

Thermal and thermomechanical properties of boron nitride-filled acrylonitrile butadiene styrene (ABS) composites

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Abstract: The present study aims at investigating the effect of hexagonal boron nitride (hBN) nanoplatelets on the properties of acrylonitrile butadiene styrene (ABS) polymer. Composites containing 0-30 vol% hBN were prepared through batchwise melt compounding, which was followed by compression molding. Subsequently, the thermal and thermomechanical properties of the fabricated samples were investigated. The dynamic mechanical analysis (DMA) revealed that the storage modulus of the samples was markedly improved in the entire examined temperature range, while the glass transition temperature also gradually increased as a function of hBN content. According to the thermogravimetric analysis (TGA), the incorporated boron nitride particles enhanced the thermal stability of ABS composites, exhibiting a notably higher decomposition onset temperature. Additionally, the thermal conductivity of the ABS/hBN composites significantly increased by 570% when the hBN content was 30 vol%.

Keywords: acrylonitrile butadiene styrene; boron nitride; thermal conductivity; thermogravimetric analysis, dynamic mechanical analysis

I. INTRODUCTION

Recent times have seen a miniaturization and functionalization in the field of electronic devices [1-3]. One of the major challenges of this trend is to provide effective heat dissipation for the respective products in order to prevent their heat accumulation. Overheating might lead to a reduced lifespan and reliability of such high power density electronic components, including LEDs, Li-ion batteries, microelectronic packaging, and solar cells [4, 5]. One of the most common and cheapest materials for such purposes are polymers owing to their low density, good electrical insulation, and simple processability, however, their use is mostly limited to protective coatings and insulating layers because of their inherently low thermal conductivity, which is typically below 0.5 W/mK [6].

In order to overcome this shortcoming of polymers, a commonly followed strategy is to pair them with thermally conductive fillers [7]. The most commonly applied thermal conductors to incorporate into polymers are metallic, carbonaceous, and ceramic materials. Metals and carbon-based fillers provide an optimal solution when the electrical insulation is not important, albeit,

when it is essential along with outstanding heat conductivity, then ceramic additives are the obvious choice since the previous types usually own high electrical conductivity too [8, 9]. Among ceramics, the most common ones to be embedded into polymers to achieve the desired properties are aluminum nitride (AlN), aluminum oxide (Al₂O₃), silica carbides (SiC), and boron nitrides [6]. Oftentimes, researchers aim to improve the interfacial affinity of these particles through functionalization, or else the lack of active groups would result in these particles clumping together and distributing poorly within the polymer matrix [10]. These approaches, however, besides inserting an additional step into the processing sequence are also rather time- and money-intensive procedures.

Hexagonal boron nitride (hBN) nanoplatelets are 2D materials that attracted considerable scientific interest as fillers for various polymers due to the fact that they exhibit several benefits over carbonaceous and metallic particles. The thermal conductivity of hBN is anisotropic because of its layered structure. Accordingly, its in-plane thermal conductivity greatly differs from the through-plane conductivity. The previous one is roughly 600 W/mK because of the strong covalent bonds between B and N atoms,

while the latter one is between 1.5 and 2.5 W/mK [11]. Besides their excellent heat conductivity, their major advantages are the outstanding electrical insulation, corrosion resistance, and high thermal stability [10]. Therefore, a large body of work has been devoted to the development of boron nitride-filled polymer composites of improved thermal conductivity throughout the last several years with various thermoplastics and thermosets used as matrix materials. Among others, polypropylene [12], polyamide 6 [13], high density polyethylene [7], and epoxy [14-16] were successfully paired with this innovative ceramic filler.

In this work, a batchwise melt mixing procedure was employed to fabricate hBN-filled acrylonitrile butadiene styrene (ABS)-based polymer composites with enhanced thermal properties. The prepared ABS/hBN samples were subjected to dynamic mechanical analysis to study their thermomechanical behavior and glass transition temperature, while the thermal stability was examined by means of thermogravimetric analysis. Furthermore, the enhancement in the thermal conductivity of ABS as a function of boron nitride content was studied by laser flash technique.

II. MATERIALS AND METHODS

1. Materials

The ABS polymer (Magnum 3453) used as matrix material was obtained from Trinseo (Wayne, Pennsylvania, USA). The hexagonal boron nitride nanoplatelets under the brand Hebofill 482 were purchased from Henze BNP (Lauben, Germany). The density of hBN is 1.88 g/cm³ and its average particle size is <30 μm according to its official datasheet. It has to be noted, that this latter value refers to the size of hBN agglomerates, while the individual particles are much smaller than that. Scanning electron microscopic image of the hBN particles is shown in **Fig.1**.

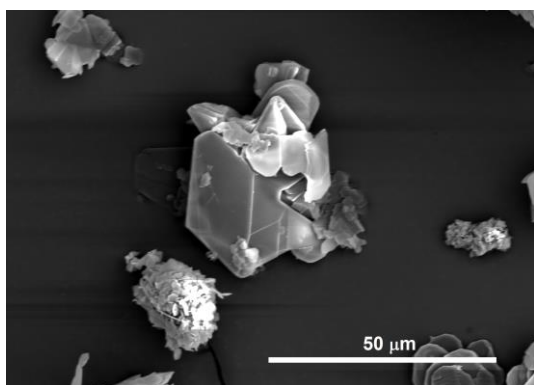


Figure 1. Scanning electron microscopic image of the applied boron nitride nanoplatelets

Table 1. Composition and designation of the prepared samples

Designation	ABS-content [vol%]	hBN-content [vol%]
ABS	100	0
ABS_1hBN	99	1
ABS_3hBN	97	3
ABS_5hBN	95	5
ABS_10hBN	90	10
ABS_20hBN	80	20
ABS_30hBN	70	30

2. Preparation of the ABS/hBN composites

The melt mixing process of ABS and hBN was performed with a Haake PolyLab internal mixer (Vreden, Germany) equipped with a chamber of 50 cm³. The compounding was carried out at a temperature of 190 °C, whereas the rotational speed of the mixing elements was 60 rpm. The procedure lasted for 10 minutes with ABS being the first material to be added into the mixer. Subsequently, after 3 minutes the hBN particles were also introduced. This way, ABS-based samples containing 0, 1, 3, 5, 10, 20, and 30 vol% hBN were prepared. The composition and designation of the prepared samples are collected in **Table 1**.

The fabricated samples were compression molded following the melt compounding. This way, sheets of ~2 mm thickness were prepared with a Carver hot press 4122 (Wabash, Indiana, USA) compression molding machine at 190 °C.

3. Characterization

Dynamic mechanical analysis (DMA) was performed with a TA Instruments Q800 device (New Castle, Delaware, USA) in the temperature range of 30 °C to 150 °C with a heating rate of 3 °C/min. The experiments were carried out using a single cantilever clamp. The frequency was 1 Hz and the strain amplitude was set to 0.02%.

Thermogravimetric analysis (TGA) was carried out with a TA Instruments Q500 device (New Castle, Delaware, USA). Samples in the range of 5-10 mg were exposed to a heating program ranging from 30 °C up to 700 °C at a linear heating rate of 10 °C/min in a nitrogen atmosphere.

The enhancement in the thermal conductivity of the samples was determined with a Netzsch LFA 467 Hyperflash (Selb, Germany) light flash apparatus. Round samples with a diameter of 12.7 mm were cut from the compression molded sheets and coated with graphite. Five pulses were performed on each specimen. The thermal conductivity enhancement

(Φ) was determined according to Equation (1) as follows [17]:

$$\Phi = \frac{k_c - k_{ABS}}{k_{ABS}} \times 100\% \quad (1)$$

where k_c and k_{ABS} represent the thermal conductivity of the composite and the unfilled ABS polymer, respectively.

III. RESULTS AND DISCUSSION

1. Dynamic mechanical properties

The dynamic mechanical behavior of the fabricated samples was analyzed in the temperature range of 30 °C to 150 °C. **Fig. 2** shows the temperature dependence of the storage modulus (E') and loss factor ($\tan \delta$) of the prepared samples. According to **Fig. 2a**, all the composites containing hBN particles exhibited considerably higher storage modulus than that of unfilled ABS in the whole analyzed temperature range. This increment can be

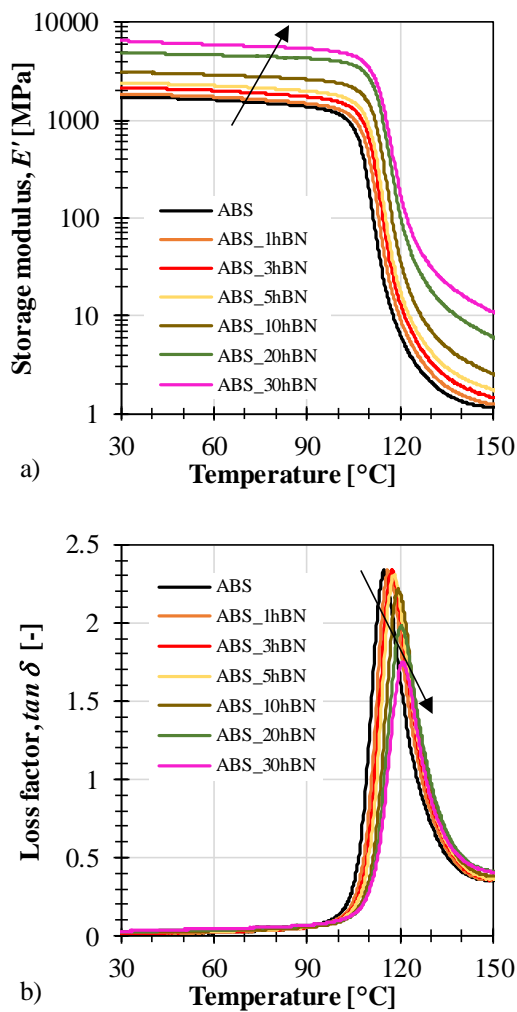


Figure 2. Storage modulus (a) and loss factor (b) versus temperature of pure ABS compared with composites containing different amounts of hBN

explained by the high rigidity of ceramics particles (such as hBN), which confers a general increase in the stiffness of the composite matrix. Meanwhile, the E' of all the prepared samples reduced with increasing temperature. At low temperatures, the amorphous part of polymers tends to be in a so-called glassy state. In the glassy state, the motion of chain molecules is restricted, resulting in high storage modulus values that only slightly decrease as a function of temperature. When exceeding the glass transition temperature (T_g) a sudden drop in storage modulus can be observed, representing the transition of the material from the glassy state into a rubber-like state. As seen in **Fig. 2a**, the decrease in storage modulus when exceeding the T_g was highest for those composite samples that contained the highest amount of hBN filler (note the logarithmic scale).

The temperature dependence of the loss factor is shown in **Fig. 2b**. The glass transition temperature of polymeric materials is mostly defined as the temperature where the $\tan \delta$ curve peaks. Apparently, with increasing hBN content, the T_g of ABS (114.8 °C) shifted towards higher temperatures, reaching 120.8 °C when the maximum of 30 vol% hBN was incorporated into the matrix. This shift to higher temperatures refers to a reduced chain mobility of the ABS molecules in the presence of hBN [18]. Additionally, it can be seen that the $\tan \delta$ peaks declined with the introduction of ceramic particles indicating a reduced damping capacity of the ABS polymer.

2. TGA behavior

The thermal stability of the samples was analyzed by means of TGA measurements. The TGA thermograms of unfilled ABS and the composites against the increasing temperature are illustrated in **Fig. 3a**, whereas **Fig. 3b** shows their derivatives (DTG). Clearly, all samples exhibited a single-step degradation process, corresponding to the decomposition of macromolecular chains of ABS polymer. The degradation manifested in a sudden drop in the TGA thermograms (**Fig. 3a**) and in a sharp peak in the DTG curves (**Fig. 3b**). The thermal stability of the fabricated samples was analyzed in the form of the onset temperature and maximum thermal degradation temperature. The onset of the decomposition (T_o) was considered as the temperature where the specimens suffered 5% of weight loss, while the temperature of the maximum degradation (T_p) was determined based on the peak points of the DTG curves. The T_o value of neat ABS was 381.8 °C, which gradually improved with increasing hBN content, reaching the highest temperature of 391.1 °C for the ABS_30hBN sample. This enhancement in thermal stability can be attributed to the high heat capacity of the hBN filler, which is embedded into the ABS matrix.

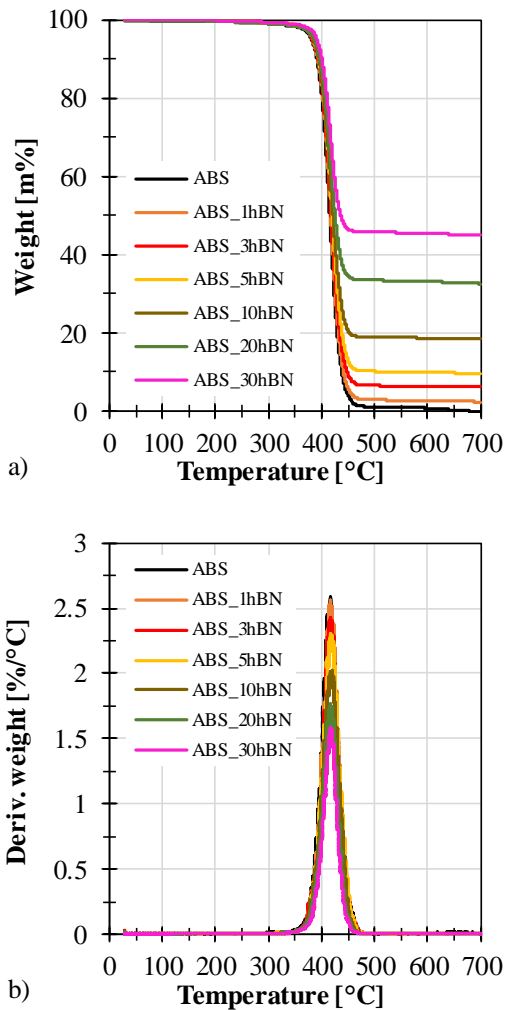


Figure 3. Thermograms of TGA (a) and DTG (b) versus temperature of pure ABS compared with composites containing different amounts of hBN

Meanwhile, the ceramic fillers did not significantly affect the T_p values. The temperature corresponding to the maximum degradation was the lowest for unfilled ABS (416.5 °C), but it only increased slightly in the presence of boron nitride particles, with all the composites being in the small temperature range of 416.6 and 418.6 °C.

3. Thermal conductivity

The thermal conductivity enhancement data of all hBN-containing composites relative to that of unfilled ABS are depicted in **Fig. 4**. The thermal conductivity of commercial ABS was determined as 0.19 W/mK, which is in good agreement with the literature [6]. As expected, with hBN nanoplatelets getting incorporated into the polymer matrix, the thermal conductivity of ABS increased simultaneously. The relative enhancement of thermal conductivity was 2.5%, 5.8%, 45.3%, 101.5%, 263.5%, and 572.0% for the composites

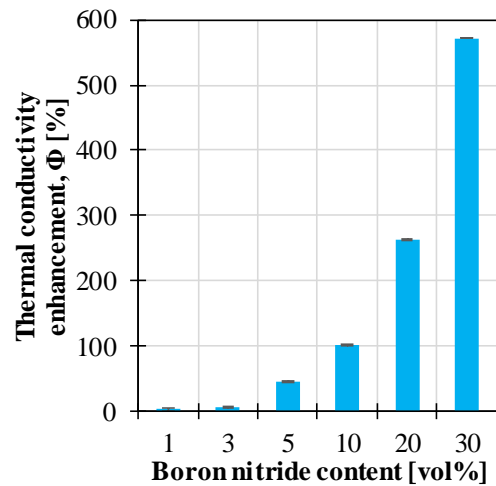


Figure 4. Thermal conductivity enhancement of ABS at various hBN concentrations

containing 1, 3, 5, 10, 20, and 30 vol% of boron nitride particles, respectively.

IV. CONCLUSIONS

In the present study, ABS/hBN composites were fabricated through batchwise melt compounding using an internal mixer. Subsequently, the composites were formed into sheets through compression molding. The thermomechanical behavior of the fabricated samples was analyzed by means of dynamic mechanical analysis. It was revealed that the hBN particles greatly enhance the storage modulus of ABS in the whole examined temperature range while also increasing its glass transition temperature prominently. Through thermogravimetric analysis it was shown that the onset of ABS shifts to a higher temperature if hBN nanoplatelets are incorporated into it, referring to an improved thermal stability. Additionally, the laser flash measurement verified that this type of ceramic filler is highly efficient in increasing the thermal conductivity of ABS polymer, reaching a maximum relative increment of 570% at 30 vol% hBN concentration.

Overall, this study provides solid evidence about all the investigated properties of ABS being markedly improved in the presence of hBN particles.

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AUTHOR CONTRIBUTIONS

L. Lendvai: Conceptualization, Experiments, Fund acquisition, Writing – original draft

D. Rigotti: Conceptualization, Experiments, Writing – review and editing

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DISCLOSURE STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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