% talc has 0.59 W/mK thermal conductivity, while with the same amount of BN fillers, the thermal conductivity is 1.14 W/mK. The polypropylene composite material with BN/talc hybrid filler presented higher thermal conductivity coefficient than those with single fillers (Figure 2.). This effect means that the two fillers has a synergetic effect as the thermal conduction is not linear between the BN and talc. The hybrid filled compounds have higher conductivity than their expected value, therefore they show positive hybrid effect. The polypropylene based compound containing 20 V% BN and 10 V% talc has the highest thermal conductivity of 1.22 W/mK, although its expected value from the rule of mixture was only 0.96 W/mK. The synergetic effect can be explained with the different size of the filler particles. The particle size distribution of the talc has higher mean value than BN has. 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 coefficient. Therefore the thermal conductivity can be about five times higher than that of the pure polypropylene, and 20% higher than the expected value of the BN-talc compound.

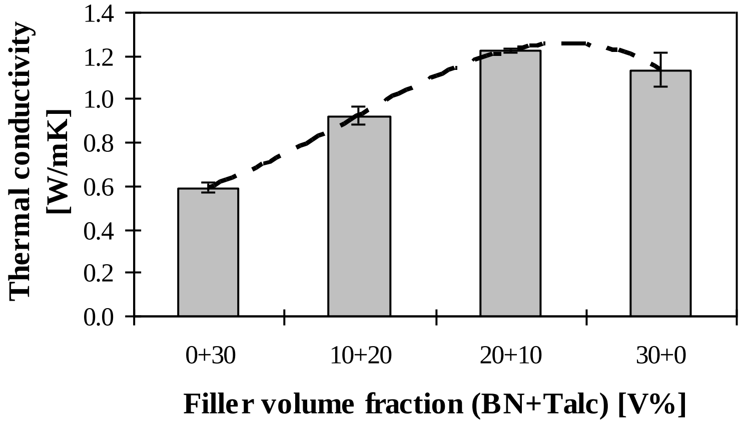


Figure 3. Thermal conductivity of polypropylene hybrid composite as a function of ratio of boron nitride and talc volume fraction

4 Conclusion

In this work the synergetic effect between talc and hexagonal boron-nitride was investigated. The hexagonal boron nitride is a kind of ideal thermal conductive agent while it keeps the electrical insulator behavior of the polymer matrix. As result, the measurements show BN has significant effect on thermal conductivity. Adding 30 V% of it the thermal conductivity of the composite is more than four times higher (1.14 W/mK) than the unfilled polypropylene (0.25 W/mK). Talc is usually used to decrease the price of the composite materials. Filling 30 V% of it into the polypropylene, the thermal conductivity is only doubled. Using talc and boron nitride as hybrid filler, synergetic effect was detected. The compound containing 20 V% BN and 10 V% talc has higher thermal conductivity (1.22 W/mK) than the compound containing 30 V% BN (1.14 W/mK). According this phenomenon, the thermal conductivity of the composite materials can be enhanced and at the same time the price of the compounds can be lowered.

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References

[1] Kalaitzidou K., Fukushima H., Drzal L. T. Multifunctional polypropylene composites produced by incorporation of exfoliated graphite nanoplatelets. *Carbon*, **45**, pp. 1446-1452 (2007).
[2] Boudenne A., Ibos L., Fois M., Majesté J. C., Géhin E. Electrical and thermal behavior of polypropylene filled with copper particles. *Composites: Part A*, **36**, pp. 1545-1554 (2005).
[3] Jones W. E., Chiguma J., Johnson E., Pachamuthu A., Santos D. Electrically and thermally conducting nanocomposites for electronic applications. *Materials,* **3**, pp. 1478-1496 (2010).
[4] Zhou W., Qi S., An Q., Zhao H., Liu N. Thermal conductivity of boron nitride reinforced polyethylene composites. *Materials Research Bulletin*, **42**, pp. 1863-1873 (2007).
[5] Han Z., Fina A. Thermal conductivity of carbonnanotubes and their polymer nanocomposites: A review. *Progress in Polymer Science,* **36**, pp. 914-944 (2011).

[6] Kemaloglu S., Ozkoc G., Aytac A. Properties of thermally conductive micro and nano size boron nitride reinforced silicon rubber composites. *Thermochimica Acta*, **499**, pp. 40-47 (2010).

[7] Yu J. H., Duan J. K., Peng W. Y., Wang L. C., Peng P., Jiangudt P. K. Influence of nano-AlN particles on thermal conductivity, thermal stability and cure behavior of cycloaliphatic epoxy/trimethacrylate system, *eXPRESS Polymer Letters*, **5**, pp. 132-141 (2011).

[8] Li T. L., Hsu S.L.C. Enhanced Thermal Conductivity of Polyimide Films via a Hybrid of Micro- and Nano-Sized Boron Nitride. *The Journal of Physical Chemistry B*, **114**, pp. 6825-6829 (2010).

[9] Yang K., Gu M. Enhanced thermal conductivity of epoxy nanocomposites filled with hybrid filler system of triethylenetetramine-functionalized multi-walled carbon nanotube/silane-modified nano-sized silicon carbide. *Composites: Part A*, **41**, pp. 215-221 (2010).

[10] Yang K., Gu M. Enhanced thermal conductivity of epoxy nanocomposites filled with hybrid filler system of triethylenetetramine-functionalized multi-walled carbon nanotube/silane-modified nano-sized silicon carbide. *Composites: Part A*, **41**, pp 215-221 (2010).

[11] Teng C.-C., Ma C.-C., M., Chiou K.-C., Lee T.-M., Shih Y.-F. Synergetic effect of hybrid boron nitride and multi-walled carbon nanotubes on the thermal conductivity of epoxy composites, *Materials Chemistry and Physics*, **126**, pp. 722-728 (2011)

[12] Yang S.-Y., Lin W.-N., Huang Y.-L., Tien H.-W., Wang J.-Y., Ma C.-C. M., Li S.-M., Wang Y.-S. Synergetic effects of graphene platelets and carbon nanotubes on the mechanical and thermal properties of epoxy composites, *Carbon*, **49**, pp. 793-803 (2011).

[13] Kovacs J.G., Kortelyesi G., Kovacs N.K., Suplicz A. Evaluation of measured and calculated thermal parameters of a photopolymer. *International Communications in Heat and Mass Transfer*, **38**, pp. 863-867 (2011).