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Effects of h-BN on the thermal and mechanical properties of PBT/PC/ABS blend based composites

Xing Jin[1], Nian Fu[1,2,], Huili Ding[1], Nan Zhao[1], Jianbing Sang[3], Xiaolei Li[3], Saleem Abbas[1], Xuewen Xu[1], Fanbin Meng[1], Jie Li[1], Ying Fan[1,*], and Chengchun Tang[1]*

[1]*School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, P. R. China*

[2]*College of Physics Science and Technology, Hebei University, Baoding, 071002, P. R. China*

[3]*School of Mechnical Engineering, Hebei University of Technology, Tianjin 300130, P. R. China*

Abstract

Hexagonal boron nitride microplatelets (h-BNMPs) or h-BN microplatelets/h-BN nanospheres (h-BNNSs) hybrids-filled polybutylene terephthalate (PBT)/Polycarbonate (PC)/Acrylonitrile Butadiene Styrene (ABS) blends with a mass proportion of 7:2:1 were prepared. The use of h-BNMPs resulted in composites with higher enhancement than h-BN hybrid fillers in terms of thermal conductivity. The addition of h-BN hybrids (h-BNMPs and h-BNNSs at the weight ratio of 8:2) achieved highest enhancement of mechanical properties, adding 6 wt% h-BN hybrids achieved a 39% increase in notched impact strength and a 4.9% increase in tensile strength. Moreover, not only did the incorporation of h-BN hybrids significantly enhance the mechanical performance of composites, but it remarkably improved the thermal conductivity of composites. Nevertheless, the doping of h-BNMPs resulted in the decrease of mechanical properties, although it availably contributed to the rise of thermal conductivity compared to the neat PBT/PC/ABS matrices.

*__Corresponding author:__ Tel.:+86-22-60204580.

E-mail addresses: funian3678@163.com (N. Fu), yfan@hebut.edu.cn (Y. Fan).

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1. Introduction

In the past decades, polymer/inorganic nanocomposites have received research attention from academic and industrial communities due to their novel functional applications, good processibility and relatively low cost.[1-7] These nanocomposites obtain the benefits by merging the advantages of inorganic and organic phases. Controlling the filler dispersion and interaction between filler and polymer matrix contributes to and achieve the outstanding performance of a composite. Meanwhile, rational and effective methods are developed for desirable properties of nanocomposites such as high thermal conductivity and excellent mechanical properties. In most cases, it is popular to functionalize the fillers or modify the surface chemistry of the fillers.

Recently, BN as a novel filling material has now been proved to produce composite with excellent performance.[8-11] BN based fillers (such as BN nanoplatelets, BN nanospheres, BN nanosheets and BN nanotubes) have attracted attention because of its low density, high thermal conductivity, electrical insulation, superb oxidation resistance, passivity to react with acids, low coefficient of friction and potential application in developing polymeric composites.[12-14]

In this study, the effect of h-BNMPs and h-BN hybrids on the thermal and mechanical properties of melt compounded PBT/PC/ABS based composites is to be investigated. The emphasis is to explore the relationship between content of h-BN fillers and the performance of h-BN/PBT/PC/ABS composites. The crucial factors are the dispersion of h-BN in composites and the interaction between h-BN and matrix. The use of twin screw extruding and injection molding machine ensures the dispersion of h-BN, meanwhile versatile and functional groups existing on the surface of h-BN contribute to improve the adhesion and affinity between fillers and matrices. The dependences of thermal conductivity and mechanical properties on the concentration and dispersion of h-BN and interaction between fillers and matrices are studied.

2. Materials and methods

H-BNNSs (50~500 nm) were synthesized by the chemical vapor deposition (CVD) reaction of trimethoxyborane ($B(OMe)_3$) with ammonia.[15] H-BN powder (purity >99.0%, 3~5 μm; Qing Zhou Materials Co., China) with platelet morphology was used. The thermal conductivity of BN along the basal planes of the hexagonal crystal structure was about 280 W/m•K at room temperature. PBT was purchased from Chang Chun Chemical Co. Ltd., China. ABS was purchased from STAREX Co. Ltd., Korea. PC was purchased from INFINO Co. Ltd., Korea.

Nowadays plain homopolymers are rarely used. Instead, the use of polymer blends dominates in many applications. The brittle or ductile behavior of polymer and the preferred mechanisms of deformation and failure are controlled principally by two molecular parameters-the entanglement density and chain flexibility, determining an initiation stress for crazing or shear yielding, respectively. Pseudoductile polymers exhibiting high entanglement density and flexibility, such as PC and polyesters (PBT, PET), tend to deform by shear yielding mechanism rather than crazing. Multiple crazes are actually the main source of ductility in polymers modified by blending with elastomers. ABS appeared very effective in increasing the craze concentration by promotion of craze nucleation at lowered overall plastic resistance.[16] Blending PBT, PC and ABS could make sure the ideal mechanical properties by improve the entanglement density and chain flexibility of neat PBT/PC/ABS matrices. The work is an exploration to blend PBT, PC and ABS at mass fraction of 7:2:1. H-BNMPs, h-BNNSs and PBT/PC/ABS blends were dried in a vacuum oven at 120 °C. After that, 4.5 g of h-BNMPs and

300 g of PBT/PC/ABS blends (PBT:PC:ABS with the mass ratio of 7:2:1)were loaded into the twin screw extruder, then the blends were extruded by the extruder through a die in the form of stands (4 mm), which are cooled and solidified in the water bath before being cut (2 mm). To make sure the degree of mixability, the barrel temperature was 180 ^{o}C, 200 ^{o}C, 210 ^{o}C, 220 ^{o}C, 235 ^{o}C, 245 ^{o}C, 200 ^{o}C, respectively, and the speed of screws was 180 r/min. The particles obtained from the pelletizer were sufficiently dried at 80 ^{o}C in the vacuum drying oven. Subsequently, the injection molding machine was used for molding PBT/PC/ABS based composites filled with 1.5 wt% h-BN microplatelets. The barrel zone temperature was 235 ^{o}C, 240 ^{o}C, 245 ^{o}C, respectively, the temperature of injecting nozzle was 240 ^{o}C, the speed of screw was 25~60 r/min and the molding cycle was 15~60 s. By using the same method, the composites of the PBT/PC/ABS filled with 3 wt%, 4.5 wt%, 6 wt% and 7.5 wt% h-BNMPs or 1.5 wt%, 3 wt%, 4.5 wt%, 6 wt% and 7.5 wt% h-BN hybrids (h-BNMPs: h-BNNSs at weight ratio of 8:2) were prepared. The mass ratio of h-BN hybrids came from the roles of h-BNMPs and h-BNNSs. H-BNMPs had higher thermal conductance than h-BNNSs. H-BNNSs made for reinforcing the mechanical properties of composites. We chose the ratio of 8:2 as an exploration to improve the mechanical and thermal properties simultaneously. The mechanical tests were performed using Instron 3365 for tensile strength and ZBC-4 impactor for notched impact strength. To remove the internal stress, the samples were placed in the test room for more than 24 hours at the temperature of 23 ^{o}C $\pm$ 1 ^{o}C before the mechanical tests. The h-BN fillers, neat PBT/PC/ABS blends and composites were characterized by X-ray diffraction (XRD) technique for phase identification. The crystal structure of boron nitride particles and composites were determined by SmartLab X-ray diffraction patterns (XRD) with Cu Ka radiation. The thermal conductivity of neat PBT/PC/ABS and PBT/PC/ABS based composites were examined by TC 3000 apparatus (Xi'an Xiatech Electronic Technology Co. Ltd.,

China). For the measurements of thermal conductivity we employed the ASTM D5470 standard method. To increase the sample density and reduce the contact thermal resistance, a constant pressure of 3 MPa was applied to a specimen during the measurements. The thermal conductivity (κ) was calculated as $\kappa = Qd/\Delta TA$, where Q is the heat flow generated from an electrical heater, ΔT is the temperature difference at the two ends of a specimen, and d is the specimen thickness.[17] These samples were characterized by scanning electron microscope (FE-SEM, Nava NanoSEM 450, FEI) to examine the fractured morphology. Thermo-gravimetric analysis (TGA) was carried out with SDT Q600 instrument, from room temperature to 700 °C, at a heating rate of 10°C/min under nitrogen flow

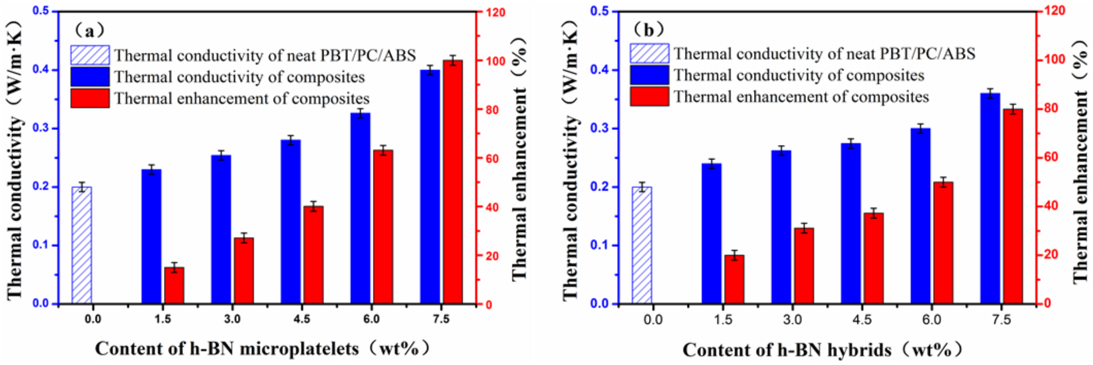

Fig.1 Effect of filler content on thermal conductivity of PBT/PC/ABS based composites.

3. Results and discussion

Fig.1 shows the thermal conductivity of neat PBT/PC/ABS matrices and PBT/PC/ABS based composites with different contents of h-BN fillers, ranging from 1.5 wt% to 7.5 wt%. Under the loading of 4.5 wt%, the thermal conductivity of composites filled with h-BN hybrids are generally higher than that of composites filled with h-BNMPs, however, the results are obviously opposite when beyond 4.5 wt%. Because of low content, the h-BNMPs cannot connect each other, the h-BNNSs works as bridges between the h-BNMPs, and the h-BNMPs can sufficiently connect and partially form the thermal conductive path and networks with the continuous increase of filler content. When adding 7.5 wt% h-BNMPs, the thermal conductivity increases by 102% (0.438 W/m•K, compared to 0.216

W/m•K of neat PBT/PC/ABS), the thermal conductivity is 0.360 W/m•K with the enhancement of only 80% (compared to neat PBT/PC/ABS) in term of filling 7.5 wt% h-BN hybrids.

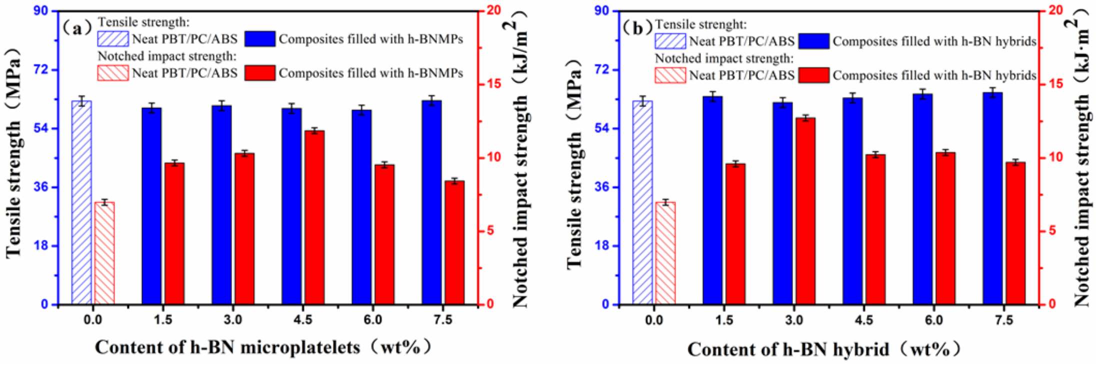

Fig. 2 Effect of filler content on tensile strength and notched impact strength of PBT/PC/ABS based composites.

Fig.2 shows that the introducing of h-BNMPs doesn't improve the tensile strength moreover it even decreases the impact strength. By contrast, the incorporation of h-BN hybrids significantly enhances the impact strength of the composites, which also remarkably improves the heat conduction of composites as shown in Fig. 1. Adding 6 wt% h-BN hybrids achieves a 39% increase in notched impact strength (9.706 kJ/m^2, compared to 6.98 kJ/m^2 of neat PBT/PC/ABS matrices) and a 4.9% increase in tensile strength (65.05 MPa, compared to 62.45 Mpa of neat PBT/PC/ABS matrices).

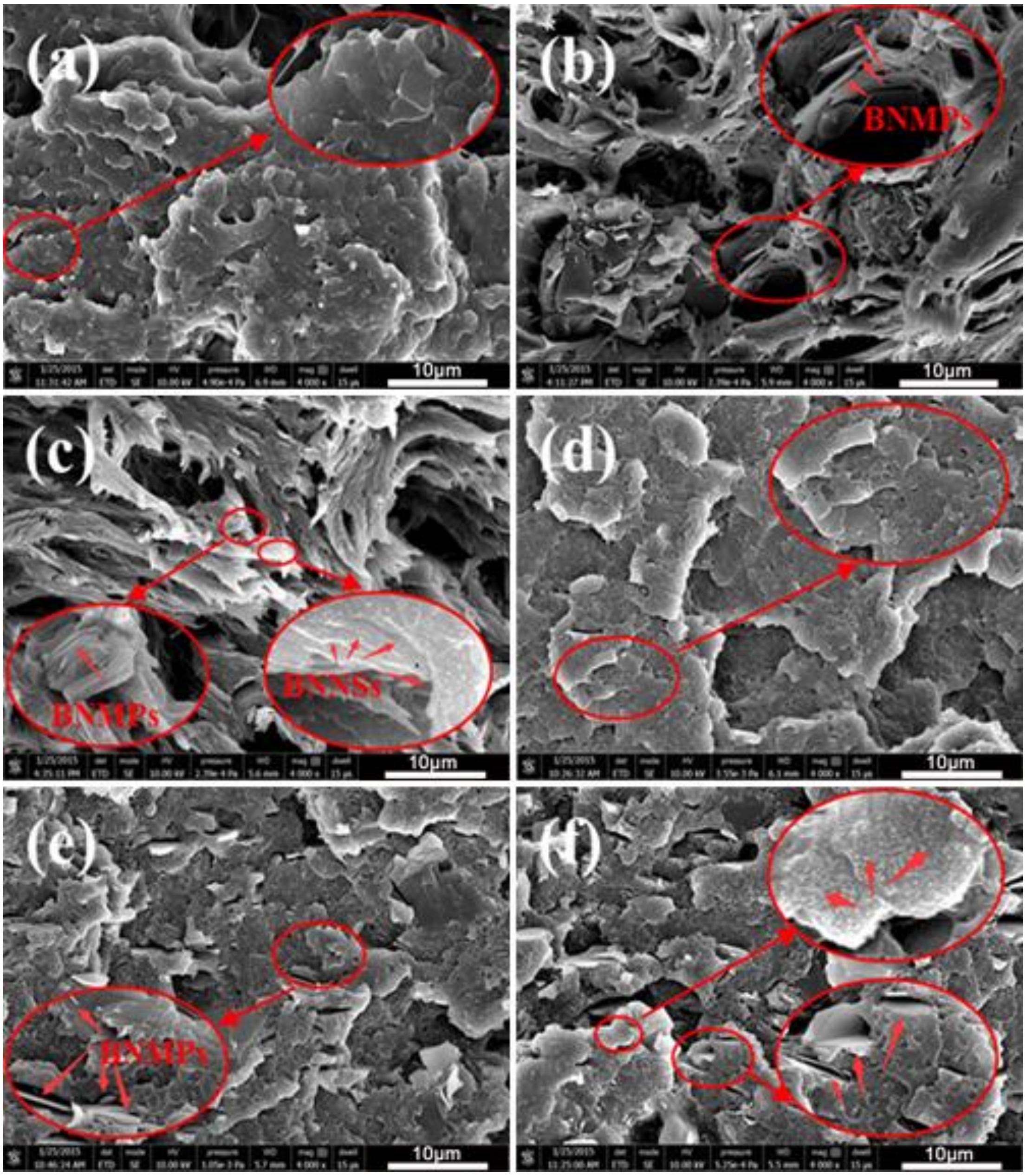

Fig.3 SEM images of the tensile fractured surface: (a) neat PBT/PC/ABS matrix, (b) composite filled with 7.5 wt% h-BNMPs and (c) composite filled with 7.5 wt% h-BN hybrids and impact fractured surface: (d) neat PBT/PC/ABS matrix, (e) composite filled with 7.5 wt% h-BNMPs and (f) composite filled with 7.5 wt% h-BN hybrids.

Fig.3 shows the morphology of neat PBT/PC/ABS and composites with 7.5 wt% h-BN content. Fig.3 (a) and (d) show the tensile fractured surface and impact fractured surface of neat PBT/PC/ABS, respectively, both of them are smooth with a typical feature of brittle fracture as shown by M. Du et al.[18] With the increasing content, the network (Fig.3 (b) and (e)) is formed by h-BNMPs embedded in matrix, which contributes to the improvement of thermal conductivity. All composites (Fig.3 (c), (d), (e) and (f)) reveal a wrinkled rough fractured surface, and the h-BN particles are embedded in matrix. This phenomenon is due to the local polymer deformation or matrix shear yielding, which could be explained by a crack deflection mechanism caused by adding BN fillers.[19,20] Especially, the homogeneous dispersion of h-BNNSs (white particles in red circles in Fig.3 (c) and (f)) effectively reinforces the mechanical properties of composites.

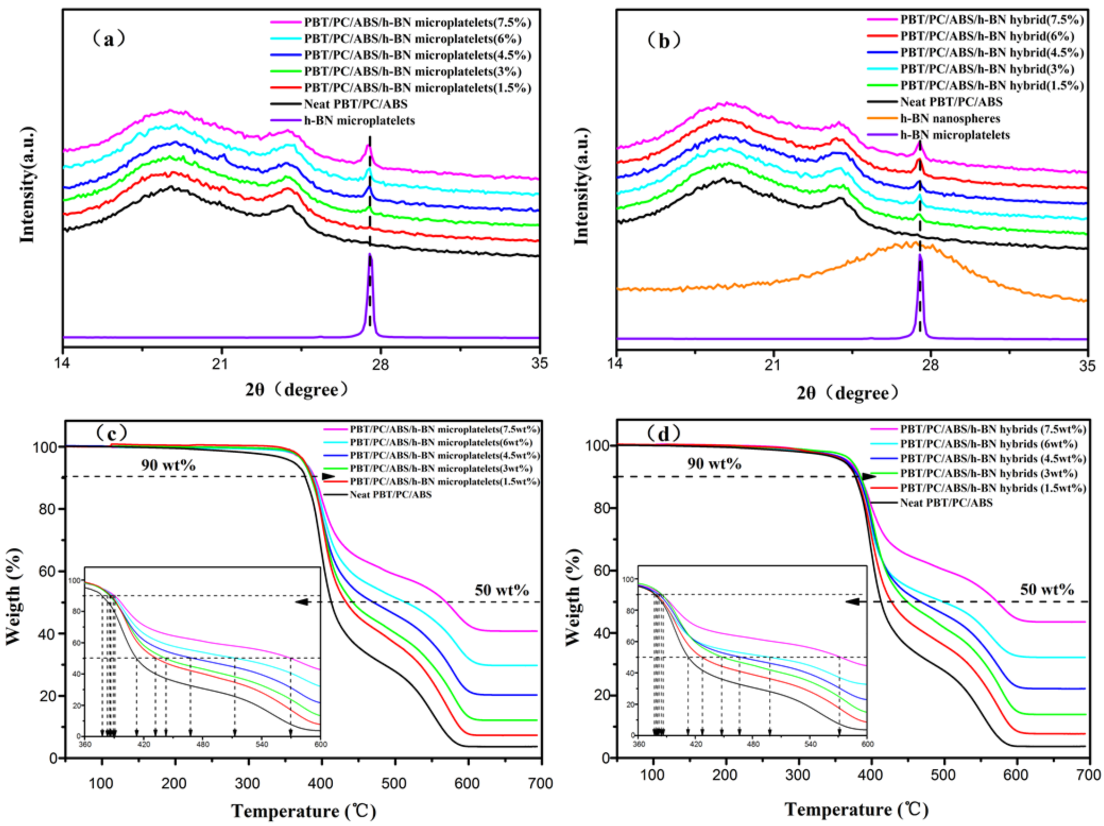

Fig. 4 XRD patterns of (a) h-BNMPs and composites filled with h-BNMPs and (b) h-BN hybrids and composites filled with h-BN hybrids and dependence of thermal stability of composites on the content of (c) h-BNMPs and (d) h-BN hybrids.

In Fig. 4, the XRD patterns of h-BN fillers, composites filled with h-BNMPs (Fig. 4 (a)) or h-BN hybrids (Fig. 4 (b)) are shown. A mutual diffraction peak corresponds to (002) plane of the hexagonal crystal of boron nitride and the intensity becomes stronger with the increase of h-BN filler content. The crystal structures of h-BN fillers and matrix have no evident influence on each other. As shown in Fig. 4 (c) and (d), the thermal stability of neat PBT/PC/ABS and composites is evaluated by TGA. All composites exhibit similar thermal degradation behavior, from room temperature to 700 ^{o}C, compared to the neat PBT/PC/ABS, indicating that the addition of BN particles does not change the thermal decomposition mechanism of the PBT/PC/ABS matrix.

4. Conclusions

In summary, the effects of h-BNMPs and h-BN hybrids on the thermal and mechanical properties of PBT/PC/ABS blends have been studied extensively. H-BNMPs were shown to have an obvious effect on the thermal conductivity of the blend; with 102% increase achieved by adding 7.5 wt% h-BNMPs. The addition of h-BN hybrids significantly enhanced the mechanical performance of composites with remarkably improvement of the thermal conductivity of the composites. The introducing of h-BN filers reinforced the thermal stability of composites with the crystal structure of PBT/PC/ABS remained.

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