

IMPROVED THERMAL PROPERTIES WITH HYBRIDIZATION OF THE FILLERS FOR THERMOPLASTIC MATERIALS

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1 Introduction

Nowadays the polymer based composite materials attract more and more attentions. The aim of the researchers is to replace the metal parts with these modern materials in numerous applications, because the polymers have several advantages (light weight, corrosion resistance and easy processability). Therefore in this field, the major part of the researches dealing with the fiber reinforced polymeric materials, which have similar or higher tensile strength than steel. But not only the mechanical properties, but the thermal properties of metals are better than polymers have. In several cases it is crucial to utilize materials, which have high thermal conductivity and are electrical insulators. Many examples can be found in the electronics [1-6].

It is well known that the polymers are good thermal insulators. Their thermal conductivity is about 0.1...0.5 W/mK. The thermal conductivity of the unfilled polymers is strongly affected by their crystallinity. Thus amorphous polymers belongs to the lower range, such as PMMA (polymethylmethacrylate), PC (poly-carbonate) and PS (polystyrene), and highly crystalline polymers, such as HDPE (high-density poly-ethylene) belong to the upper range [7, 8].

Adding fillers to plastics, for example carbon based, metallic or ceramic fillers, the thermal behavior of polymers can be increased significantly. Furthermore the thermal properties depend on several factors: the filler concentration, the ratio between the properties of the components, the size and the shape of the filler particles, the manufacturing process and the filler matrix interactions [7]. Among the fillers, the carbon based

ones seem to be the best promising, because of their high thermal conductivity, low density and relative low cost. Traditional carbon-based fillers are the carbon black (CB), the graphite and the carbon fiber (CF). Beyond that nowadays the carbon nanotube (CNT) and graphene are in the focus of the researches, which promises by far the best properties. The drawback of these fillers are that the composites will be not only thermally, but electrically conductive [7, 9]. When dielectric behavior is important, ceramic fillers should be used such as boron-nitride (BN), silicon carbide (SiC) or aluminum-oxide (Al_2O_3). The ceramic filled polymer composites are important mainly in electronic application [7, 10]. Metallic particles (for example copper, silver and aluminum powder) increase the thermal conductivity and also the electrical conductivity of the polymer compounds. The disadvantage of the metallic fillers is the high density, thus it limits the applicability when lightweight is required [7, 11].

Thermally conductive polymer composites offer new possibilities for replacing metal parts in several applications: power electronics, electric motors, generators, heat exchangers, microelectronics, and many others, thanks to the polymer advantages such as light weight, corrosion resistance and ease the processability. In some instruments, such as LED lamps or memory chips, the efficient heat dissipation is necessary. The generated heat can raise the temperature of the device and over the critical temperature lifespan decreases significantly or the instrument may be damaged.

To achieve a sufficient level of thermal conductivity coefficient in conductive polymer composites, usually higher than 30 vol% filler is necessary. This

high filler content generate an unavoidable processing challenge, because the viscosity of the compounds increases significantly. Thus the extrusion and injection molding limit the amount of fillers and the maximal achievable thermal conductivity. Moreover, high filler loading dramatically changes the mechanical behaviors and density [12].

According the researches higher efficiency can be reached by using two or more different fillers in the same composite material obtain the synergetic effect between the particles [5-6]. It is an efficient method, to improve the thermal conductivity while using the same amount of filler. Teng et al. [13] investigated the hybrid effect between boron nitride and multi-walled carbon nanotubes in epoxy based composite. They found that hybrid fillers provide 740% increase in thermal conductivity of epoxy resin (1.9 W/mK), using 30 vol% boron nitride and 1 vol% MWCNT. Yang and Gu [14] investigated the effect of hybrid carbon nanotubes and silane-modified silicon carbide fillers on the thermal conductivity enhancement of epoxy nanocomposite. They established that a hybrid filler system could provide a synergetic effect and also reduces costs.

In this work the aim was to analyze the synergetic effect between the talc and boron-nitride as hybrid filler for thermal conductivity enhancement. Further aim was to investigate the applicability of the compounds, thus the change in mechanical properties, the flowing behavior and the crystallinity.

2 Materials and methods

In the experiments the thermoplastic matrix material was H145 F homo-polypropylene (PP) (Tiszai Vegyi Kombinát Nyrt., Hungary). As filler hexagonal boron nitride (BN) (grade A 01; H.C.Starck GmbH, Germany) and talc (Novia Kft., Hungary) was selected. The thermal conductivity coefficients of the fillers are respectively about 60 and 10 W/mK.

In the polypropylene matrix material different amount of boron-nitride and talc was filled, while keeping the total filler content of 30 V%. 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. After that 80x80x2 mm samples produced with injection molding on an Arburg Allrounder 370s 700-290 injection molding

machine. The injection molding parameters can be seen in Table 1.

Parameters	Value
Injection volume	49 cm ³
Injection rate	50 cm ³ /s
Switch-over point	12 cm ³
Holding pressure	80% of injection pressure
Holding time	20 s
Cooling time	10 s
Clamping force	650 kN
Screw rotation speed	15 min ⁻¹
Temperature profile	200-195-190-185-180°C
Mold temperature	50°C

Table 1. Injection molding parameters

To characterize the processability and compare the flow behavior of the composite materials, their melt flow rate was determined on CEAST 7027.000 capillary rheometer. The measurement was performed according to the EN ISO 1133:2005 standard. On the samples mechanical (tensile test) and thermal analysis (thermal conductivity and DSC measurements) were also performed. The mechanical tests were performed on Zwick Z020 tensile test machine using a cross-head speed of 2 mm/min. Charpy impact strength was measured by using a Ceast Resil Impactor Junior impact testing machine equipped with a 2 J hammer. The result was determined with the following equation (Eq. 1.):

$$a_{cU} = \frac{W_B}{b \cdot h} \cdot 10^3 \quad (1)$$

where a_{cU} [kJ/m²] is the Charpy impact strength, h [mm] is the height and b [mm] is the width of the specimen, W_B [J] is the energy at break.

The thermal conductivity measurement was performed according to transient hot plate method on a single specimen apparatus. The lower plate of the apparatus was cooled by four Peltier cells. The upper plate was heated by heating wire. The temperature was measured with 4 thermistors (Fig. 1.). The thermal contact resistance between the plates and the specimen was minimized by using ceramic filled thermally conductive grease. The point of the process is to reach a steady state condition in heat flow, thus simplifying the

measurement to a one-dimensional case to use the Fourier's law (Eq.2) [15].

$$\lambda = \frac{P}{S} \cdot \frac{L}{T_2 - T_1}, \quad (2)$$

where λ [W/mK] is the thermal conductivity of the sample, P [W] is the electrical power, S [m²] is the cross section area and L [m] is the thickness of the specimen, T_1 [K] is the temperature of the cold plate and T_2 [K] is the temperature of the hot plate.

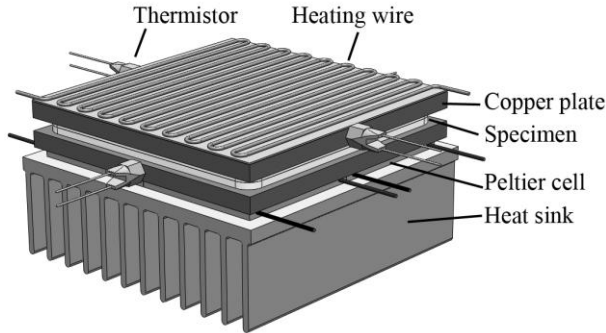


Fig. 1. Hot-Plate apparatus

The crystallinity of the samples was determined with Differential Scanning Calorimetry (DSC) measurements on TA DSC Q2000 calorimeter. A heating/cooling/heating scan cycle was used at a heating and cooling rate of 10°C/min between 25 and 225°C. The crystallinity was determined by Eq. 3.

$$X = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f \cdot (1 - \phi)}, \quad (3)$$

where ΔH_m [J/g] is the enthalpy at melting point, ΔH_{cc} [J/g] is the enthalpy of cold crystallization, ΔH_f [J/g] is the enthalpy of the fully crystalline polymer and ϕ [m%] is the mass fraction of the filler [16]. According to the literature the theoretical value of ΔH_f for the polypropylene is 165 J/g [17]. Finally the size and the shape of the fillers were investigated with Scanning Electron Microscop (SEM) (Jeol JSM 6380LA).

3 Results and discussion

According to the SEM analysis the talc and boron-nitride have a plate-like shape. The average size of boron-nitride particles is under 10 μm but particles in the nanometer range can also be found but in the aggregates. The thickness of the plates is in the nanometer range. The average particle size of talc is between 5 and 50 μm which is higher than that of the BN, while the thickness of the particles is also in

the micrometer range, although the individual plates are thinner than one micrometer. In spite of the bigger size of talc particles, the final material could contain much smaller particles, as talc is a very soft material, and thus high shear during the molding process can break them.

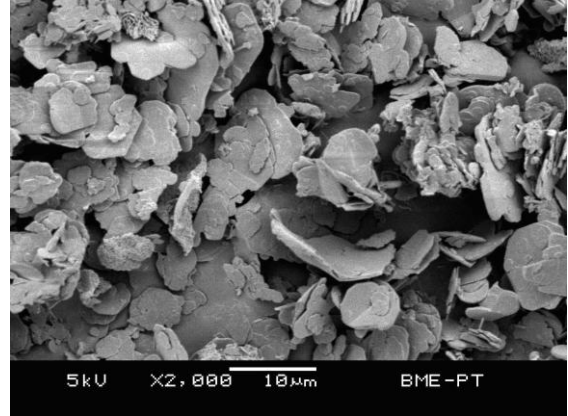


Fig. 2. SEM picture of the boron-nitride powder

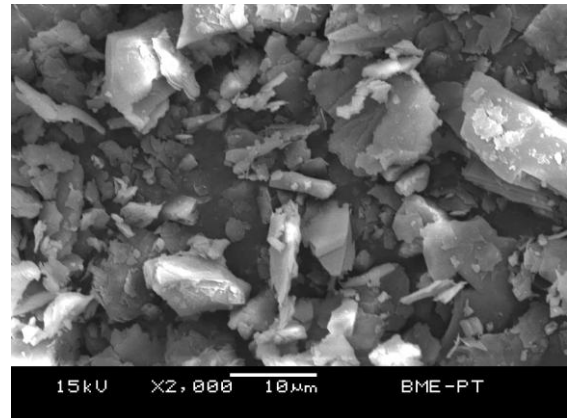


Fig. 3. SEM picture of the talc powder

The SEM pictures of the fracture surfaces (Fig. 4. and Fig. 5.) shows that the fillers were smoothly dispersed in the matrix material. The surfaces of the particles were no modified with coupling agent (like silane surface modifier) thus stronger adhesion and in this way better mechanical properties can be developed using this kind of additives. However the filler content was quite high (30 vol%), large aggregates could not be found. Thanks to the high filler content particles could form a conductive network in the compound through the wall thickness of the products and this way the thermal conductivity can be improved more efficiently. The

compound is densely packed, the interparticle distance is small and thus the particles could make contacts with each other. As Fig. 5. shows in the extruder and in the injection molding machine the high shear rate do not break the soft talc powder. Thus the size different of the fillers in the hybrid material can improve the synergetic effect.

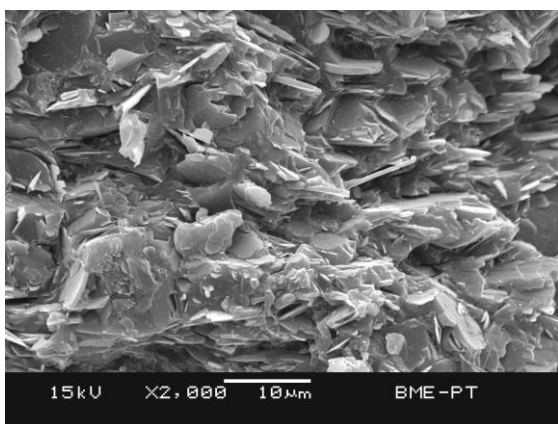


Fig. 4. SEM picture of the polypropylene/boron-nitride compound

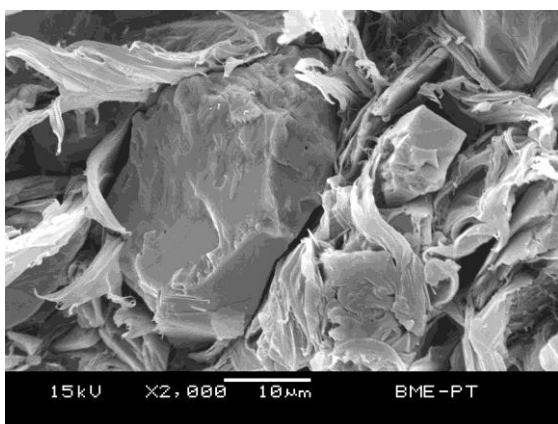


Fig. 5. SEM picture of the polypropylene/boron-nitride compound

The fillers have a great influence on the flowing behavior of the polymer materials. Increasing the filler content the viscosity of the material increasing also. This phenomenon can worsen the processing of the material, such as injection molding and extrusion. With the MVR measurement the compounds can be characterized aspect of the processability. The MVR values of the single and hybrid filled compounds is shown on Fig. 6. The

melt volume rate of the unfilled polypropylene is 44 cm³/10min. Filling 30 vol% talc into the matrix, the MVR decrease to 11.8 cm³/10min and at the case of 30 vol% boron-nitride this value is only 2.5 cm³/10min. 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 cm³/10min) than that of the 30 vol% boron-nitride filled PP.

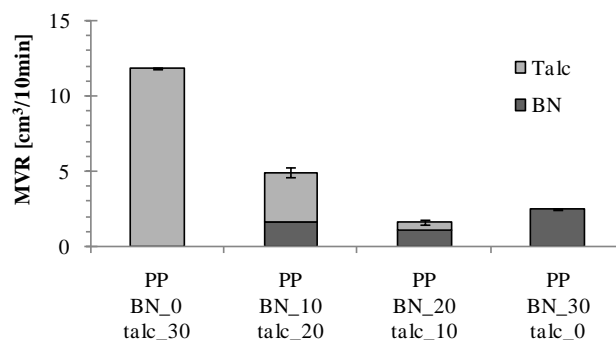


Fig. 6. Melt volume rate of the compounds (melt temperature: 230°C, load weight: 2.16 kg)

To characterize the changes in mechanical properties of the compounds, quasistatic and dynamic tests were performed. The results of tensile test (as quasistatic test) can be seen on Fig. 7. and Fig. 8. In comparison to the unfilled polypropylene, the particle filled compounds have significant smaller tensile strength. The unfilled PP tensile strength (31.9 MPa) decreased by 6-10 MPa by adding 30 vol% filler.

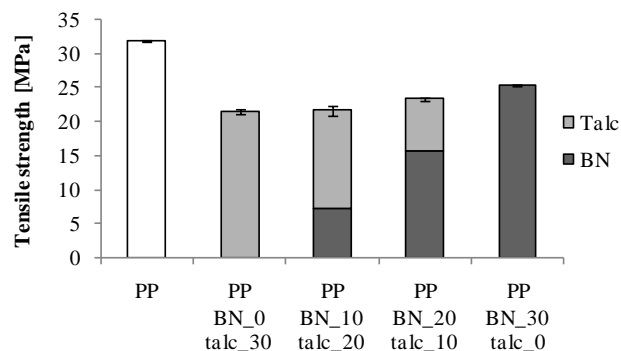


Fig. 7. Tensile strength of the compounds

The tensile modulus shows reverse tendency (Fig. 8.). Adding fillers to the polypropylene, the modulus increased significantly. While the unfilled H145 F PP has 2.1 GPa tensile modulus, the PP/10 V% BN 20 V% talc compound has three times higher (6 GPa) modulus. It means that the particles as reinforcement raise the compounds rigidness. Furthermore it was found that BN has better reinforcing effect than talc. Filling 30 V% talc into the matrix, the modulus increased by 2.8 GPa, and using the same amount of BN, it increased by 3.7 GPa. In addition using hybrid fillers higher reinforcing effect can be achieved. It means that synergetic effect exists between talc and BN.

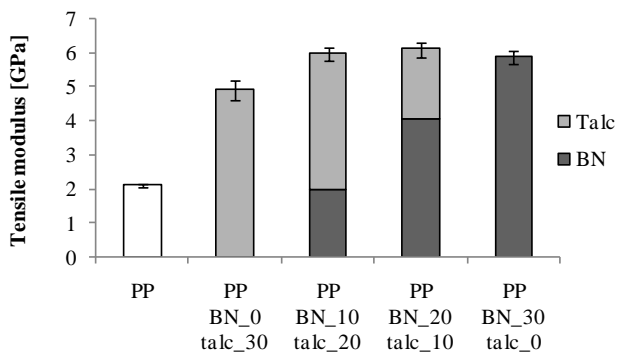


Fig. 8. Tensile modulus of the compounds

As the typical loads of the polymer parts have dynamic characteristic, charpy tests were also performed. The results of the measurements can be seen on Fig. 9. The unfilled H145 F polypropylene has 72 kJ/m² impact strengths. Adding 30 V% talc to the matrix, a significant drop can be observed, as the impact strength lowered to the tenth of the unfilled polypropylene. This drop is much more remarkable than the drop in the tensile strength. The most rigid material of the compounds is the polypropylene containing 20 V% BN and 10 V% talc of which impact strength is only 3.6 kJ/m². The results show that in contrast the tensile modulus, in the impact strength the hybrid material has negative synergetic behavior.

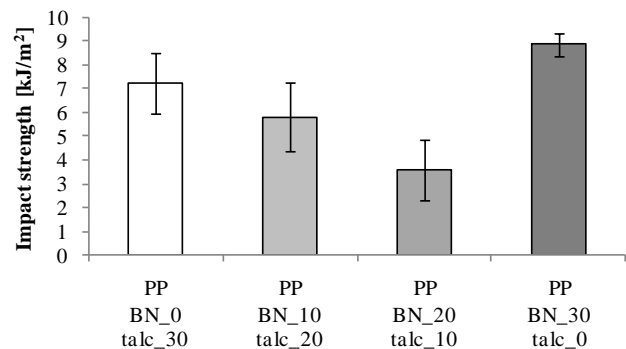


Fig. 9. Impact strength of the single filled and hybrid materials

Further positive hybrid effect can be appointed between the talc and boron-nitride by analyzing the thermal properties of the single filled and hybrid filled compounds. The PP based compound, containing 20 V% BN and 10 V% talc has also the highest thermal conductivity, higher than the 30 V% BN compound has. It can be explained with the size effect: smaller boron-nitride particles help to established more contact between the larger talc particles to obtain higher thermal conductivity coefficient. in this way the price of the product can be lowered by using hybrid filler in addition higher thermal conductivity can be obtained. Furthermore the improved thermal conductivity shortens the cycle time as the molded product cools faster. Thus the production will be more efficient and economic.

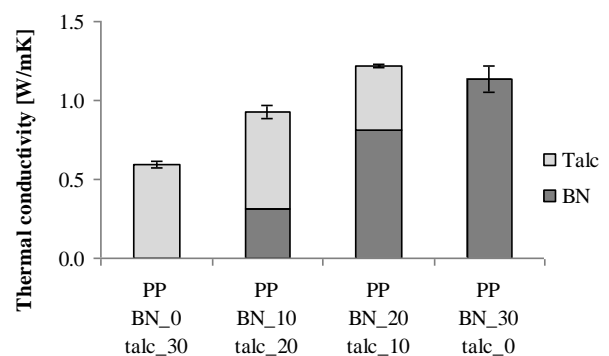


Fig. 10. Thermal conductivity of the single filled and the hybrid materials

The crystallinity of the injection molded samples was also investigated. The crystallinity significantly depends on the cooling rate in the mold. The higher

the cooling rate is, the lower the arisen amount of crystals. This phenomenon is shown in Table 2. and on Fig. 11. During the DSC measurement, where the heating and cooling rate was 10°C/min, both of the fillers (boron-nitride and talc) shows good nucleating agent behavior. The crystallinity of the unfilled PP is 62.6%. Adding 30 vol% BN and talc the crystallinity increased by 3-4%. According to Fig. 11. it can be established that during injection molding less crystals can be arisen when using fillers with higher thermal conductivity, because the cooling rate is higher in the specimens. This phenomenon can worsen the nucleating effect of the fillers. As the unfilled PP crystallinity is 66.7% after injection molding, 30 vol% talc increased it by 9%. Adding 30 vol% BN, the crystallinity decreased by 4%. The thermal conductivity of the talc is about 2-10 W/mK [18], and its value of the boron-nitride is 60-65 W/mK [19]. It shows the theory, that the filler, which has higher thermal conductivity lower the crystallinity on account of the higher cooling rate.

Material	X	St.dev
	[%]	[%]
H145 F	62.64	0.13
H145 F + 30talc	66.42	1.71
H145 F + 20t/10BN	57.28	0.65
H145 F + 10t/20BN	58.28	0.15
H145 F + 30BN	64.88	2.28

Table 2. Crystallinity of the samples using 10°C/min heating and cooling rate

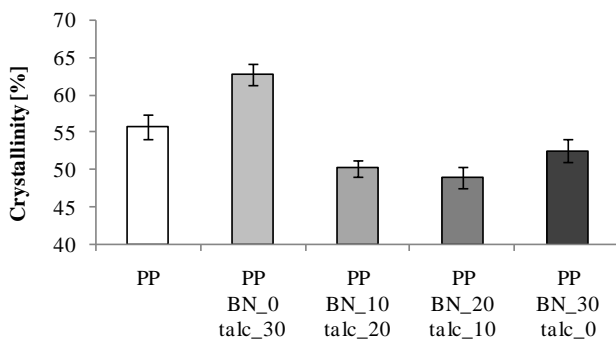


Fig. 11. Crystallinity of the samples after injection molding

Conclusion

In this study the effect of the hybridized fillers on the thermal and mechanical properties of polymer compounds was analyzed. The matrix material was a homo-polypropylene and the fillers were hexagonal boron-nitride and talc. Both of the fillers are relative soft material, thus it can not damage the processing machines. The compounds were prepared with a twin screw extruder and the 80x80x2 mm plate like samples were injection molded for the tests.

According to the SEM analysis talc and boron-nitride have plate-like shape. The average size of the boron-nitride is smaller (under 10 µm), than that of the talc (5-50 µm), thus they can act as efficient hybrid fillers. The pictures of the fracture surface of compounds show even filler distribution and bigger aggregates can not be discovered. The compounds are densely packed (filler content is 30 vol%) thus particles could form a conductive network in the compound through the wall thickness of the products and improve the thermal conductivity more efficiently.

The MVR measurements show the change in the flowing behavior of the compounds and represent its processability. The 44 cm³/10min MVR of the unfilled polypropylene decreased by 36 cm³/10min filling 30 vol% talc into the matrix and by 41.4 cm³/10min adding 30 vol% BN. Furthermore boron-nitride and talc hybrid filler has a negative hybrid effect to the viscosity.

Quasistatic and dynamic tests were also performed to characterize the mechanical properties of the materials. The unfilled PP tensile strength (31.9 MPa) decreased by 6-10 MPa by adding 30 vol% filler. In contrast to the tensile strength adding fillers to the polypropylene, the modulus increased significantly. It was found that BN has better reinforcing effect than talc. Furthermore a synergetic effect between the talc and boron-nitride was shown. Charpy tests (as dynamic test) were also performed. 30 V% talc to the matrix, a significant drop can be observed, as the impact strength lowered to the tenth of the unfilled polypropylene.

Further positive hybrid effect was appointed between the talc and boron-nitride regarding to the thermal conductivity. The thermal conductivity coefficient was determined with a hot-plate apparatus. The compound containing 20 V% BN and 10 V% talc (1.22 W/mK) has higher thermal

conductivity than the 30 V% BN (1.14 W/mK) compound has. It can be explained with the size effect. Further benefit of the hybridization is the shorter cycle time and the cost efficiency.

The crystallinity of the compounds was determined with DSC measurements. As a result, talc and also boron-nitride show an efficient nucleating agent behavior, when the heating and cooling rate was 10°C/min. Analyzing the effect of the injection molding, when the cooling rate was very high, lower crystallinity was developed. It can be established when using fillers with higher thermal conductivity and the cooling rate is also high, lower crystallinity can be arisen. This phenomenon can worsen the nucleating efficiency of the fillers.

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References

- [1] J. H. Yu, J. K. Duan, W. Y. Peng, L. C. Wang, P. Peng, P. K. Jiangudt "Influence of nano-AlN particles on thermal conductivity, thermal stability and cure behavior of cycloaliphatic epoxy/trimethacrylate system", *eXPRESS Polymer Letters*, Vol. 5, pp 132-141, 2011.
- [2] W. E. Jones, J. Chiguma, E. Johnson, A. Pachamuthu, D. Santos "Electrically and thermally conducting nanocomposites for electronic applications". *Materials*, Vol. 3, pp 1478-1496, 2010.
- [3] J. G. Kovács, G. Körtélyesi, N. K. Kovács, A. Suplicz "Evaluation of measured and calculated thermal parameters of a photopolymer". *International Communication in Heat and Mass Transfer*, Vol. 38, pp 863-867, 2011.
- [4] A. Suplicz, J. G. Kovács "Development of thermally conductive polymer materials and their investigation". *Materials Science Forum*, Vol. 729, pp. 80-84, 2013.
- [5] A. Suplicz, J. G. Kovacs "Development of thermal conductive hybrid composites". *ECCM15-European Conference on Composite Materials*, Venice, Italy, 24-28 June 2012.
- [6] T. L. Li, S.L.C. Hsu "Enhanced Thermal Conductivity of Polyimide Films via a Hybrid of Micro- and Nano-Sized Boron Nitride". *The Journal of Physical Chemistry B*, Vol. 114, pp 6825-6829, 2010.
- [7] Z. Han, A. Fina "Thermal conductivity of carbonnanotubes and their polymer nanocomposites: A review". *Progress in Polymer Science*, Vol. 36, pp. 914-944, 2011.
- [8] P.E. Slade, L.T. Jenkins "*Thermal Characterization Techniques*". Marcel Dekker, 1970.
- [9] R. Sengupta, M. Bhattacharya, S. Bandyopadhyay, A. K. Bhowmick "A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites". *Progress in Polymer Science*, Vol. 36, pp. 638-670, 2011.
- [10] Thermally Conductive Boron Nitride/SEBS/EVA Ternary Composites: "Processing and Characterization" *Polymer Composites*, Vol. 31, pp 1398-1408, 2010.
- [11] J. A. Molefi, A. S. Luyt, I. Krupa "Comparison of the influence of Cu micro- and nano-particles on the thermal properties of polyethylene/Cu composites". *Express Polymer Letters*, Vol. 3, pp 639-649, 2009.
- [12] W. Michaeli, T. Pfefferkorn "Electrically Conductive Thermoplastic/Metal Hybrid Materials for Direct Manufacturing of Electronic Components". *Polymer Engineering and Science*, Vol. 49, pp 1511-1524, 2009.
- [13] C.C. Teng, C.C.M. Ma, K.C. Chiou, T.M. Lee, Y.F. Shih" Synergetic effect of hybrid boron nitride and multi-walled carbon nanotubes on the thermal conductivity of epoxy composites". *Materials Chemistry and Physics*, Vol. 126, pp 722-728, 2011.
- [14] K. Yang, M.Gu "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*, Vol. 41, pp 215-221, 2010.
- [15] K. D. Maglic, A. Cezairliyan, V. E. Peletsky "*Compendium of Thermophysical Property Measurement Methods*". Plenum Press, 1984.

- [16] S. L. Gao, J. K. Kim “Cooling rate influences in carbon fibre/PEEK composites. Part 1. Crystallinity and interface adhesion”. *Composites: Part A*, Vol. 31, pp 517-530, 2000.
- [17] J.E. Mark “*Polymer Data Handbook*”. 2nd edition, Oxford University Press, 2009.
- [18] W. Zhou, S. Qi, Q. An, H. Zhao, N. Liu “Thermal conductivity of boron nitride reinforced polyethylene composites”. *Materials Research Bulletin*, Vol. 42, pp 1863-1873, 2007.
- [19] B. Weidenfeller, M. Höfer, F.R. Schilling “Thermal conductivity, thermal diffusivity, and specific heat capacity of particle filled polypropylene”. *Composites: Part A*, Vol. 35, pp 423-429, 2004.