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Improved thermal conductivity of polypropylene filled with exfoliated hexagonal boron nitride (hBN) particles

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Abstract

In this work, we show the route to obtain thermoplastic based composites with an enhanced thermal conductivity that was achieved by using exfoliated hexagonal boron nitride (hBN) particles as a filler material. Reports on composites with bulk or nano hBN showed, that while increasing the filler load improves thermal properties it could aggravate the composite melt rheology and mechanical properties. On the other hand, exfoliated hBN particles compared to bulk or nanopowder hBN could provide even better thermal properties with no degradation in composite mechanics, which was shown for epoxy. Taking into account the above, we obtained exfoliated hBN particles by ultrasound treatment in isopropyl alcohol and then used them as a filler in polypropylene based composites to increase the thermal conductivity. The composites with 29% wt. of exfoliated hBN showed a thermal conductivity of 0.721 W m−1 K−1 which is 4 times higher than for pristine polypropylene.

1. Introduction

Composite materials based on polymers with thermally conductive fillers have attracted much attention of the scientists due to the low cost of raw materials and wide range of potential applications. A list of commonly used polymer matrix materials for such composites includes polyethylene (PE) [1, 2] polypropylene (PP) [3], poly (methyl methacrylate) (PMMA) [4], polyurethane and more complex systems [5–8], while hexagonal boron nitride (hBN) [1, 2, 4, 7] aluminium nitride (AlN) [9, 10] and aluminium oxide (Al2O3) are most often used as a filler. The methodology of composite material preparation largely determines its final physical and mechanical properties. At the moment several methods for introducing filler material into the matrix volume were described, the most commonly used are: solution mixing [11, 12], melt blending [13, 14] and in situ polymerization [15, 16]. Nonetheless, in the case of hBN, not only the method of introducing the filler into the matrix volume determines the final properties of the composite, but also the thickness of the particles which can be reduced by the exfoliation process. Such a process is carried out to obtain two-dimensional flakes of hBN which have incredibly high thermal conductivity [17], high tensile strength combined with high flexibility and both thermal and chemical stability [18].

Most of the reports on exfoliation of hBN from the bulk describe three main routes to obtain a few-layered flakes: a) micromechanical exfoliation involving simple scotch-tape approach which has very low performance and is time and labour consuming [19]; b) milling and attrition, which can provide decent performance but tend to lead to a very broad size and thickness distribution of the resulting flakes [20, 21]; c) liquid phase exfoliation under the action of ultrasound in proper solvent or solvent with addition of some kind of exfoliating chemical agent which tend to intercalate between hBN layers (lithium salts, alkali or acids) [22–24]. Compared to the first
two methods liquid-phase exfoliation is more scalable and requires only solvent and an ultrasound bath or horn to proceed. When exfoliated hBN particles are introduced into liquid epoxy the resulting thermal conductivity (TC) of such composite significantly increases from 0.15 to 0.624 W m$^{-1}$ K$^{-1}$ [25]. This effect is still not very promising as compared to bulk or nano-hBN fillers described elsewhere [26], when TC values are almost ten times higher. We should also notice that introduction of exfoliated hBN into liquid polymers is much simpler than the extrusion method commonly used for thermoplastics like PP or PE. However, epoxy by itself is not recyclable, which is an ecological problem, and replacing it with a more environmentally friendly polymer is in demand [27]. The usage of hBN exfoliated by an ultrasonic treatment in organic solvents produces a dispersion which cannot be easily dried without suffering from agglomeration of already thin nanosheets. To avoid the agglomeration we devised a method in which we used a dispersion of exfoliated hBN nanosheets in isopropyl alcohol and mixed it with the solution of polypropylene in hot toluene from which both of the solvents should be evaporated. The resulting product is a composite in a form of flakes, that could be used for further processing.

As discussed elsewhere [28], when filler content is higher than 50% by weight the composite based on high-density polyethylene (HDPE) and modified hBN has thermal conductivity as high as 2 W m$^{-1}$ K$^{-1}$, but becomes brittle and hard to handle. We tried to address this problem in the current study by using more flexible exfoliated hBN particles [29] as a filler to increase the thermal conductivity with no significant drop in mechanical properties.

Therefore here we show a technique for production of thermoconductive composites with polypropylene matrix and exfoliated hBN as a filler. Exfoliation of boron nitride particles leads to a higher level of elasticity of the composite compared to the addition of untreated powder and should result in higher thermal conductivity at the same amount of filler.

### 2. Materials and methods

#### 2.1. Exfoliation technique and materials used

We used hexagonal boron nitride powder (hBN) with mean particle size of 12-13 um (Momentive, AC6004) for exfoliation which was conducted in 150 ml round bottom flask filled with 100 ml of isopropyl alcohol (IPA). The flask was placed into ultrasonic bath for 24 hour treatment. Resulting dispersion was then centrifuged at 5000 rpm for 7 minutes and supernatant was collected. We also tried high-power ultrasonic treatment with Heilsher UIP1000HD for a short time period as well as replacing the centrifugation with simple 20 min decantation for higher hBN concentration in the resulting composites. Exfoliation process scheme and scanning electron microscopy pictures are shown in figure 1. The dispersion has translucent appearance and demonstrates the Tyndall effect when lit by a red laser pointer as shown in figure 1 (b).

#### 2.2. Composite preparation

Composites with exfoliated hBN particles and low viscosity polypropylene (Borealis) were prepared in a two step process. Firstly, polypropylene granules were dissolved in hot toluene at 100 °C on the hotplate under vigorous stirring. Secondly, the supernatant of hBN/IPA dispersion was poured into polypropylene solution and the temperature on the hotplate raised up to 200 °C to evaporate all the solvents. Obtained viscous mass was then poured into a glass beaker and put for 2 hours into an air oven to evaporate residual solvents.

Resulting dry composite flakes were grind into a powder and put into a press form to obtain the platelets (10 mm in diameter) for thermal conductivity measurements. The composite platelets were pressed at 170 °C under the pressure of 5 MPa. A square-shaped composite sheets with 25 mm sides and 1 mm thick containing approximately 3% of exfoliated and pristine hBN were prepared on the glass substrates at 170 °C to visually compare the changes in flexibility.
2.3. Experimental setup

Atomic force microscopy was done using AIST-NT SmartSPM 1000 instrument in semi-contact mode. Raman spectra were collected using Thermo DXR with a green 532 nm laser. Fourier-transform infrared spectroscopy (FTIR) was performed using Thermo Nicolet 380 with Smart-ATR attachment and a diamond ATR crystal. Boron nitride powder before and after ultrasound treatment as well as brittle fracture of the composites surface were imaged by Tescan Vega 3 scanning electron microscope (SEM). Filler load and thermal stability of the resulting hBN/PP composites was devised from thermogravimetric data, which was measured on SDT Q600 at constant heating rate of 10 °C min⁻¹ from room temperature to 600 °C. Thermal conductivity was calculated using thermal diffusivity, density and heat capacity measured by Laser flash method (LFA) on Netsch 447, hydrostatic weighing and differential scanning calorimetry on Netsch 204F1 Phoenix respectively.

3. Results and discussion

Ultrasound treatment of hBN powder in IPA for 24 hours with further centrifugation produces a dispersion which is stable for more than a week. Coleman group [22] reported that some of hBN particles after this treatment undergo almost full exfoliation producing few-layered hBN sheets and unexfoliated part could be separated by centrifugation. Stable hBN nanosheet dispersion after the centrifugation demonstrates clearly seen Tyndall effect, which is shown in figure 1 (b). The dispersion obtained by this method could be used to produce thin hBN films and coatings by Langmuir-Blodgett [30] or even screen-printing [31] methods. After the treatment, hBN particles are 5 to 10 times smaller in lateral size compared to the untreated powder and have a thickness less than 15-20 nm, as can be seen in figure 2 (c). We should note that while the majority of the particles in the dispersion are thin, monolayer hBN sheet formation takes place only for the particles which have very small lateral size of 150-300 nm which is due to the tearing of hBN sheets as described in [28], and the concentration of such particles is low.

Thermogravimetric analysis (figure 3) showed that maximum obtained filler load was 29 wt.%, which is close to the numbers reported elsewhere [32] for silane-modified hBN. Two other samples prepared with slightly lower hBN dispersion concentration resulted in composites with 18 and 2% hBN by weight. The samples with 29 and 18% of hBN also showed that weight loss process in TGA experiment starts at slightly higher temperature compared to the sample with low hBN content or pristine PP. This could indicate higher thermal stability of composites with at least 18% of the filler.

FTIR spectra of composite samples and pristine PP for comparison are shown in figure 4. While on the samples with 2 and 18% of hBN its main peaks at 1374 and 817 cm⁻¹ are not seen clearly, the baseline slope change in the regions around 1300-1350 cm⁻¹ and 800-900 cm⁻¹ is apparent. The sample with the highest filler content has very intense 1373 and 817 cm⁻¹ bands attributed to in plane and out of plane B-N bond vibrations respectively. More detailed image of 817 cm⁻¹ band is shown in the (b) inlet of figure 4, where the asymmetrical shape of this band is clearly seen on spectra of the composites with 2% and 18% of exfoliated hBN and is due to overlap of PP and hBN bands in this region. The spectrum of a composite with 29% wt. of hBN has more expressed B-N bands which can be seen in figure 4 (a). We did not find any significant band shifts in the spectra of PP matrix in all analyzed composite samples, which indicates no changes in the structure of PP.

Raman spectra (figure 5 b) of the composites show the increase of relative intensity of hBN peaks (1376 cm⁻¹) with the growth of filler content. We did not notice a significant shift in the position of hBN peak in pressed composite samples compared to pristine untreated hBN powder, which could occur for monolayer hBN particles [19]. The intensity of hBN peak may vary by the sample surface, but all spectra collected for composites with both 18 and 29% of hBN showed that it is two times more intense in relation to the highest PP peak.
Scanning electron microscopy images of a liquid-nitrogen brittle fracture surface of composites with exfoliated hBN particles and pristine hBN are shown in figure 6 (a) and (b) respectively. A typical image of a composite with 2% of hBN does not have filler particle agglomerates, sometimes not even a single particle on the whole image at 500x magnification. However, both composites with 18 and 29% have a lot of individual hBN particles and most of them are separated by the polymer. When the filler content is 29% hBN particles are still appear to be evenly distributed in the matrix polymer, which should provide better thermal and mechanical properties as compared to PP filled with untreated hBN. Moreover, we did not have a solid evidence for the formation of interpenetrating networks (IPN) of the filler particles, therefore a percolation threshold in the composites with 29% of hBN probably was not reached. Images of the composite with pristine hBN particles (figure 6 (b)) clearly show large particle aggregates that reduce the strength of the composite without contributing much to its thermal conductivity due to uneven filler distribution.

Figure 3. Thermogravimetric curves of PP/hBN composites filled with various amount of exfoliated hBN.

Figure 4. FTIR spectra of PP/hBN composites filled with various amount of exfoliated hBN (a) and peak at 817 cm$^{-1}$ for pristine PP, 2% hBN and 18% hBN to show the band overlap (b).
While the main focus of this work is to address thermal properties of composites with exfoliated hBN particles, some discussion of the problems with materials processing and composite mechanics is needed. Due to a low performance of the ultrasound equipment available and a required further centrifugation step for hBN dispersion it is hard to produce highly concentrated suspensions of few-layered hBN nanosheets, therefore resulting composites either have low concentration of a filler or produced samples tend to be very small. As described in section 2 the LFA measurement requires small 10 mm disks, while thorough analysis of mechanical properties should be carried out on 4 mm thick and 80 mm long bars. We managed to produce 25 by 25 mm square sized samples with the thickness of 1 mm, which is inappropriate for tensile strength or bend strength measurements. However, we assessed the flexibility of the composites with exfoliated and pristine hBN by simple visual approach that is shown in figure 7. The figure shows that composites with untreated hBN have clearly seen particle agglomerates while the materials with the same amount of exfoliated hBN has better filler distribution. Moreover, the lower part of the figure shows that material with 3% of exfoliated hBN can be bent at
much higher degree (c) compared to the composite with the same amount of pristine hBN (d) and same exact dimensions.

We used a standard formula (1) to calculate the thermal conductivity ($\alpha$) using measured values of thermal diffusivity ($\chi$), density ($\rho$) and heat capacity ($C_p$).

$$\alpha = \chi C_p \rho$$  \hspace{1cm} (1)

Thermal conductivity values for the obtained composites and the data used to calculate it are presented in table 1. The plot in figure 8 shows how thermal conductivity of the composites depends on exfoliated hBN content. Additionally, DSC curves for the composites with exfoliated hBN particles are shown in figure S1. We can argue that with 29% wt. of exfoliated hBN nanosheets the composite has thermal conductivity four times higher compared to pristine polypropylene. This is also higher than for PP filled with 33% wt. of silane-modified hBN. The plot also show that that 29% of filler is close to the percolation threshold, even though we measured the samples in the direction perpendicular to the orientation of hBN sheets in the volume of the platelet. Usually,
thermal conductivity of such composites have strong anisotropy due to pressure application direction at the stage of composite preparation. Lower filler amount leads to insignificant decrease of thermal conductivity compared to pristine PP. It is well known, that sample density in the case of such composites can highly impact the final thermal conductivity numbers. Therefore higher density leads to an increase in overall thermal conductivity. Quite the opposite was observed for the composites with exfoliated hBN, which have lower density than the composites with silane-modified hBN, but significantly higher temperature diffusivity (0.474 and 0.306 mm² s⁻¹ respectively). Hence the usage of exfoliated hBN particles as a filler results in better thermal conductivity without affecting the density of the composite so much. Moreover, higher amount of exfoliated hBN filler or its combination with silane-modified hBN nanoparticles could in principle lead to even better thermal properties, which is a subject of further research.

4. Conclusions

Exfoliated hexagonal boron nitride particles with mean thickness of 15-30 nm were used as a filler for polypropylene based composites. The developed method of introduction of the particles into the polymer matrix from the dispersion resulted in the composites with maximum filler load of 29% by weight. We showed that at the same amount of filler the materials with exfoliated hBN are more flexible and tend to break at much higher levels deformation. The density of the composites with the load of 29% was 1046kg m⁻³, which is lower as compared to our previous report, but with higher thermal diffusivity (0.474 mm² s⁻¹). Obtained thermal conductivity of the hBN/PP composite with a maximum filler load was more than four times higher compared to pristine PP (0.721 and 0.18 W m⁻¹ K⁻¹ respectively) and more than 1.5 times higher if compared to PP with silane-modified hBN with reported thermal conductivity of 0.468 W m⁻¹ K⁻¹ [32]. According to SEM images and thermal conductivity values in relation to the filler load the percolation threshold for this type of composite is higher than 29% of exfoliated hBN by weight. Improved thermal properties combined with additional data on the mechanical properties of such composites will open many promising application cases in the future.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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