Supplementary Information

Covalently Bonded Interface for Polymer/Boron Nitride Nanosheets Composite Toward Enhanced Mechanical and Thermal Behaviour

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I: Sample Preparation with Solvent blending method (SBM)

High density polyethylene (HDPE) used in this work was supplied by Reliance industries Pvt. Ltd. with the following specifications (melting point: 135–150 °C, melt flow rate (MFR): 8 g/10 min at 190 °C, 2.16 Kg, and density: 960 g cm^{-3}). BN nanoplatelets (BNNP) were supplied by Lower Friction Canada; with average lateral size in the range of 150-250 nm. The received BNNP was further high-energy ball milled to produce BN nanosheets (BNNS). Toluene was supplied by RANKEM Chemicals, which was used as a solvent medium with a molecular weight of 58.08 g mol^{-1}, boiling point: 55.5–56.5 °C, density: 0.79 g cm^{-3} at 20 °C. Xylene and sodium hydroxide (pallets) was also purchased from RANKEM chemicals. Pristine BN nanosheets were modified with silane coupling agent (3-Aminopropyl)triethoxysilane (APTES) and was supplied by Sigma Aldrich (CAS: 919-30-2).

II: Sample Preparation with Solvent blending method (SBM)

The solvent blending method is a popular technique used for the preparation of nanocomposites[1-4]. In Solvent blending method, the measured amount of pristine PE pallets was initially dissolved in the toluene solvent in the ratio of 1:10 (polymer to solvent ratio) on hot plate magnetic stirrer at 140 ºC. Simultaneously, the PE-g-BN nanosheets was also sonicated in toluene for 60 min. The sonicated solution (Toluene+PE-g-BN) was added to the solution after complete dissolution of PE pallet in the toluene. Further, the whole solution (PE+PE-g-PE+Toluene) was stirred at 140ºC and 300 rpm until the toluene is removed from the solution as depicted in Fig.S2. After removing toluene, highly viscous gel was obtained and kept in the vacuum oven at 70 ºC for next 24 hours to ensure the complete removal of the toluene from the solution. A thin layer of (PE/PE-g-PE) was obtained and cuts into small pieces. Further these small pieces were fed into the micro injection molding machine (as shown in Fig.S1) at 170ºC to fabricate the tensile and flexural sample as per the ISO 527 (Specimen type 1BA) and ISO 178 standard, respectively. The details dimensions of the tensile and flexural samples are shown in the Fig.S2.

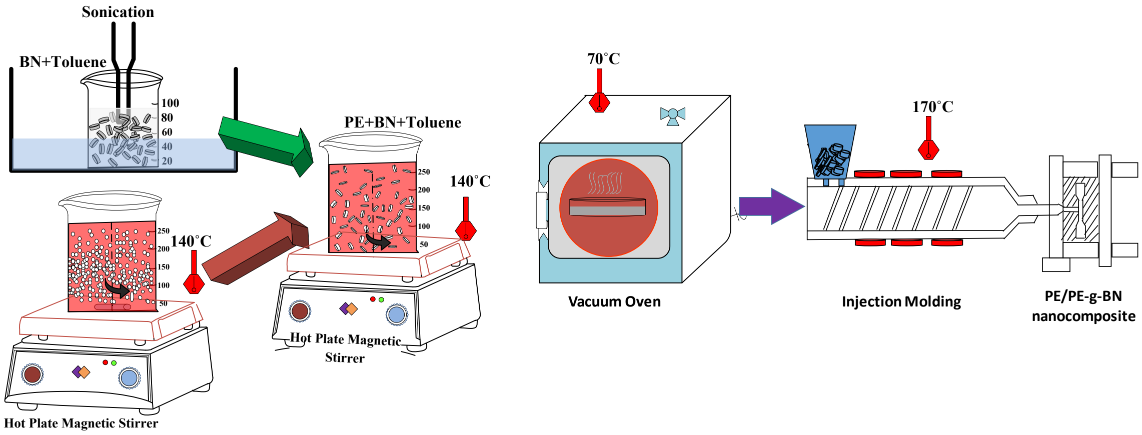

Figure S1. Schematic diagram of solvent blending method used in nanocomposites sample fabrication

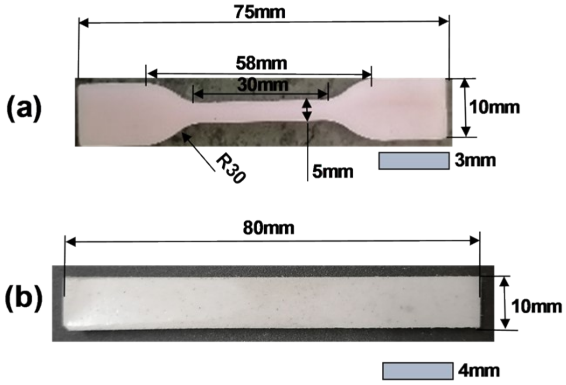

Figure S2. Dimensions of the (a) tensile and, (b) Fluxural samples of the nanocomposites

III: Differential scanning calorimetry (DSC) analysis

DSC analysis is a technique used to measure the changes in heat flow in a sample as a function of temperature or time. The resulting DSC thermogram provides information about the thermal properties of the sample, including melting and crystallization behavior. The analysis of the thermogram can be used to determine the heat capacity, enthalpy, and other thermodynamic parameters of the sample. To determine the percentage crystallinity of all the specimens, the following equation (Eq.1) was employed (5).

$$X_c = \frac{1 \qquad \Delta H_m}{(1 - weight\%)\Delta H'_m} \times 100 \qquad \text{---------------------------} \qquad (1)$$

The degree of crystallinity (X_c) was calculated using the weight percentage of pBN and PE-g-BN nanofiller, the heat of fusion of the material (pure PE or PE/BNnanocomposite) (ΔH_m), and the heat of fusion of fully crystalline polyethylene ($\Delta H'_m$), which was taken as 290 J/g from literature (6).

All the samples of were heated twice to eliminate the thermal history. Further, samples were recrystallized during the cooling at the same ramp rate of 10 ˚C/min. In order to quatifying the percentage crystallinity of the pure PE and nanocomposites samples of PE/pBN(5%) and PE/PE-g-BN(5%) with same concentration of nanofiller, DSC thermograms of are plotted in

Fig.S3.

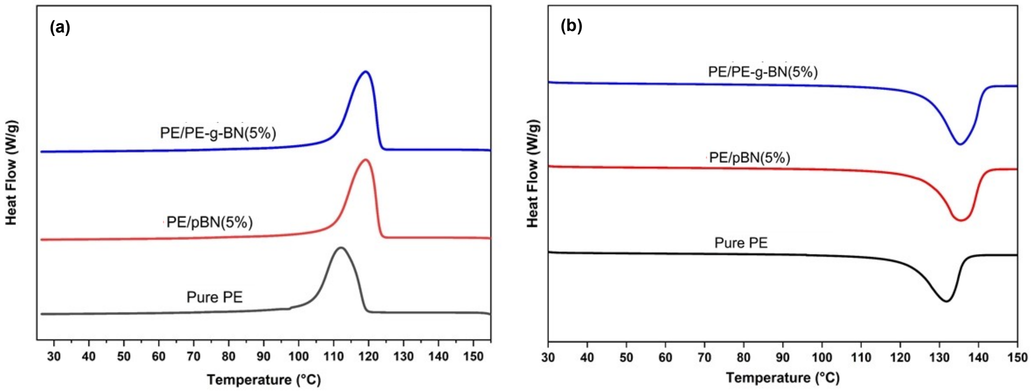

Fig.S3. DSC thermograms of pure PE, PE/pBN(5%) and PE/PE-g-BN(5%) nanocomposites (a) Exothermic cooling curve and, (b) second heating curve

It can be percieved from the Fig.S3(a) that refers to cooling curves of pure PE, PE/pBN(5%) and PE/PE-g-BN(5%) nanocomposites that the bell shaped cooling exotherms becomes broader with the addition of the BN nanofiller in the PE matrix. A silimar trend was also observed for second heating exotherm curves, broadening of curve attributed to the formation of PE crystallites over wide range of temperature with diffrenent crystallite sizes. However, on comparing the DSC thermograms of nanocomposites samples at same weight concentration, broadening is more significant for nanocomposites reinforced with funcitonalized nanosheet (PE-g-BN). Uniform dispersion of functionalized nanosheet (PE-g-BN) in the PE matrix leads to the higher peak broadening and crystallinity. The details of percentage crystallinity of pure PE and nanocomposites samples are given in the Table1. It can be seen in the table S1 that crystallinity is 62.65%, 70.20% and, 73.55% for pure PE, PE/pBN(5%) and, PE/PE-g-BN(5%) nanocomposites, respectively.

Table S1. Percentage crystallinity of pure, PE/pBN(5%) and, PE/PE-g-BN(5) nanocomposites

Configuration	Crystallinity (%)
Neat PE	62.65
PE/pBN(5%)	70.20
PE/PE-g-BN(5%)	73.55

IV: Dispersion stability of pristine and functionalized BN nanosheet

In this study ,the authors have also dispersed the pristine BN, OH-BN, sBN, and PE-g-BN in the water to a nominal concentration of 1mg/ml using ultrasonication, and the dispersed solution were kept for one week. Fig.S4 shows the digital snapshot of all dispersed solutions after one week. It can be seen in Fig.S4 that, dispersion stability increases with covalent functionalization.

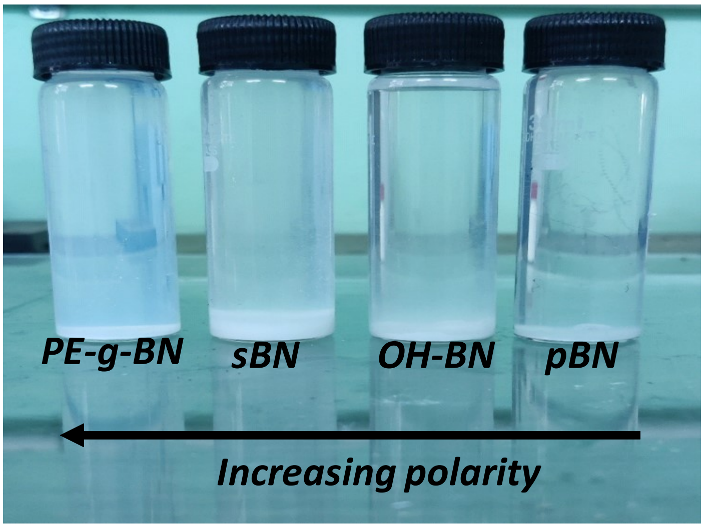

Fig.S3. Digital photograph of dispersed solution of pBN, OH-BN, sBN, PE-g-BN in water after one week of sonication.

V: Grafting of MA-g-PE onto silane functionalized BN

It can be seen from the below figure of FTIR spectra of PE-g-BN that the broadening of FTIR absorption peak at 3450 cm^{-1} (shown with blue color arrow) attributing non-hydrogen bonded N-H stretching, the peak at 796 cm^{-1} attributing N-H rocking, peak at 1547 cm^{-1} shows secondary amide N-H bending and C-N stretching, and the peak at 1663 cm^{-1} shows secondary amide C=O stretching, indicated the presence of the primary amide bonding (-CO-NH-)(7)(8). Peak broadening at 3400 cm^{-1} represents enhanced -OH stretching, and the peak at 1260 cm^{-1} shows C-O stretching, representing the presence of the -COOH bonding. These results demonstrate the successful covalent grafting of the polyethylene onto the s-BN through the chemical reaction of the –NH$_2$ group with the maleic anhydride. The table below lists some assignments of the s-BN and PE-g-BN using FTIR spectrum.

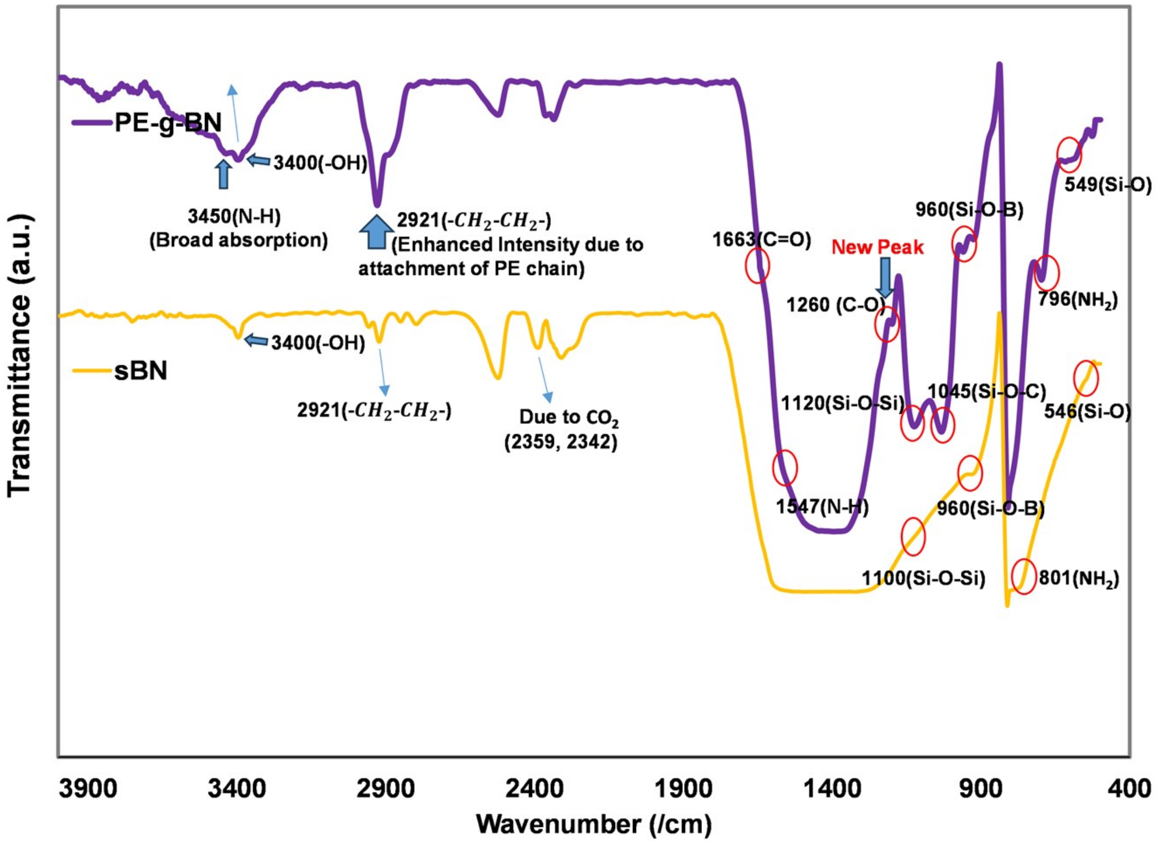

Fig.S4: FTIR Spectra for s-BN and PE grafted BN with all visible peaks.

Table: Assignments on the silane functionalized BN and PE-g-BN

Nanocomposites configuration	Wavenumber (cm^{-1})	Assignment	Bond
	1100	Si-O-Si asymmetric stretching	Si-O-Si
	3400	-OH stretching	-OH

s-BN	960	Hydrolyzed silane bond with BN surface hydroxyl group	Si-O-B
	801	-N-H rocking	$-NH_2$
PE-g-BN	3400-3450	Overlap of -OH stretching and N-H stretching (non-hydrogen bonded) -	-CO-NH-
	1663	Secondary amide C=O stretching	-COOH
	1547	Secondary amide -N-H bending and C-N stretching	N-H
	1260	C-O stretching	C-O
	1120	Si-O-Si asymmetric	Si-O-Si
	1060	Si-O-C stretching	Si-O-C
	796	N-H rocking	NH_2

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