Surface Manipulation of Thermal-Exfoliated Hexagonal Boron Nitride with Polyaniline for Improving Thermal Stability and Fire Safety Performance of Polymeric Materials

You-Ran Zhi,† Bin Yu,*‡ Anthony Chun Yin Yuen,§ Jing Liang,§ Lin-Qiang Wang,∥ Wei Yang,*,§∥ Hong-Dian Lu,∥ and Guan-Heng Yeoh§

†School of Mechanical Engineering, Nanjing Institute of Technology, 1 Hongjing Avenue, Nanjing, Jiangsu 211167, People’s Republic of China
‡Department of Architecture and Civil Engineering, City University of Hong Kong, 88 Tat Chee Avenue, Kowloon, Hong Kong, People’s Republic of China
§School of Mechanical and Manufacturing Engineering, University of New South Wales, Sydney, NSW 2052, Australia
∥Department of Chemical and Materials Engineering, Hefei University, 99 Jinxiu Avenue, Hefei, Anhui 230601, People’s Republic of China

Supporting Information

ABSTRACT: In this article, the polyaniline (PANI)/thermal-exfoliated hexagonal boron nitride (BNO) hierarchical structure (PANI−BNO) was constructed via in situ deposition to improve the dispersion and interfacial adhesion of boron nitride in multi-aromatic polystyrene (PS) and polar thermoplastic polyurethane (TPU). Because of the conjugated structure and polar groups in PANI, the uniform dispersion and strong interfacial adhesion between PANI−BNO and PS and TPU were achieved. Thermogravimetric analysis results showed that the incorporation of PANI−BNO enhanced the thermal stability of PS and TPU, i.e., the temperatures at both 5 and 50 wt % mass loss. In addition, PANI with high charring ability also acted as a critical component to generate a synergistic effect with BNO on reducing the fire hazards of PS and TPU. This well-designed structure led to a remarkable reduction of flammable decomposed products and CO and CO2 yields. Meanwhile, a dramatic decrease in the real-time smoke density and total smoke production was observed for PS and TPU nanocomposites with 3 wt % PANI−BNO hybrids, respectively. The multiple synergistic effects (synergistic dispersion, char formation, and barrier effect) are believed to be the primary source for these enhanced properties of polymer nanocomposites.

1. INTRODUCTION

Polymer nanocomposites reinforced by two-dimensional (2D) nanomaterials are highly attractive because of their enhanced comprehensive performances, such as thermal,1–3 mechanical,4,5 and electrical properties,6 as well as fire safety.7–10 Recently, there has been an increasing interest in graphene-like 2D nanomaterials, i.e., hexagonal boron nitride (HBN), because of its unique structure and outstanding properties, such as excellent mechanical properties, thermal conductivity, and electrical insulation, as well as superb oxidation resistance.11–14 With these extraordinary characteristics, HBN is regarded as a promising nanoadditive to fabricate high-performance polymer nanocomposites. Owing to the barrier effect and catalytic action, 2D HBN has been demonstrated as a promising flame retardant and smoke suppressant for polymer materials.15,16 However, the application of HBN in polymer nanocomposites is usually limited by difficult delamination and poor dispersion of HBN in the polymer matrix due to the strong layered interaction in bulk HBN. Therefore, it is necessary to explore an effective approach to achieve exfoliation and functionalization of HBN. Liquid exfoliation is widely used to produce HBN nanosheets in scalable quantities.17,18 Unfortunately, the obtained bare HBN nanosheets are easy to restack and incompatible with the polymer matrix, thus, the desirable reinforcing effect is hardly achieved by directly introducing the stacked HBN into the polymer matrix. Recently, Cui et al.19 reported large-scale thermal exfoliation and functionalization of HBN via a simple thermal oxidation process. After thermal treatment, there are many hydroxyl groups on the surface and edges of functionalized HBN (BNO) which is hydrophilic, resulting in superior dispersion of BNO in water. Such process provides a simple approach to exfoliate and functionalize HBN for applications in polymer nanocomposites.
HBN–polymer nanocomposites have been extensively developed in terms of enhanced thermal conductivity, thermal stability, and mechanical properties. However, up to now, only a few efforts have been made to fabricate well-dispersible 2D HBN nanomaterials in polymers with outstanding flame-retarded properties. Gu et al. first incorporated a novel hybridized multifunctional filler (CPBN), cyclotriphosphazene/HBN hybrid (CPBN) functionalized with hexachlorocyclotriphosphazene and p-phenylenediamine into bismaleimide/o,o′-diallylbisphenol A resins, achieving superior thermal conductivity, thermal stability, and flame retardancy. In spite of the improved properties, the CPBN is not well exfoliated in solvents, which is not an ideal enhancer due to the poor dispersion. In our previous work, thermal-exfoliated HBN was synthesized by thermal treatment, accompanying a subsequent sol–gel process to enhance fire safety of epoxy resin (EP). Although the thermal stability, flame retardancy, and smoke suppression of the EP nanocomposites were significantly improved, the procedure was complicated. More importantly, such an approach is not suitable to prepare flame retarding thermoplastic materials. More recently, ordered alignment of super paramagnetic zinc ferrite (ZF) decorated boron nitride nanotube (BNNT) interaction. The well-ordered ZF–BNNS nanoadditive remarkably reduced the peak of heat release rate (PHRR) (48.5%), peak smoke production release (46.0%), and carbon monoxide production (66.6%), respectively. The well-aligned BNNS functions as a physical barrier to slow down the release of gaseous pyrolysis products via the so-called “tortuous path” effect, while ZF increases the synergistic effect by promoting carbonization and char layer formation. Despite the progress in HBN-based flame retardant polymer nanocomposites, manipulating the surface properties of HBN with suitable modifiers which can form strong interfacial adhesive with most polymers is still necessary for general polymeric materials.

Polyaniline (PANI) with a conjugated structure has been used as a flame retardant additive for polymers due to its char formation ability. Guo et al. demonstrated that PANI could serve as a coupling agent to improve the dispersion state of nanoadditives within the epoxy matrix as well as enhance the interfacial adhesion by forming covalent bonding between PANI and epoxy chains. In previous work, mechanically tough PANI–BNNTs films were obtained through the strong PANI–boron nitride nanotube (BNNT) interaction. Recently, the construction of PANI/2D nanomaterial hybrids, such as PANI/graphene and PANI/MoS2, has been reported, whereas most of the efforts have been focused on the electrical properties and catalysis performances of these hybrids. Because of the conjugated structure and adjustable morphology, it was speculated that PANI could directly deposit on BNO nano-sheets to promote the dispersion state of hybrid sheets and strengthen the interface adhesion from PANI to general polymers, such as multi-aromatic polystyrene (PS) and polar thermoplastic polyurethane (TPU). However, to the best of our knowledge, the surface manipulation of HBN and the synergistic effect of PANI–BNO hybrids upon reducing the fire hazards of polymer nanocomposites have not been reported yet.

In this work, we presented a facile strategy for in situ preparation of PANI–BNO hybrid sheets by the heterogeneous polymerization process, where thermal-exfoliated HBN (BNO) was prepared according to our reported method. Benefiting from the high specific area, BNO nanosheets could act as a template to induce the growth of PANI. The thermal properties and flame retardancy of both TPU and PS nanocomposites were investigated and the possible flame retarding mechanism was proposed.

2. RESULTS AND DISCUSSION

2.1. Structure and Thermal Analysis of HBN and its Derivatives. The chemical composition on the surface of HBN, BNO, and PANI–BNO was investigated by X-ray photo-
electron spectroscopy (XPS) (Figure 1a). Four peaks at approximately 397.5, 190.3, 284.2, and 532.8 eV corresponding to N 1s, B 1s, C 1s, and O 1s, respectively, are observed in the XPS spectrum of HBN. The XPS spectrum of BNO is similar to that of HBN, while the elemental contents are different (see Table S1, Supporting Information). Obviously, the oxygen atom percentage for BNO (7.5%) is much higher than that of HBN (2.2%), due to the presence of hydroxyl groups on the surface of BNO. Noticeably, the carbon atom content of PANI−BNO is much higher than that of BNO due to the incorporation of carbon-rich PANI (49.2% for PANI−BNO vs 7.1% for BNO).

Figure 1b shows the X-ray diffraction (XRD) patterns of HBN, BNO, and PANI−BNO. Typical peaks at 26.6, 41.7, 44.0, 50.2, 55.1, and 76.0° are indexed as (0 0 2), (1 0 0), (1 0 1), (1 0 2), (0 0 4), and (1 1 0) planes of HBN, respectively.16 Compared to HBN, BNO exhibits a new peak at 27.9°, resulting from B(OH)3 (010),29 further confirming the formation of hydroxyl groups. Different from BNO, the characteristic (0 1 1), (0 2 0), and (2 0 0) crystal planes of polyaniline (PANI) appear in the XRD pattern of PANI−BNO.30 Fourier transform infrared (FTIR) spectroscopy was employed to further confirm the structures of HBN, BNO, and PANI−BNO. The FTIR spectrum of HBN reveals two strong absorptions at 1370 and 815 cm\(^{-1}\) corresponding to the B−N stretching and deformation vibrations, respectively. By hydroxylation, a new peak at 3210 cm\(^{-1}\) ascribed to O−H stretching vibrations appears. For the FTIR spectrum of PANI−BNO, the intense peaks at 1581 and 1130 cm\(^{-1}\) can be correlated to the quinoid structure of PANI. The peak at 1497 cm\(^{-1}\) is attributed to benzenoid rings. The peak at 1291 cm\(^{-1}\) is due to the C−N stretching of secondary aromatic amines.31−33 The thermal stability of HBN, BNO, and PANI−BNO was investigated by thermogravimetric analysis (TGA) (Figure 1d). HBN is highly thermally stable with little weight loss until 700 °C. By contrast, BNO begins to lose weight at low temperature i.e., 200 °C, resulting from the removal of unstable hydroxyl groups at the surface, while 94.4 wt % residue is left at 700 °C. After the growth of PANI on BNO, PANI−BNO undergoes two-stage degradation, corresponding to the PANI. At 700 °C, the weight residue is approximately 66.6 wt %. On the basis of the results and discussion aforementioned, it can be concluded that the hierarchical PANI/BNO hybrids have been successfully prepared.

2.2. Morphology and Dispersion. Both scanning electron microscopy (SEM) and transmission electron microscopy
(TEM) were employed to observe the morphology of HBN, BNO, and PANI–BNO. Figure 2a shows the thick layered structure of bulk HBN with micro-dimension, and the surface and edge of HBN are very smooth. After thermal treatment and exfoliation, large amounts of very thin BNO sheets are observed (Figure 2b). Compared to BNO, the edges of PANI–BNO nanosheets (Figure 2c) become much rougher and some particles are distributed on the surface of the nanosheets. Similar results are further verified by TEM. Bulk stackable sheets, ultra-thin nanosheets, and rough and particle-loaded nanosheets are respectively demonstrated for HBN, BNO, and PANI–BNO. These results indicate that the surface of BNO has been functionalized with PANI via in situ polymerization. The dispersion and interfacial interaction of PANI–BNO within polymeric materials are critical to fabricate advanced flame retarding nanocomposites. Figure 2g–j show TEM images of BNO/PS, PANI–BNO/PS, BNO/TPU, and PANI–BNO/TPU, respectively. Figure 2h reveals the uniform dispersion of PANI–BNO in PS with the formation of exfoliated and intercalated structures. PS is a nonpolar polymer with aromatic-rich structures. Thus, such excellent dispersion is due to the strong adhesive of PANI to PS caused by the π–π interaction. Conversely, BNO nanosheets could not achieve ideal distribution within the PS matrix while some agglomerations are observed. For TPU/PANI–BNO nanocomposites, PANI–BNO sheets with mainly exfoliated structures are dispersed in the matrix. Through thermal exfoliation and subsequent functionalization with PANI, the surface of PANI–BNO is polar, which is beneficial to the dispersion of nanosheets in the polar TPU matrix by electrostatic interaction. Therefore, PANI–BNO with polar groups and rich aromatic structures improves the compatibility and interfacial interaction of HBN within both polar and nonpolar matrices by preventing the restacking and agglomeration.

2.3. Thermal Stability of Polymer Nanocomposites.

Thermal degradation behavior of polymer materials is closely related to their combustion performance. TGA has been widely employed to investigate thermal degradation behavior of polymer materials.34–36 The thermal stability and degradation behaviors of PS, TPU and their corresponding nanocomposites were evaluated by TGA, and the detailed data are listed in Table 1. $T_{0.05}$ and $T_{0.5}$ are defined as the temperatures at 5 and 50% weight loss, respectively. Neat PS undergoes one-stage thermal decomposition with nothing left at 700 °C under nitrogen, and the $T_{0.05}$ and $T_{0.5}$ is 397 and 430 °C, respectively. Both PS/BNO and PS/PANI–BNO show similar degradation behavior to neat PS, but the thermal stability of PS/PANI–BNO is higher than the other two samples, demonstrated by the higher $T_{0.05}$ and $T_{0.5}$. The improved thermal stability is further verified by the increased residue at 700 °C (1.8 vs 0.0 wt %). Noticeably, the only small amount of residue is obtained for PS/BNO (0.1 wt %), indicative of the heterogeneous dispersion of BNO in PS. For the thermal-oxidative degradation of PS and its nanocomposites, all the PS samples exhibit lower degradation temperature compared to these counterparts under nitrogen, but a higher increase in $T_{0.05}$ and $T_{0.5}$ are observed with the incorporation of PANI–BNO, which exhibit 14 and 19 °C improvement relative to neat PS, respectively. As expected, PS/PANI–BNO shows better thermal stability than PS/BNO. The so-called tortuous path effect of nanosheets, delaying the escape of volatile degradation products, and the formation of additional char residues are the main reasons for the enhanced thermal stability. Different from the thermal stability change, the addition of BNO or PANI–BNO has a negligible impact on the degradation rate of PS under nitrogen (See Figure S1, Supporting Information), and even adverse impact on the mass loss rate under air. This phenomenon is probably attributed to the catalytic activity of HBN. However, the degradation rate of PS/PANI–BNO under air is lower than that of PS/BNO, indicating the better barrier effect of nanosheets. Similar to PS and its nanocomposites, the presence of nanoadditives does not change the degradation pathway of TPU, while there are also increases in the $T_{0.05}$ and $T_{0.5}$ under nitrogen. By contrast, adding PANI–BNO promotes the char formation of TPU from 2.9 wt % for neat TPU to 6.0 wt % (nitrogen), indicating that PANI–BNO is a more significant charring effect in TPU than PS, which may cause larger reduction in the total heat release. It is noteworthy that the residues of TPU nanocomposites against thermal oxidation over 450 °C is improved, suggesting the superior thermal stability at elevated temperatures. Interestingly, both PANI–BNO and BNO reduce the degradation rate of the corresponding TPU nanocomposites, and PANI–BNO contributes to a larger reduction than BNO resulting from the ideal dispersion. This result is indicative of the main contribution of the barrier activity of BNO over the catalytic effect. Overall, the TGA results demonstrate that PANI–BNO improves the thermal stability and promotes the charring of polymer substrates, especially TPU.

2.4. Combustion Performance of Polymer Nanocomposites.

Cone calorimeter (CC) has been demonstrated to provide data that correlate well with medium to full-scale fire tests.37–40 The combustion performance of pristine polymers and their nanocomposites was evaluated by cone calorimeter, as shown in Figures 3 and 4, and the corresponding parameters are summarized in Table 2. Pristine PS is flammable and releases large amounts of heat with the peak of heat release rate (PHRR) of 896 kW/m² once ignited. Compared to pure PS, PS/BNO shows notable flame retardancy, corresponding to a 28.9% reduction in the PHRR with much lower time to ignition (TTI), probably due to the high thermal conductivity and catalytic effect of BNO. The barrier effect of the BNO nanosheets is responsible for the increased full width at half maximum for the HRR curves of PS/BNO nanocomposites, which is confirmed by the negligible change of total heat release (THR) values (Figure 4c). A higher reduction in the PHRR (31.3%) relative to PS/BNO is observed for PS/PANI–BNO, suggesting the lower fire hazards. The reduction is attributed to the fact that the barrier effect will prolong the release of combustible gases derived from PS, but the total heat release is not reduced. By contrast, the PHRR of TPU/PANI–BNO is decreased by 32.6% relative to neat TPU (Figure 4b). Noticeably, a decrease of 8.9% in THR is observed, indicating that PANI–BNO is more
efficient on promoting the char formation of TPU than PS, as revealed by TGA results.

Fire hazards of polymeric materials are usually composed of thermal hazards and nonthermal hazards. Smoke and toxic gases belong to the nonthermal hazards, which are mainly responsible for fire deaths.41,42 Therefore, reducing smoke and toxic gases release polymeric materials during a fire are of vital importance for rescue. Figure 5 plots the SPR and TSP curves of PS and its nanocomposites (a, c), and TPU and its nanocomposites (b, d). The pSPR, TSP, pCOP, and pCO₂P values for polymer nanocomposites follow the reduction change trend similar to the PHRR (Figures S2 and S3, Supporting Information). The additional char formation and barrier effect of PANI–BNO leads to the reduction of total smoke release, while the presence
of PANI−BNO has little effect on the CO production, implying the incomplete combustion. All these reductions in smoking and toxic gases are attributed to multiple synergistic catalytic and barrier action of PANI−BNO.

2.5. Flame Retardant Mechanism. To well understand the flame retardant mechanism, residue analysis of samples after combustion are very crucial. Figure 6 shows the digital photos of char residues for all samples after cone calorimeter tests. Neat PS (Figure 6a) has no residue left, while both PS/BNO and PS/PANI−BNO (Figure 6b) produces a little char due to the presence of temperature-tolerant HBN. Because of the intumescent characters of TPU during burning, all the TPU samples (Figure 6d−f) have large amounts of residues, which are not much different from each other. To further analyze the quality of these residues, FTIR and XRD were used to investigate their components and structures. Figure 6 presents FTIR spectra (g) and XRD patterns (h) of these char residues for PS/PANI−BNO, TPU, and its nanocomposites after cone calorimeter tests. The FTIR spectra of the char residues for PS/PANI−BNO, TPU/BNO, and TPU/PANI−BNO reveal the peaks at approximately 750 cm$^{-1}$ due to multi-aromatic structure. Different from the char structure of TPU, PS/PANI−BNO, TPU/BNO, and TPU/PANI−BNO exhibit absorption peaks at 1375 and 815 cm$^{-1}$ due to the vibration of B−N, indicating the presence of HBN. In the XRD pattern of the residue for pure TPU, a weak and broad diffraction peak at approximately 23° is attributed to (002) diffraction of graphite. These XRD patterns of PS/PANI−BNO, TPU/BNO, and TPU/PANI−BNO reveal the diffraction peaks for (0 0 2), (1 0 0), (1 0 1), (1 0 2), (0 0 4), and (1 1 0) planes of HBN, respectively. Hence, the char layer composed of multi-aromatic carbon and temperature-tolerant HBN functions as an effective barrier to retard mass and heat transfer.

TG-IR was used for the real-time detection of the evolved volatile products of PS and its nanocomposites during the thermal degradation process. The FTIR spectra of the volatile pyrolysis products emitted from PS, PS/BNO, and PS/PANI−BNO nanocomposites are observed from the FTIR spectra. In addition, the presence of BNO and PANI−BNO delays the degradation of the PS substrate, which is consistent with the TGA analysis under nitrogen.

Table 2. Cone Calorimetry Data of PS, TPU, and Their Nanocomposites$^{a}$

| samples            | TTI (s) | PHRR (kW/m$^2$) | THR (MJ/m$^2$) | pSPR (m$^3$/s) | TSP (m$^2$) | pCOP (g/s) | pCO$_2$P (g/s) |
|--------------------|---------|-----------------|----------------|---------------|------------|-----------|---------------|
| PS                 | 65      | 896             | 80.6           | 0.47          | 37.8       | 0.038     | 0.92          |
| PS/BNO             | 36      | 637             | 81.7           | 0.31          | 36.8       | 0.023     | 0.60          |
| PS/PANI−BNO        | 35      | 616             | 79.4           | 0.28          | 36.1       | 0.021     | 0.61          |
| TPU                | 62      | 1400            | 69.1           | 0.22          | 11.6       | 0.015     | 1.52          |
| TPU/BNO            | 56      | 1081            | 63.7           | 0.16          | 11.1       | 0.012     | 1.05          |
| TPU/PANI−BNO       | 51      | 944             | 61.7           | 0.24          | 10.1       | 0.015     | 1.03          |

$^{a}$TTI: time to ignition; PHRR: peak heat release rate; THR: total heat release; TSP: total smoke production; pSPR: peak smoke production rate; pCOP: peak CO production; pCO$_2$P: peak CO$_2$ production.

Figure 5. SPR and TSP vs time curves of PS and its nanocomposites (a, c), and TPU and its nanocomposites (b, d).
chemical inertness of HBN, it mainly functions in physical modes, while the PANI on the surface plays its role in chemical modes by both self-charring and reacting with the char from PS or TPU. The proposed flame-retarded mechanisms are illustrated in Figure 8. As clearly demonstrated in the sections above, HBN nanosheets can improve the thermal stability of the char. For intumescent char layers, i.e., TPU, high specific surface area and thermal stability of PANI−BNO nanosheets are responsible for the increase in the barrier effect and mechanical properties of the formed char. Superior barrier performance of HBN can also retard the release of combustible decomposition products and limit the supply of fuel and oxygen. Moreover, the catalytic action of HBN leads to the reduction of the smoke and
nanocomposites, Shi et al. reported a large reduction in the stability of the polymer matrix. For to reduce the PHRR, but simultaneously lower the thermal GNS (Zhou et al.), and montmorillonite (MMT, Cai et al.) were also not e double hydroxide (Matusinovic et al.) were also not e.

Obviously, graphite nanosheets (GNPs, Quan et al.), Co3O4 was very di triple layered zirconium phosphate (Tai et al.), and layered

CO release, as seen from the cone calorimeter results. PANI on the surface not only improves the dispersion of BNO by non-covalent interaction with the polymer matrix reaching an ideal barrier effect of nanosheets, but also reacts with char residues from polymer substrates under high temperature to improve char quality, which further reinforces the barrier effect of char layers.

2.6. Comparison on Thermal Stability and Flame Retardancy. To highlight the large progress achieved by this strategy, the comparison of flame retardancy of PS, TPU, and their 2D nanomaterial-based nanocomposites in this work to the results reported in the previous literature is summarized in Table 3. MCC refers to the micro-combustion calorimeter, which was used to investigate polymer combustion at a small scale (5–10 mg). Zhou et al. revealed that pristine graphene nanosheets (GNS) or MoS2 exhibited a small reduction in the PHRR. Cetyltrimethyl ammonium bromide (CTAB)-modified MoS2 caused serious deterioration of the thermal properties of PS. Bao et al. improved flame retardancy efficiency of graphite oxide (GO) by grafting phosphazene units, but the thermal stability was reduced. More importantly, GO is much more expensive than HBN, accompanying a large amount of pollutant output in the preparation process. Other 2D nanomaterials, such as organic-modified layered zirconium phosphate (OZrP, Zhang et al.), layered zirconium phosphate (Tai et al.), and layered double hydroxide (Matusinovic et al.) were also not effective to reduce the PHRR, but simultaneously lower the thermal stability of the polymer matrix. For flame-retarded TPU nanocomposites, Shi et al. reported a large reduction in the PHRR (37%) with improved thermal stability (16.1 °C increment in T1/2) by using CuCo2O4-loaded graphitic carbon nitride (C-CuCo2O4-7). However, other loading of CuCo2O4 on g-C3N4 had an adverse effect on the thermal stability, thus, it was very difficult to control the loading to achieve ideal flame-retarded TPU nanocomposites with improved thermal stability. Obviously, graphite nanosheets (GNPs, Quan et al.), Co3O4–GNS (Zhou et al.), and montmorillonite (MMT, Cai et al.) are not effective enough to reduce the PHRR. Although ultrathin β-Co(OH)2 nanosheets were demonstrated to be an efficient nanoaditive to improve the fire safety of TPU, the greatly reduced thermal properties of the TPU matrix was not suitable for practical applications. Herein, both thermal stability and fire safety of PS- and TPU-based nanocomposites are considerably improved when the PANI–BNO is added into PS and TPU. Because the surface of BNO is manipulated with PANI via in situ deposition, and PANI–BNO forms non-covalent bonds to PS or TPU, PANI–BNO is reasonably believed to be well dispersed in these polymer materials. Therefore, the excellent dispersion of PANI–BNO, and synergistic flame retardancy between BNO and PANI result in the high fire safety and thermal stability of PS and TPU nanocomposites.

3. CONCLUSIONS

The surface of thermal-exfoliated hexagonal boron nitride was facilely manipulated by in situ depositing PANI, which was compatible with multi-aromatic PS and polar TPU. Through the combination of PANI and BNO preventing their aggregation while maintaining the layer-like structure, the superior dispersion of PANI–BNO in polymeric materials were achieved. Benefiting from the uniform dispersion of nanosheets with an ideal barrier effect, the thermal stability of PS and TPU nanocomposites (T20%, T5%) was improved, which was much better than other reported 2D nanomaterial-based reinforced polymers. Incorporating 3 wt % PANI–BNO hybrid showed an obvious suppression effect on fire hazards of PS and TPU in terms of the reduced PHRR and low smoke yield. These obvious improvements resulted from the multiple synergistic effects (synergistic dispersion, char formation, catalytic effect, and barrier effect) of PANI–BNO hybrids within polymer nanocomposites. Such a simple strategy will be promising for 2D nanomaterial functionalization with potential application in flame retarding general polymeric materials.

4. EXPERIMENTAL SECTION

4.1. Raw Materials. PS was obtained from BASF-YPC Co., Ltd. (China). TPU was obtained from Baoding Bangtai Chemical Industry Co., Ltd. (Baoding, China). HBN powder with a purity of 99.9% was obtained from Shandong Mingyao new materials Co. Ltd. (Shandong, China). N,N-dimethylformamide (DMF, AP) (DMF, AR), absolute ethanol (AR), sodium dodecyl sulfate (SDS), and aniline were all purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).
4.2. Preparation of PANI−BNO. BNO was prepared according to the method described in our prior work.13 The PANI−BNO hybrid was prepared by in situ polymerization, using SDS as the surfactant. More specifically, 0.3 g of BNO was dispersed in 500 mL of deionized (DI) water assisted with ultrasonic treatment for 2 h. Subsequently, 0.5 g of SDS and 0.9 g of aniline were introduced into the above suspension and the reaction system was kept at room temperature for 24 h. After completion of the reaction, the suspension formed was centrifuged, washed, and dried, and the PANI−BNO hybrid was collected. The preparation process of PANI−BNO hybrids are illustrated in Scheme 1a.

4.3. Preparation of PANI−BNO/Polymer Nanocomposites. PANI−BNO/polymer nanocomposites were fabricated by a co-coagulation plus compression molding technique, as shown in Scheme 1b. The loading of nanoadditive for all the nanocomposites was kept at 3 wt %. Prior to manufacturing, PS and TPU were dried in an oven at 80 °C, for 24 h to remove residual water. Briefly, the preparation of PANI−BNO/polymer nanocomposites was described as follows. 1.5 g of PANI−BNO was dispersed in 200 mL of DMF with sonication for 1 h. Subsequently, 48.5 g of PS or TPU pre-dissolved in DMF was introduced into PANI−BNO dispersion until the formation of uniform dispersion. Finally, the above solution was poured into DI water accompanying slight magnetic stirring. The flocculate obtained was dried in an oven at 100 °C for 12 h to remove the residual solvent. The sample was hot-pressed at 180 °C and 10 MPa for 10 min into sheets of appropriate size.

4.4. Characterization. Chemical structures of samples were studied by Fourier transformed infrared (FTIR) spectroscopy using a Nicolet 6700 spectrophotometer (Nicolet Instrument Co.). X-ray photoelectron spectroscopy (XPS) was employed to investigate the surface chemical composition of samples using a VG Escalab Mark II spectrometer equipped with an Al Kα excitation radiation (hν = 1486.6 eV). X-ray diffraction (XRD) patterns of samples were recorded on an X-ray diffractometer (Rigaku Co., Japan) with Cu Kα radiation (λ = 0.1542 nm). Morphology and dispersion of samples was observed using a scanning electron microscope (SEM) and a transmission electron microscope (TEM). SEM images were acquired from a FEI Sirion 200 scanning electron microscope at an acceleration voltage of 10 kV. TEM was evaluated on a JEOL JEM-2100 instrument with an acceleration voltage of 200 kV. Prior to observation, power samples were dispersed in DI water assisted with ultrasonic treatment and solid samples with dozens of microns in thickness were obtained using an ultramicrotome. Thermogravimetric analysis (TGA) was conducted on a TGA Q5000IR thermo-analyzer (TA Instruments Inc.) at a heating rate of 20 °C/min. Combustion performance of samples was evaluated using a cone calorimeter (Fire Testing Technology, UK) under an incident flux of 35 kW/m². All the samples with the dimensions of 100 × 100 × 3 mm³ are required for the tests. Thermogravimetric analysis-infrared spectrometry (TG-IR) was performed using a PerkinElmer TGA analyzer coupled with a Fourier transform infrared spectrophotometer at a heating rate of 20 °C/min under nitrogen. The temperature between stainless steel transfer pipe and gas cell were maintained at 230 °C to avoid the condensation of pyrolysis products. Raman spectroscopy was performed using a LabRAM-HR Confocal Raman Microprobe (Jobin Yvon Instruments, France) with a 514.5 nm argon ion laser.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02316.

Element content of HBN, BNO, and PANI−BNO measured from XPS analysis (Table S1); DTG curves of PS and its nanocomposites (a, b) and TPU and its composites (c, d) under nitrogen and air, respectively (Figure S1); CO production and total CO release vs time curves of PS and its nanocomposites (a, c), and TPU and its composites (b, d) (Figure S2); CO₂ production and total CO₂ release vs time curves of PS and its nanocomposites (a, c), and TPU and its composites (b, d) (Figure S3) (PDF)

**AUTHOR INFORMATION**

*E-mail: yubin2-c@my.cityu.edu.hk (B.Y.).
*E-mail: weyang@ustc.edu.cn (W.Y.).
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The authors declare no competing financial interest.

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