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Supporting Information

Uniaxially Stretched Polyethylene/Boron Nitride Nanocomposite Films with Metal-like Thermal Conductivity

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Material processing
The HDPE pellets were firstly ground, at room temperature, into a powder using a Wedco SE-12 UR pilot plant grinder operating at 7000 rpm and with a gap size set to 400 μm. Then the HDPE powder was premixed for 2 minutes with BNNPs at a speed of 2000 rpm/min using a PRISM Pilot 3 high speed mixer. The HDPE/BNNP blends containing BNNP of loadings 5 w.t.%, 10 w.t.% and 15 w.t.%, respectively were prepared.

The PE/BNNP dry blends were melting-mixed in a Collin ZK 25 twin-screw extruder with a 30:1 length to diameter ratio (L/D) and a temperature profile of 175, 220, 220, 215, 210, 200 ºC from zones 1 to 6. An additional mixing element was employed in the mixing zone to produce a more intensive mixing and a reverse conveying element was employed after the mixing zone to increase mixing time. The screw speed was set at 150 rpm and the feeding rate was 25%. The residence time of melt in the extruder is about 1.5 min. The extruded strand was cooled in a water bath and pelleted. Finally, the extruder pellets were then extruded into a 1 mm thick and 100 mm wide sheet by a single-screw extruder (Collin GmbH) with a finishing calendar/chill roll unit. The screw speed was set at 85 rpm and temperature was in the range of 170 ~ 200 ºC. Afterwards, the extruded sheets were cut into 76 mm × 76 mm squares for uniaxial stretching.
Figure S1 | Chill rolls in three roll up stack configuration (left), Collin GmbH single screw extruder(right).

Uniaxial stretching (Figure S2) of the extruded sheets (76 mm × 76 mm × 1 mm) was performed using the Queen’s in-house biaxial stretcher. The sheets were clamped by pneumatic grippers and heated rapidly, from room temperature, to 160 °C at a heating rate of about 5 °C/s and hold for 4 min to erase any materials processing history and achieve a uniform temperature distribution before stretching. The sample was then cooled down to 110 °C at a cooling rate of 80 °C/min, followed by uniaxial stretching at various Λ (2, 3, 4 and 5) in air. After that the stretched sample was cooled down naturally to room temperature.

Figure S2 | Schematic of uniaxial stretching test

Characterization

SEM sample preparation
The specimens were etched at 25 °C for 48 h to remove the amorphous phase on the surface. The etching reagent is 0.5 w.t.% solution of potassium permanganate in a mixture of concentrated sulfuric acid (98%) and concentrated nitric acid (65%). After that, the etched surfaces were washed by dilute sulfuric acid (30%) for 10 min (twice), hydrogen peroxide solution for 5 min (twice), distilled water for 10 min (twice), and acetone for 10 min in sequence under sonication. After completely drying in vacuum oven, the etched surface was gold sputtered for observation using a field-emission SEM (Nova NanoSEM450, FEI, USA) operating at 20 kV.

X-ray analysis

WAXD measurements were carried out to characterize the structure of the composite films in the Hefei National Synchrotron Radiation Laborator (NSRL). A 2D CCD X-ray detector (MARUSA) was employed for detection of 2D-WXAD images, having a resolution of 1024 × 1024 pixels (pixel size =150 ×150 μm), λ = 0.154 nm. The data acquisition time was 30 s for each scattering pattern. The sample to detector distance was 112.6 mm for WAXD. The scattered intensities were registered in the range of scattering angles 2θ from 10 to 30°.

Linear WAXD profiles were obtained from circularly integrated intensities of 2D-WAXD image patterns acquired. The intensity was plotted as a function of the scattering vector, q, where |q| = 4π(sin θ)/λ, λ is the wavelength of the incident beam, and 2θ is the scattering angle. Subsequently, through deconvoluting the peaks of linear WAXD profiles, the overall crystallinity (Xc) was calculated by

\[ X_c = \frac{\sum A_{cryst}}{\sum A_{cryst} + \sum A_{amorph}} \]
where \( A_{\text{cryst}} \) and \( A_{\text{amorph}} \) are the fitted areas of crystal and amorphous, respectively.

Herman’s method was used to determine the degree of orientation of the lamellae crystals in the composite films. The crystalline orientation can be characterized by the average orientation of the normal to the crystalline plane with respect to an external reference frame. Here, the flow direction was taken as the reference direction. For a set of \( hkl \) planes, the average orientation, expressed as \( \langle \cos^2 \phi \rangle_{hkl} \), can be calculated mathematically using the following equation:

\[
\langle \cos^2 \phi \rangle_{hkl} = \frac{\int_0^{\pi/2} I(\phi) \cos^2 \phi \sin \phi \, d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi \, d\phi}
\]

where \( \phi \) is the Azimuthal angle and \( I(\phi) \) is the scattered intensity along the angle \( \phi \).

Herman’s orientation function, \( f \), can be defined as

\[
f = \frac{3\langle \cos^2 \phi \rangle_{hkl} - 1}{2}
\]

where \( f \) has a value of -0.5 when the normal of the reflection plane is perpendicular to the reference direction (\( \phi = 90^\circ \)), a value of 1 when normal of the reflection plane parallel is the reference direction (\( \phi = 0^\circ \)), and a value of 0 when the orientation is random. For evaluation of the degree of orientation, the Azimuthal intensity distribution \( I(\phi) \) at \( q = 1.20 \text{ Å}^{-1} \) is analyzed.

Typical WAXD patterns of the composite films extracted from 2D-WAXS images are displayed in Figure S3a. All samples display distinct characteristic peaks at angles of 21.7 ° and 24.1 °, which correspond to the (110) and (200) planes of PE respectively. A very weak peak at 26.8 ° of BN (002) was also observed. Such low diffraction intensity is caused by low loading of BNNPs in the composites. The azimuth patterns of the
composite films are presented in Figure S3b-e. The typical oriented characteristic peaks for all samples were shown for $A > 2$.

![Figure S3](image)

Figure S3 | WAXD diffraction patterns and Azimuth angle of (110) plane for stretched composite film under various stretch ratios ($A$).

<table>
<thead>
<tr>
<th>BN loadings (w.t.%)</th>
<th>Crystallinity ($\pm 5%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$SR = 1$</td>
</tr>
<tr>
<td>0</td>
<td>59.6</td>
</tr>
<tr>
<td>5</td>
<td>57</td>
</tr>
<tr>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>15</td>
<td>63</td>
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