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PMMA functionalized boron nitride sheets as nanofillers

Zhenhua Cui,[a] Andre P. Martinez[b] and Douglas H. Adamson*[a,b]

We report the functionalization of hexagonal boron nitride (hBN) with polymer chains. These chains are grown by atom transfer radical polymerization (ATRP) from hBN following thermal treatment. When used as a nanofiller, the material shows improved dispersion resulting in significantly improved toughness as compared to pristine hBN without polymer functionalization. The polymer functionalized BNO is also characterized by TGA, FTIR and FESEM.

Hexagonal boron nitride (hBN) is a synthetic material commonly used as a high temperature lubricant or as an additive in cosmetics.[1] It is similar in many ways to graphite: it has a stacked sheet morphology, high thermal conductivity, and excellent mechanical strength.[2] However, it is an electrical insulator and is more chemically inert and temperature stable than graphite.

Similar to other high aspect ratio stacked materials, in order to fully utilize its extraordinary properties in composites[3-8], the sheets must be exfoliated and be well dispersed in the matrix. Thus the tendency for the sheets to aggregate or restack must be suppressed. In the case of graphite, a common route to controlling aggregation in polymer composites is to oxidize the graphite to graphene oxide (GO), lessening the sheets' tendency to form stacked structures.[9] The oxidation conditions used for graphite do not work with hBN however, necessitating a different approach for dispersing the sheets in a composite. Grafting polymer chains to the particle surface is one such approach. In this article we describe the synthesis and characterization of hBN sheets with grafted polymer chains and their incorporation into a nanocomposite. Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) are used to analyse the grafted sheets, and the mechanical properties of composites are shown to be superior to those of control samples.

Previous studies of hBN composites[10-12] have started with hBN materials exfoliated to various degrees by mechanical means without chemical functionalization. These fillers are normally referred to as boron nitride nanosheets (BNNS). Zhi et al. reported fabrication of PMMA/BNNS composites with unfunctionalized hBN nanosheets.[11] Coleman et al. reported composite films of BN using a solution sonication method involving 48 hours of sonication followed by filtering and adding the filter cake to thermoplastic polyurethane dissolved in DMF. An improvement in modulus was reported at 5 and 20% loadings at the cost of reduced strain at break.[5] While encouraging, these approaches rely on extended mechanical treatment of the BN to produce exfoliated material at very high dilution, and do not utilize grafted polymer chains to aid in dispersion. Boron nitride nanotubes have also been investigated,[13] with some success. Direct mixing of the tubes into a PMMA matrix resulted in an increased modulus, but a decrease in strength and elongation.

In order to attach polymer chains to hBN, the sheets must first be functionalized, but due to boron nitride's chemical inertness, reports of hBN functionalization[14-17] are scarce. The examples we are aware of are the work by Bhimanapati et al.[16] using a mixture of phosphoric and sulphuric acid and the work of Sainsbury et al.[14] by solution-phase oxygen radical functionalization. While Bhimanapati did not report the growth of polymers from their functionalized hBN, the work of Sainsbury described the stoichiometric addition of peroxides to BNNS that enabled the addition of isocyanate functional groups to the hBN. These reactive groups were then proposed to react with the polymer matrix, specifically polyurethane.

Our approach is fundamentally different. We start with hydroxylated hBN (BNO) produced at a large scale by an oxidation method published previously.[15] We then grow polymers from the BNO sheets as outlined in Scheme 1. This approach allows for the polymerization of a wide variety of monomers from BN sheets by controlled radical polymerization, leading to a wide

choice of polymer matrices into which well dispersed BN nanofillers can be mixed.

Initiator is attached through the hydroxyl groups by first adding 4, 4'-Methylene di-*p*-phenyl diisocyanate (MDI) in excess, resulting in isocyanate functional groups on the sheets. An excess is used to avoid the difunctional MDI linking the sheets together. This is

followed by adding water to form aniline groups. The addition of α-bromoisobutyryl bromide (BiBB) then places an ATRP initiator on the sheets. FTIR is used to analyse the intermediate compounds as shown in Figure S1 and Figure S2.
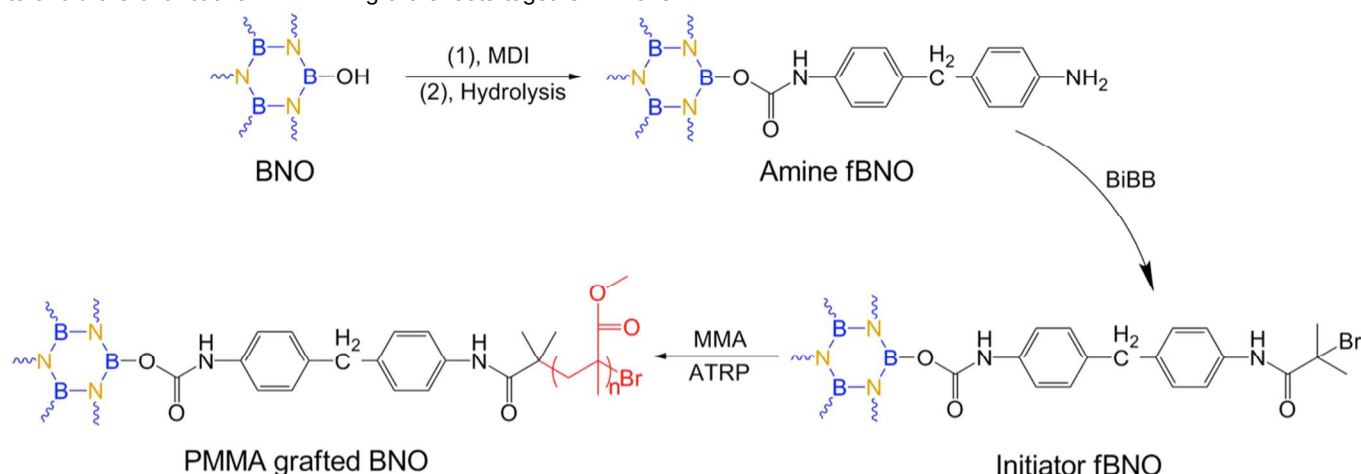
Scheme. 1 Reactions to graft PMMA from BNO

Polymerization of methyl methacrylate to form poly(methyl methacrylate) (PMMA) from the attached initiator is accomplished as described in the experimental section. The polymer-functionalized sheets are then washed with tetrahydrofuran (THF) several times to remove any polymer not attached to the sheets. The wash containing unattached polymer is analysed by gel permeation chromatography (GPC) to estimate the molecular weight of the PMMA chains attached. GPC indicates a molecular weight of 174k and polydispersity of 2.52 (Figure S5). As a control, PMMA is prepared by the ATRP of MMA using the same procedure but without the sheets, giving a MW of 199 K and a PDI of 1.15. The high polydispersity in the BNO system compared with the control PMMA reflects the effect of growing from nanosheets versus from solution, and similar result has been observed when growing polymer chains from graphene nanosheets.[18]
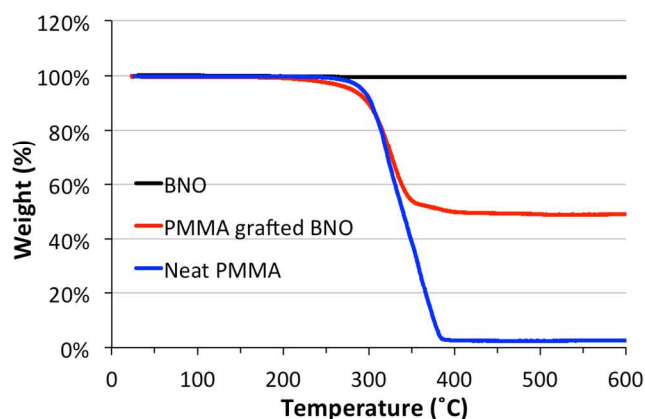
In order to determine the mass of polymer grafted to the sheets, TGA is used and the results shown in Fig. 1. As the base BNO is stable in air up to 800 °C, any weight loss below that temperature is due to the degradation of PMMA. We find that 53% by mass of the grafted and washed material is PMMA. For comparison, Fig. 1 also shows that no mass loss is observed with BNO and pure PMMA displays complete mass loss. SEM images of the grafted sheets after TGA analysis show nanosheets with the typical morphology of BNO (Figure S6).
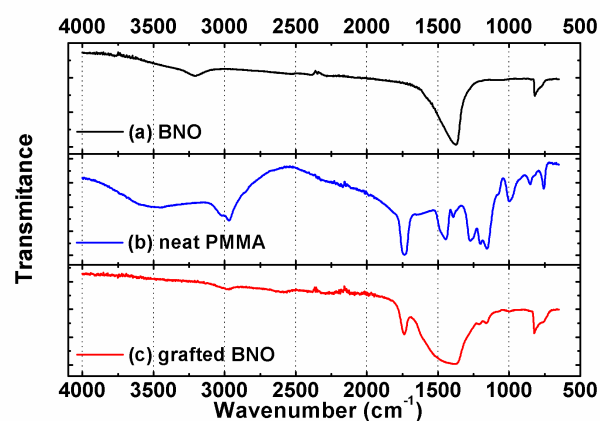

Fig.2 FTIR spectra of (a) BNO, (b) neat PMMA and (c) PMMA grafted BNO.

Fig.1 TGA of BNO, PMMA grafted BNO and neat PMMA

FTIR spectra of the grafted material and controls are shown in Fig. 2. The upper spectra, Fig. 2a, shows the starting BNO

material, consistent with previously published work,[15] having the characteristic peaks corresponding to B-N in-plane stretching at 1370 cm^{-1}, B-N-B out of plane at 810 cm^{-1} and the B-O-H peak at ~3200 cm^{-1}. Fig. 2b is the spectrum of neat PMMA, shown for comparison, with a strong peak at ~1700 cm^{-1} from the carbonyl group and weaker peaks around 1150 cm^{-1} and 3000 cm^{-1} assigned to C-O-C single bond stretching vibration and C-H stretching. The BNO with PMMA chains attached after washing with THF to remove unattached chains is shown in Fig. 2c. The spectrum is dominated by the characteristic BN peak at 1370 cm^{-1}, but also contains the carbonyl peak near 1700 cm^{-1} observed in the neat PMMA. Repeated washings with THF result in no change in the spectrum. In the filtrate, shown in Figure S3, no BN peak is found and the spectrum is nearly identical to pure polymer from the control reaction. Figure S4 shows the material after heating to 600 °C. The spectrum is identical to that of the starting BNO. Additionally, the FTIR reveals the reappearance of the B-O-H peak at ~3200 cm^{-1}. This peak is not seen in the FTIR of the grafted BNO, but is visible in the BNO prior to grafting, supporting the contention that the functionalization reaction occurs through the hydroxyl groups on the BNO.
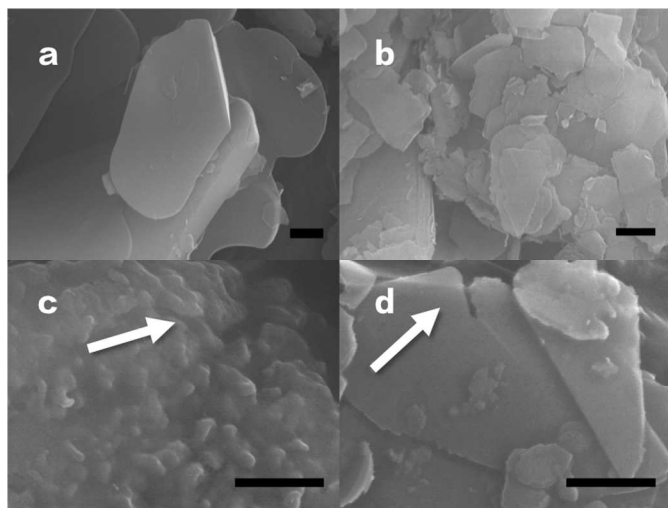

Fig.3 SEM of (a) pristine hBN, (b) BNO, (c) PMMA grafted BNO and (d) a mixture of BNO and PMMA dissolved in THF and then precipitated out by methanol. White arrows point out the polymer coated smooth edges of grafted BNO and sharp edges on unfunctionalized BNO. Another difference is rough surfaces of PMMA chemically bonded BNO and the flat surfaces of unfunctionalized BNO sheets in the mixture. The scale bar is one micron.

The presence of PMMA covalently attached to the BNO sheets is also supported by SEM images of BNO and PMMA grafted BNO shown in Fig. 3 (b) and (c). The functionalization of the sheets with ATRP initiator makes no observable difference in the sheet morphology as show in Fig. S7. After the polymerization reaction, the grafted BNO sheets are coated by PMMA as seen in SEM images (Fig. 3(c) and Fig. S6). Grafted BNO sheets appear to have a continuous polymer coating with smooth edges and lumpy surface structure in contrast to the sharp edges and flat surface of the starting BNO. In order to be sure the morphology changes are not simply due to physically adsorbed polymer,

50/50 by mass mixture of BNO and neat PMMA in THF is precipitated by methanol. As shown in Fig. 3d, the BNO morphology is similar to the starting BNO (as pointed out by the arrow in Fig. 3 (d)), suggesting that polymer does not adsorb on the sheet surface and that Fig. 3c shows polymer covalently bound to the sheet.
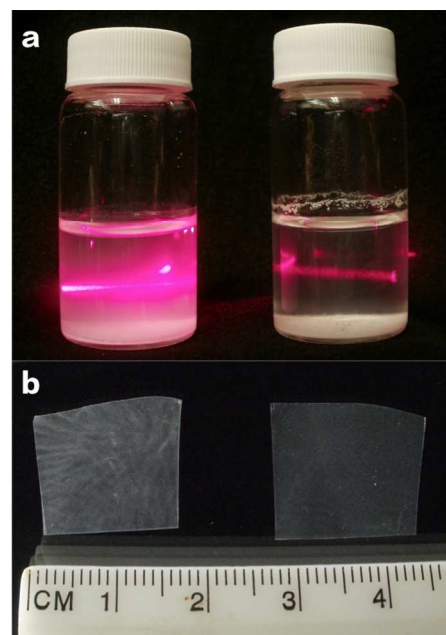

Fig.4 (a) Water suspension of BNO (left) and an equal mass of BNO that has been grafted with PMMA (right). (b) Films of equal thickness of hBN filled PMMA (left) and PMMA grafted BNO filled PMMA (right).

The attachment of polymer chains to the sheets is also seen to result in differences in the suspendablity of the sheets in liquid and their dispersibility in a polymer matrix as compared to controls. It has been shown previously that BNO forms a stable suspension in water, while hBN precipitates.[15] In Fig. 4a, two samples are compared in terms of their ability to form stable suspensions in water. The control on the left is an aqueous suspension of BNO that had been mixed with PMMA in THF, precipitated in methanol, dried, then bath sonicated in water. On the right is an equal mass of BNO that is grafted with PMMA and sonicated in the same manner the control sample in water. Simply mixing with PMMA does not change the hydrophilicity of BNO; after sitting overnight, the sheets are still suspended in water with the PMMA particles precipitated out. Conversely, the grafted BNO is hydrophobic and settles out of suspension. The clear solution implies the PMMA is chemically attached to BNO. The improved dispersion of the nanofiller in a polymer matrix is shown visually in Fig. 4b. BNO without polymer grafting (on the left) and grafted BNO (on the right) are added to PMMA in THF and cast onto glass slides. The aggregated inhomogeneous composite on the left is in sharp contrast to the uniform dispersion of the grafted BNO on the right.

Tab. 1 Tensile test result of PMMA and composites

	Toughness (MJ/m^3)	Young's modulus (MPa)	Elongation (%)
Neat PMMA	7.96	739	24.2
hBN filled	6.68	793	18.9
Grafted BNO filled	13.5	803	34.4

The improved dispersability of the grafted BNO in PMMA leads to superior mechanical properties in grafted BNO/PMMA composites. To demonstrate this, PMMA composites with 1% (w/w) loadings of PMMA grafted BNO are prepared. Two control samples are also prepared using the same procedure; one with neat PMMA without any filler and the other with 0.5% (w/w) unfunctionalized pristine hBN, maintaining the same weight percentage of BN as in the grafted BNO/PMMA composite. To compare the mechanical properties of these three samples, composites are hot pressed into sheets and cut into dog-bone shape tensile bars. Tensile tests are then performed and the results shown in Table 1. Compared with blank PMMA, the grafted BNO filled samples show significant improvements in elongation and toughness as well as an 8.7% improvement in Young's modulus. The effect of ungrafted hBN on the properties of the PMMA is consistent with results found by others[5] in which the addition of hBN to thermoplastic polyurethane leads to an increase in modulus with a corresponding decrease in extension at break.

The improved modulus of the composite is a result of the high modulus of hBN.[19] The force required to deform hBN sheets that are not perpendicular to the stretching direction contributes to the overall force needed to stretch the composite. That the modulus benefits from the nature of hBN, even when not exfoliated or well dispersed,[20] is known from studies of graphene nanocomposites. Such nanosheets result in increased Young's modulus even while reducing the elongation and toughness of the materials.[21] This effect is significantly diminished in control hBN composites, however, compared to the well-dispersed BN sheets with grafted polymer chains. The attached chains are expected to increase the interaction of the nanofillers with the matrix, improving dispersion and strengthening the filler/matrix interface. We find that this effect only exists in the grafted BNO filled composites. Therefore, the mechanism of strengthening is a combination of the high modulus of BN, well dispersed fillers, and increased strength of the filler/matrix interface. Similar results and conclusions have been reported in other filler systems.[14]

The improvement in elongation can be explained by a similar mechanism. The improved dispersity of grafted BNO nanosheets and the interaction of the PMMA matrix and grafted sheets leads to larger deformation prior to ultimate failure, as shown in Tab. 1, where we observe greater elongation for the PMMA/grafted sheets based composites compared with the PMMA/hBN based composites. The grafted filler increases elongation by 42.1%, while the hBN filler actually reduces elongation by 21.9%. This is an important result, and clearly demonstrates a fundamental difference arising from grafted polymer chains on the sheets.

Finally, the toughness of the composites is calculated as the work per unit volume of samples, which is the total area under the stress/strain curve. As shown in Table 1, grafted BNO enhances PMMA considerably, improving toughness by 69.6%, while hBN reduced the toughness of PMMA by 16.1%.

Conclusions

We have developed a method to graft polymer chains to hBN sheets, thus improving the properties of hBN nanocomposites. Owning to the chemical inertness of hBN, the growth of polymer chains from hBN has not been previously reported. The formation of a covalent bond between PMMA and nanosheets is supported by FTIR, changes in the appearance of the sheets after extensive washing, and the lack of suspended polymer functionalized sheets in water as compared to unfunctionalized sheets. The effect of polymer grafting on the dispersion of the nanofillers and on the properties of composites made with these materials is demonstrated by comparison to various controls. Significant increases in Young's modulus, elongation and toughness are observed relative to neat polymer and ungrafted hBN filler.

Experimental Section

Preparation of initiator functionalized hBN

590mg amine functionalized BNO was added to 15ml 1-methyl-2-pyrollidinone, 0.18ml triethylamine, and 72mg 4-dimethylaminopyridine in a scintillation vial. The mixture was chilled on an ice bath, then 0.30ml BiBB was added under a stream of dry N_2. The vial was sealed and the mixture stirred overnight coming without heating. The powder appeared brown but lightened to off-white upon vacuum filtration and rinses with methanol. The powder was dried overnight under vacuum.

Polymerization from hBN sheets

In an N_2 atmosphere glovebox, 108mg copper (I) bromide, 75mg copper (II) bromide, 0.17ml N,N,N',N",N"-pentamethyldiethylenetriamine, and 8.0ml acetone was stirred in a scintillation vial until homogenous. Next, 300mg Initiator functionalized BNO was added to the vial followed by 8.0ml of methyl methacrylate and the mixture was stirred for 19 hours at room temperature. The reaction was diluted with THF and the material collected by vacuum filtration. Free polymer in the filtrate was precipitated in methanol and saved for later analysis. The powder was rinsed with THF and re-filtered several times before drying under vacuum. New FTIR peaks were observed at 1732cm^{-1}, 1199cm^{-1}, and 1155cm^{-1} corresponding to stretching modes of the polymer carbonyl and carbon-oxygen bonds.

Preparation of the composite thin films

For the control with unfunctionalized hBN, 0.05g hBN was added to THF followed by bath sonication for 15 min. 0.95g PMMA was then added and stirred for 3 days, then allowed to sit overnight to let large particles to settle down. Lastly, the solution was cast on a glass plate and dried for two days. Based on the TGA results indicating that the functionalized material was roughly have PMMA by mass, the weight percentage of grafted BNO in PMMA

was doubled to maintain the same percentage of BN sheets in all samples. All mechanical measurements were repeated at least five times with different samples.

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Notes and references

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Electronic Supplementary Information (ESI) available: More information on the details for characterization of reaction intermediates by FTIR, FESEM, GPC and stress-strain curve of composites. See DOI: 10.1039/c000000x/

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