Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

PMMA functionalized boron nitride sheets as nanofillers

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Materials

Hexagonal boron nitride powder (UK Abrasives, Inc.), Methylene di-p-phenyl diisocyanate (MDI) (Acros organics, 98%), α-bromoisobutyryl bromide (BiBB) (Acros, 98%), copper (I) bromide (Strem Chemicals, 98%), copper (II) bromide (Fisher, reagent grade), 4-dimethylaminopyridine (DMAP) (Aldrich, 99%), dimethlyformamide (DMF) (Fisher, certified ACS grade), N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99+%), methanol (Aldrich, 99.8%), and tetrahydrofuran (THF) (Fisher, histological grade) were used without further purification. Acetone (Fisher, histological grade) was dried with $CaSO_4$ then distilled and stored over 3Å molecular sieves. Methyl methacrylate (Aldrich, 99%) was rinsed three times with 5%wt. $NaOH_{(aq)}$ to remove monomethyl ether hydroquinone, three times with distilled water to remove NaOH, then dried with $CaCl_2$, distilled under reduced pressure, and stored over CaH_2 at -32^{o}C. 1-methyl-2-pyrollidinone (NMP) (Fisher, laboratory grade) was dried with CaH_2 then distilled under reduced pressure. Triethylamine (Acros, 99%) was dried with $CaSO_4$, distilled under reduced pressure, and then stored over CaH_2.

Synthesis

Preparation of hydroxylated hBN (BNO)

BNO was prepared by the thermal treatment of hexagonal boron nitride in air. In a typical experimental run, 20 g BN powder was placed in a quartz tube in a tube furnace. The furnace was heated to 1000 °C and held at that temperature for two hours in air. After cooling, the material was washed with hot water and spray dried.

Synthesis of Isocyanate functionalized BNO (fBNO)

800mg BNO and 31g MDI were added into 100ml flask, 3 drops of triethylamine was then added as catalyst. The mixture was heated up to 120^{O}C to react overnight. After reaction is over, white powder was obtained by vacuum filtration, rinsed three times with dichloromethane and dried under vacuum.

Synthesis of Amine fBNO

700mg Isocyanate fBNO was dispersed into about 5ml DMF then added drop-wise while stirring to approximately 100ml distilled water at room temperature. The mixture was degassed to promote isocyanate hydrolysis and allowed to stir overnight. The white powder was collected by vacuum filtration, rinsed several times with acetone and dried under vacuum.

Instruments

FESEM measurements were performed using a JEOL JSM-6335F cold cathode field emission (12 kV) scanning electron microscope. TGA was carried out on a TA Instruments Q 500 Thermogravimetric Analyzer at a heating rate of 10 °C min^{-1} in a platinum pan. IR transmission measurements were conducted on a Nicolet 560 instrument coupled with SpectraTech IR Plan 0044-003 microscope. Gel permeation chromatography (GPC) was performed using a Waters 717 plus autosampler with THF as eluent, a Waters 1515 isocratic HPLC pump, a Jordi fash gel DVB column, and a Varian 380-LC ELS detector. The thin film sample thickness was determined using a thickness gauge (Model LE1000-2, MeasureItAll) as the average of three data points. The composites were hot pressed into sheets and then cut into dog-bone shapes for mechanical tests. Five samples of each composite were prepared and tested. Tensile tests were performed on a computer interfaced Instron-1011 with a 500 N load cell at room temperature. The rate of crosshead motion was 1 mm/min with the data acquisition rate of 10 points per second.

FTIR

FTIR of reaction intermediates were performed to confirm reactions.

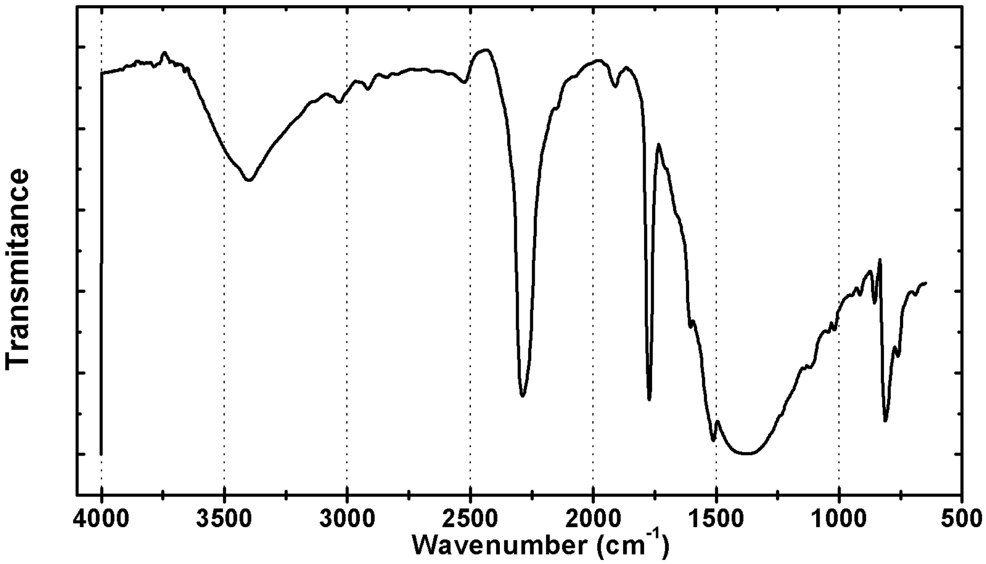

Figure S1. FTIR of amine functionalized BNNS

Figure S1 shows a peak at 3400 cm^{-1} arising from N-H bonds. Peaks at 1770 cm^{-1} and 1610 cm^{-1} correspond to C=O of the carbamate and urea respectively. A small peak at 1510 cm^{-1} from the benzene ring can be seen but overlaps with the broad B-N in-plane stretching peak at 1375 cm^{-1}. A peak centered at 2250 cm^{-1} corresponds to the N=C=O stretch of unreacted isocyanate. The B-N-B out of plane bending peak can be found at 819 cm^{-1}.

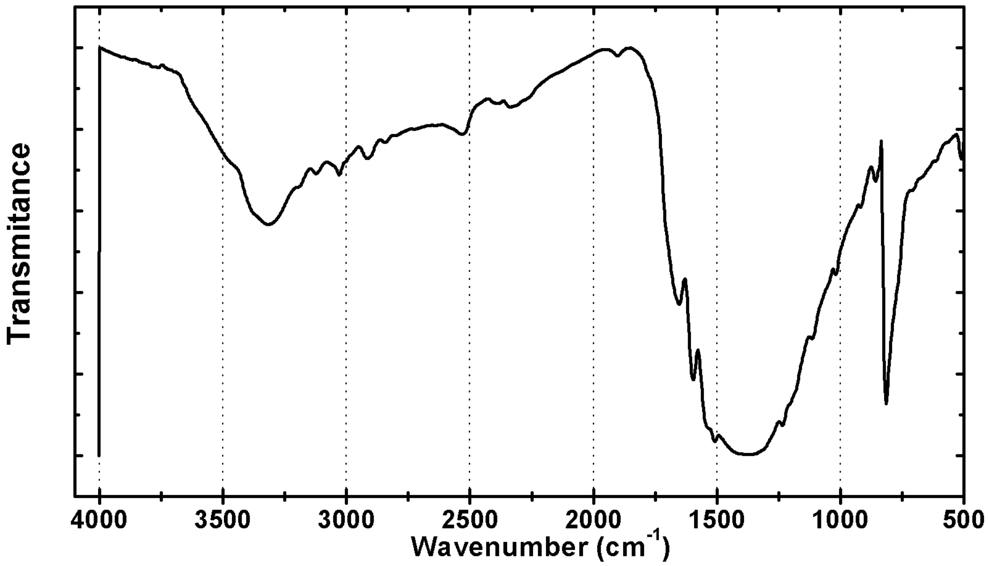

Figure S2. FTIR of BiBB functionalized BNNS

After the reaction with the acid bromide BiBB, followed by multiple washing, the FTIR in figure S2 confirms reaction with BiBB. The large peak at 1770 cm^{-1} remains, but has greatly decreased in area due to washing out unattached carbamates. A new peak at 1663 cm^{-1} shows the carbonyl stretching of the C=O in the BiBB initiator. The presence of the small peak at 1610 cm^{-1} suggests that the linkage between BN sheets and initiator may contain more than one MDI molecule, with a urea linkage between them.

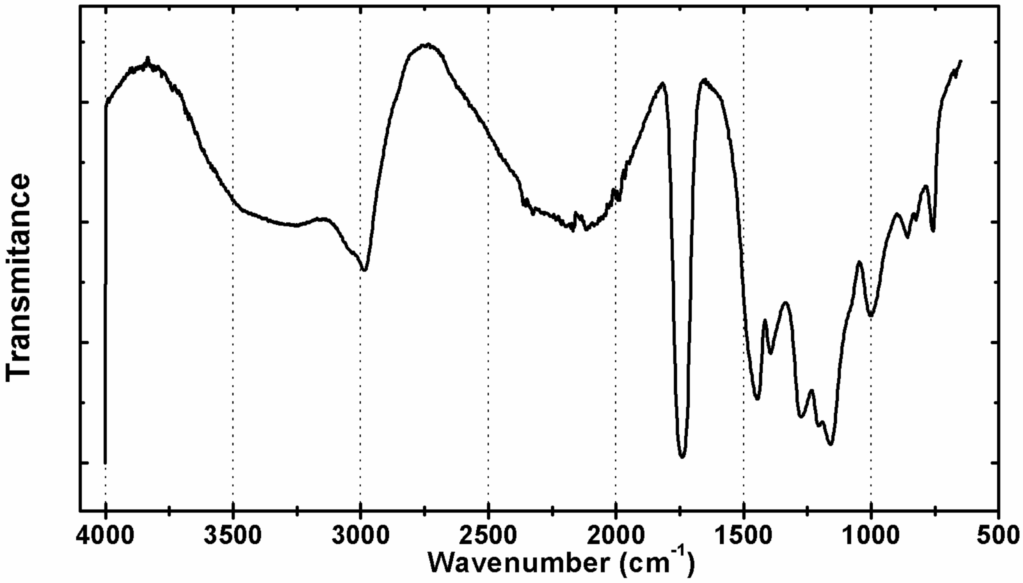

Figure S3. FTIR of free polymer in the filtrate, which is almost identical with the spectrum of neat PMMA.

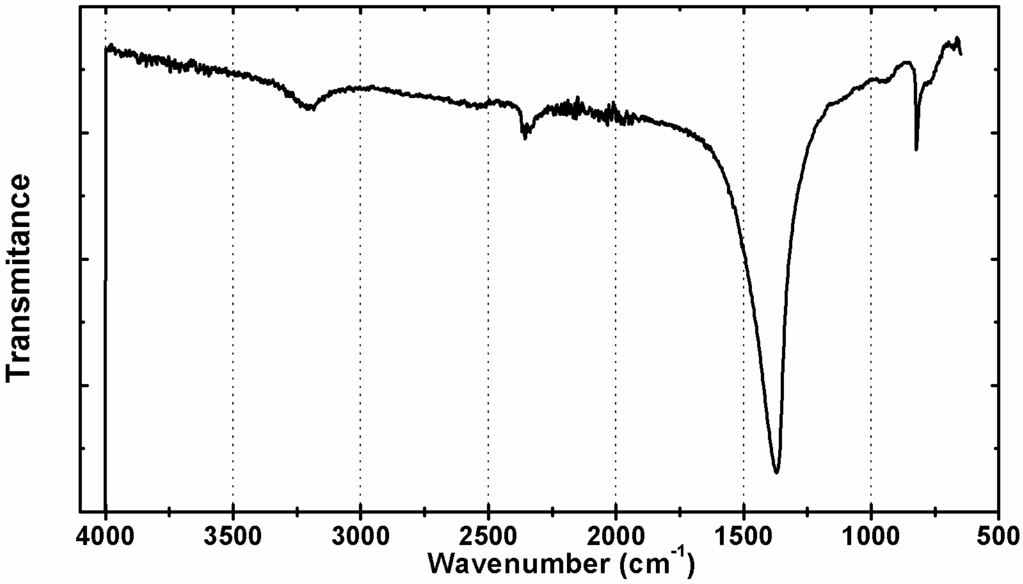

Figure S4. FTIR of TGA residue of PMMA grafted BNO.

GPC

GPC results and traces of neat PMMA as control group and free polymer from grafted BNO are shown below.

	Retention Time (min)	Mn (kg/mol)	Mw (kg/mol)	Polydispersity
Neat PMMA	16.28	199	231	1.16
Free polymer	15.164	174	439	2.52

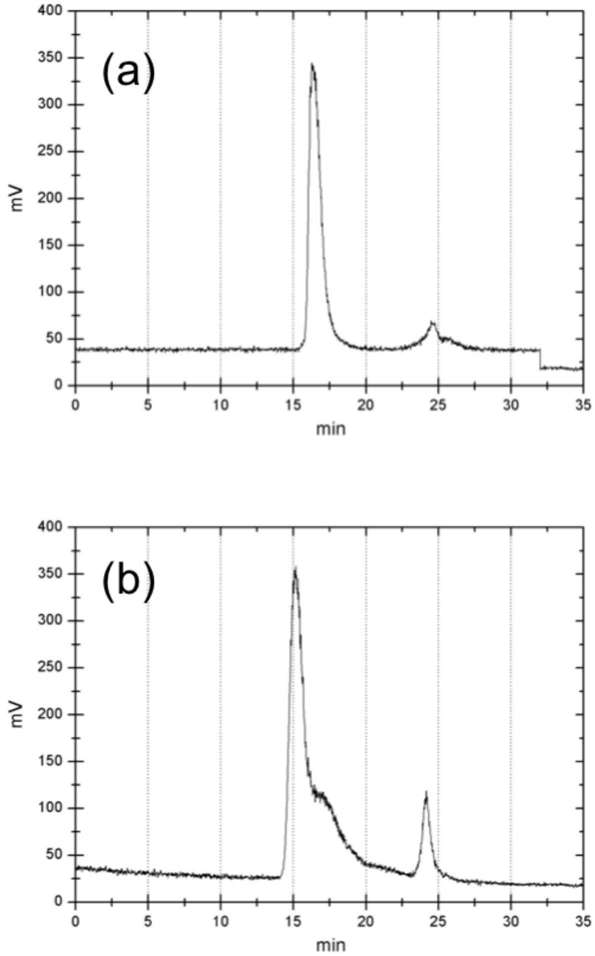

Figure S5. GPC of (a) neat PMMA as control and (b) free polymer in the filtrate of product from ATRP reaction

FESEM

To study and compare the morphology of fBNOs and neat polymer, SEM images of neat polymer and fBNOs are shown below.

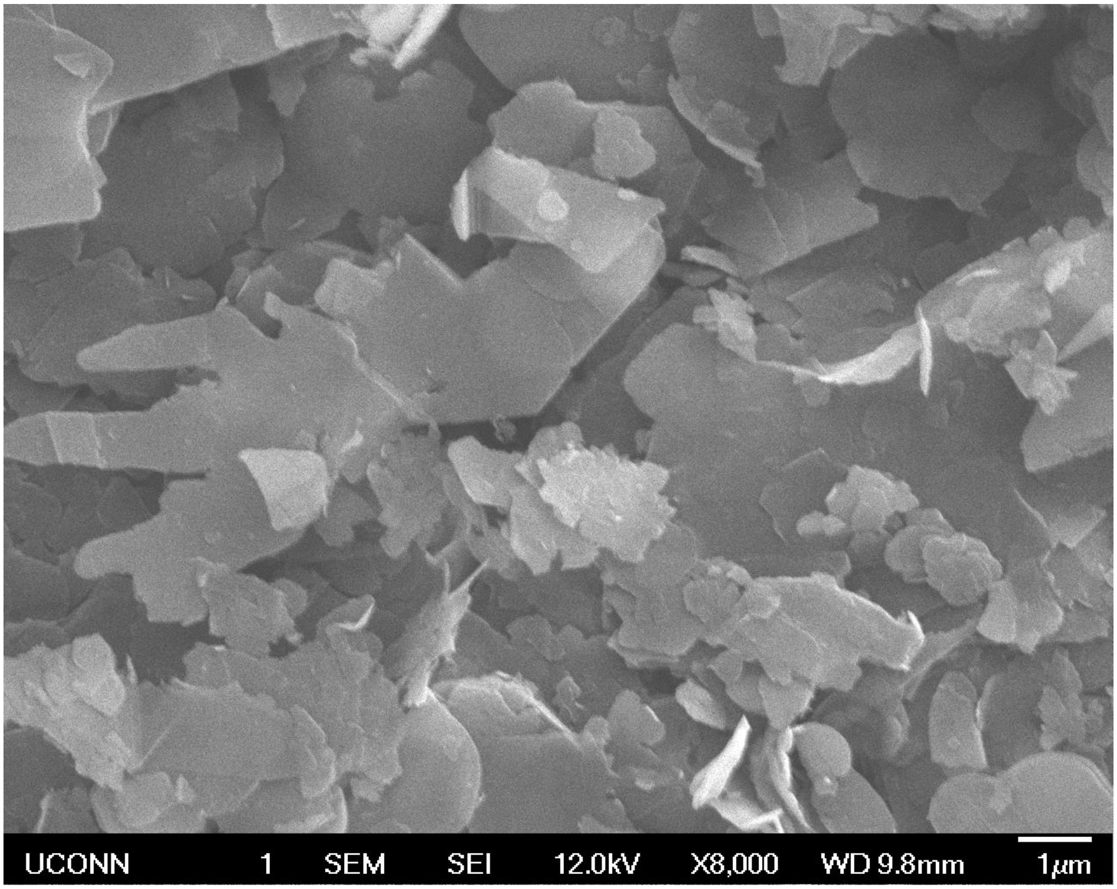

Figure S6. SEM of TGA residue of PMMA grafted BNO

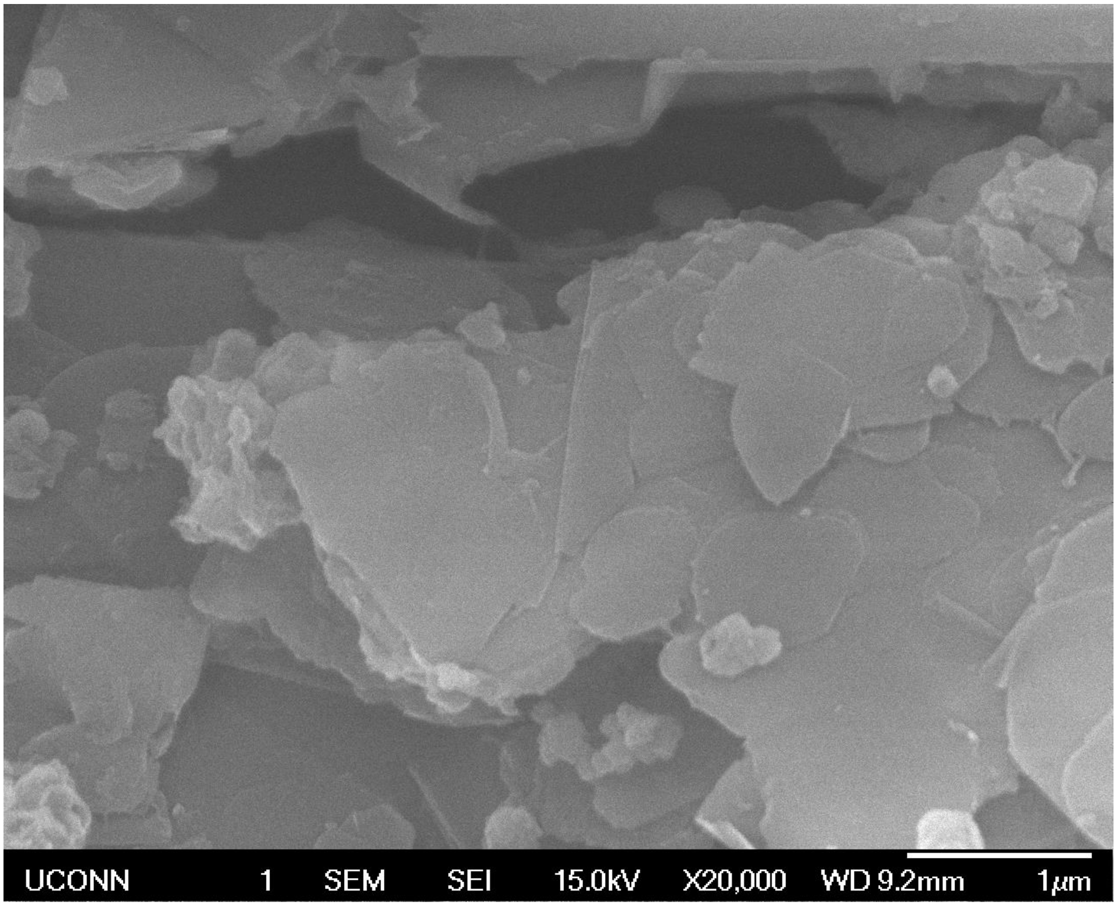

Figure S7. SEM of BiBB functionalized BNNS

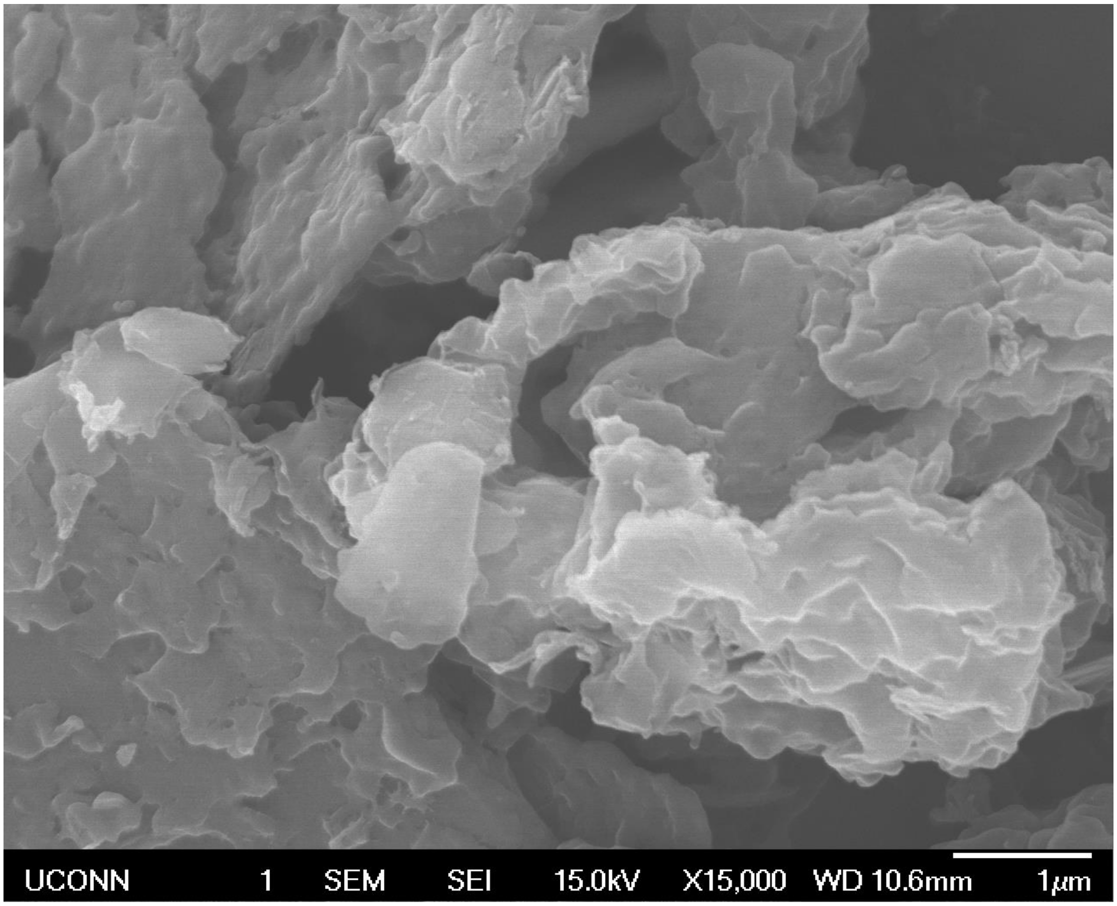

Figure S8. Low magnification SEM of PMMA grafted BNO

Thickness measurement of films in Fig. 4(b)

Thicknesses of three point of each thin film sample in Fig 4(b) are shown below.

composites	Thickness(mm)		
grafted BNO /PMMA	0.03695	0.04505	0.03130
hBN/PMMA	0.03255	0.03935	0.03280