Enhanced Mechanical Properties of Epoxy Nanocomposites by Mixing Noncovalently Functionalized Boron Nitride Nanoflakes

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The influence of surface modifications on the mechanical properties of epoxy-hexagonal boron nitride nanoflake (BNNF) nanocomposites is investigated. Homogeneous distributions of boron nitride nanoflakes in a polymer matrix, preserving intrinsic material properties of boron nitride nanoflakes, is the key to successful composite applications. Here, a method is suggested to obtain noncovalently functionalized BNNFs with 1-pyrenebutyric acid (PBA) molecules and to synthesize epoxy–BNNF nanocomposites with enhanced mechanical properties. The incorporation of noncovalently functionalized BNNFs into epoxy resin yields an elastic modulus of 3.34 GPa, and 71.9 MPa ultimate tensile strength at 0.3 wt%. The toughening enhancement is as high as 107% compared to the value of neat epoxy. The creep strain and the creep compliance of the noncovalently functionalized BNNF nanocomposite is significantly less than the neat epoxy and the nonfunctionalized BNNF nanocomposite. Noncovalent functionalization of BNNFs is effective to increase mechanical properties by strong affinity between the fillers and the matrix.

1. Introduction

Engineered polymers have drawn attention due to their high specific strength, flexibility, processability, and relatively low cost. [1-2] However, unreinforced polymers have low absolute strength and poor fracture toughness, thus limiting their general usage in mechanical components. Numerous attempts such as mixing with superior nanofillers in various dimensional forms have been made to improve the mechanical properties of polymers, and numerous significant enhancements in mechanical, optical, thermal, electronic, or magnetic properties have been reported. [3-8] Even though the strengthening mechanism is not the same as that with conventional macro-scale fillers,[9] nanofillers in the shape of zero dimensions (0D, i.e. fullerene, nanoparticle), 1D (i.e. CNT, whisker), and, most recently, 2D (i.e. graphene, boron nitride) can strengthen matrix polymers. This strengthening capacity originates from the outstanding mechanical properties of the nanomaterials, which are close to the intrinsic strength of the nanomaterials, as well as inhibition of crack propagation.[10,11] Accordingly, the key factors that affect the final properties of polymer nanocomposites are the chemical composition, geometry of additives (shape and size), and the compatibility between the nanofiller and the polymeric matrix. The compatibility, generally achieved from chemical functionalization, determines the dispersion and interface interaction of constitutive phases.[12-16]
Hexagonal boron nitride (h-BN) in various forms (BN nanoplatelets, BN nanotubes, and BN nanosheets) is an attractive nanofiller material due to its low density (2.1 g/cm³), high mechanical strength (Young’s modulus: 0.7–0.9 TPa, yield strength: ∼35 GPa), superior thermal (stable up to 1000 °C under atmospheric conditions) and chemical stabilities, and intrinsic electrical insulating property. Nevertheless, the layered structure of h-BN has been considered bad filler materials for the mechanical strengthening of polymer because of the highly anisotropic mechanical strengths. However, the recent development of few layer 2D BN nanosheets, mostly produced by liquid exfoliation, provides new opportunities to use them as nanofiller material. The true in-plane strength of the 2D BN facilitates it to apply for mechanical strengthening of polymer composites, although the high surface area of BN nanosheets and strong van der Waals interaction between them cause irreversible aggregation.

Chemical modifications such as covalent and noncovalent functionalization are effective methods of manipulating the physical and chemical properties of nanofillers to improve the compatibility, dispersion, and interfacial interaction of 2D nanofillers in a polymer matrix. The covalent functionalization of BN nanomaterials has been reported by Terao et al. and Zhi et al. They connected a long alkyl chain to a BN nanotube and enhanced the solubility in various solvents. Covalent functionalization introduces functional groups, but it inevitably goes with a chemical reaction onto the surface of BN. On the other hand, noncovalent functionalization enables the attachment of target functional groups onto the surface without any loss of material properties. Zhi and coworkers showed the noncovalent functionalization of BN nanomaterials by polyaniline (PANI), DNA, and a conjugated polymer, poly[m-phenylenevinylene-co-(2,5-dioctoxy-phenylenevinylene)] (PmPV). The functionalized BN preserves its desired properties while significantly improving its solubility. However, this method still needs to further study because of the limitation of solvents and the synthesis process involves numerous steps. Our group recently introduced a novel approach to generate noncovalent functionalization of CNTs and graphene flakes to improve their solubility in various solvents by using pyrene molecules.

Here, we provide a method to obtain noncovalently functionalized h-BN nanoflakes (BNNFs) by 1-pyrenebutyric acid (PBA) molecules. The functionalized BNNFs, produced by the nondestructive method, were used to synthesize BNNF–epoxy nanocomposites showing enhanced mechanical properties at low loadings. Graphene makes the epoxy electrically conductive, while h-BN is electrically insulating. In many applications such as electric motors it is important to keep the epoxy electrically insulating. Also, graphene turns the composite black, while h-BN appears to maintain the transparency. This is also an important functionality that graphene cannot provide. The incorporation of noncovalently functionalized BNNFs into epoxy resin yielded an elastic modulus of 3.34 GPa and ultimate tensile strength of 71.9 MPa at the loading of 0.3 wt%. Moreover, the toughness value has increased as high as 107% compared to the value of neat epoxy, which is remarkable values than that of previously reported two-dimensional nanofillers-epoxy composites measured by uniaxial tensile test. The overall mechanical properties of nanocomposites provided by the noncovalently functionalized BNNFs are much better than those of nonfunctionalized BNNFs.

2. Results and Discussion

2.1. Preparation of PBA-Functionalized BNNFs and their Epoxy Nanocomposites

Figure 1 schematically illustrates the overall procedure of PBA functionalization to BNNFs and their epoxy nanocomposites. Figure 1a shows the mixture of BN particles and 1-pyrenebutyric acid (PBA) molecules in IPA. The mixture was sonicated, washed, and centrifuged to prepare noncovalently functionalized BNNFs (PBA–BNNFs) (Figure 1b). PBA–BNNFs were dispersed in acetone to prepare the mixed solution (Figure 1c). The mixed solution was cured to prepare epoxy nanocomposites with PBA–BNNFs (Figure 1d).
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PBA molecules in isopropylalcohol (IPA). Sequentially, the mixture solution is sonicated and centrifuged in order to fabricate surface functionalized BN nanoflakes via PBA treatment, as shown in Figure 1b. The PBA-functionalized BNNFs (PBA–BNNFs) are homogeneously mixed with epoxy monomers in acetone and then the mixture is casted into a stainless steel mold (Figure 1c). Following the casting, rigorous drying and degassing at 70 °C for 6 h under a mechanical vacuum condition are required to achieve high density (∼99%) composites. The composite resin is subjected to an additional curing process at 175 °C for 1 h. Figure 1d presents a bone-shaped nanocomposite used for measuring the mechanical properties and a schematic illustration of the nanocomposite structure.

2.2. Characterization of PBA–BNNFs

The morphology of BNNFs obtained from the solvent exfoliation was examined by transmission electron microscopy (TEM). Figure 2a shows low-magnification TEM images indicating that there are thin 2D flakes in the solution. The inset of Figure 2a is the selected area electron diffraction (SAED) pattern measured along the [0001] zone axis. The SAED pattern presents a typical sixfold symmetry of h-BN diffraction, suggesting that the hexagonal lattices of the obtained BNNFs are not damaged during the exfoliation and functionalization processes. The spacing of the folded edges is observed to be about 0.33 nm, which corresponds to the theoretical layer to layer distance of h-BN (Figure 2b). Statistics of the thickness and lateral size of the BNNFs are shown in Figures 2c,d. Most of the BNNFs in the dispersion consist of thin flakes with less than 20 layers (<7 nm) and the average value is ~200–500 nm size. The thicknesses of PBA–BNNFs could also be estimated from the height profiles of the nanoflakes using atomic force microscopy (AFM) as illustrated in Figure S1. The observed objects are hundreds of nanometers wide and 3.4 nm of thickness, in agreement with the TEM data.

The surface functionalization of BNNFs is verified by spectroscopic methods and a thermo-gravimetric analysis (TGA). Figure 3a presents a comparison of FT-IR spectra of PBA, BNNFs, and PBA–BNNFs. In the case of BNNFs, the strong absorption at 1348 cm⁻¹ is due to B-N stretching (in-plane ring vibration (E₁u mode)) and the peak at 782 cm⁻¹ is attributed to B-N bending (out-of-plane vibration (A₂u mode)), which is consistent with previously reported spectroscopic data. The spectra of PBA–BNNFs are obviously different from those of BNNFs. The peaks at 1674 and 1260 cm⁻¹ are assigned to the carboxylic C=O and C–O stretching vibrations, and the peaks at 840 cm⁻¹ and 712 cm⁻¹ are due to...
to the =CH out-of-plane vibration, respectively. After noncovalent functionalization, PBA–BNNFs show the signals similar to the sum of PBA curve and BNNF curve, but these peaks in PBA–BNNFs are relatively shifted. Figure 3b indicates the UV-Vis spectra for PBA, BNNFs, and PBA–BNNFs. The spectrum of PBA has characteristic peaks at 235, 266, 275, 312, 327, and 339 nm, which arise from the π–π* transitions of pyrene rings. The shift of characteristic peaks of PBA–BNNFs in both the FT-IR and UV-Vis spectra might be attributed to π–π stacking between hexagonal rings of BNNFs and pyrene molecules of PBA. In addition, the characteristic photoluminescence band of PBA at 365 nm was extensively quenched after functionalization on the surface of BNNFs, indicating effective electron or energy transfer between these two components. (Figure 3c). TGA curves provide further evidence of successful noncovalent functionalization of BNNFs with PBA molecules. Figure 3d presents the TGA curves of PBA, BNNFs, and PBA–BNNFs in air. As shown in Figure 3d, BNNFs exhibit high thermal stability and do not decompose up to 900 °C. The PBA did not show any significant decomposition below 180 °C. However, above 180 °C, the PBA exhibits thermal degradation, which can be attributed to decomposition of the carboxylic acid group and oxidation of aromatic molecules. On the other hand, the thermal degradation behavior of the PBA–BNNFs has been found to be qualitatively similar to the sum of PBA curve and BNNF curve. TGA results for the PBA–BNNFs up to 900 °C, the quantity of functionalized PBA is estimated to be ~4 wt%.

The concentration of BNNFs and PBA–BNNFs in solution can be calculated by the Lambert-Beer law. The concentration of dispersed BNNFs is obtained in IPA with a mass concentration of 0.004 mg/mL, while the suspended PBA–BNNFs has the values of 0.039 mg/mL, which is 9.7 times higher than that of BNNFs (Figure S2). As colloidal dispersions often carry electrical charges in solution, zeta potentials of the samples need to be measured to confirm a stability of the suspension. The BNNFs and PBA–BNNFs in IPA are all negatively charged, with zeta potentials of −24.58, and −57.21 mV, respectively. The high surface charge ensures that the nanosheets repel each other in the solution, which

Figure 3. a) FT-IR spectra of PBA, BNNFs, and PBA–BNNF powders. b) UV-Vis spectra results for suspensions of PBA, BNNFs, and PBA–BNNFs in IPA. c) Photoluminescence spectra of PBA, BNNFs, and PBA–BNNFs at an excitation of 365 nm. d) Thermo-gravimetric analysis (TGA) of PBA, BNNFs, and PBA–BNNFs in a temperature range from RT to 900 °C at heating rate of 10 °C/min in air.
explains their excellent stability.[45] Also, XPS analysis gives further information of the chemical bonding between PBA–BNNFs (Figure S3). The C1s signal consisted of four different peaks: the C–C bond (284.5 eV) of sp2 carbon, a C–O bond (286.3 eV), C–O–H bond (287.6 eV), and the O=C–OH bond (288.9 eV) originated from the carboxylic moieties of PBA.

2.3. Mechanical Properties of PBA Functionalized BNNF–Epoxy Nanocomposites

Representative stress-strain curves for PBA–BNNF and BNNF nanocomposites are plotted in Figure 4a and Figure S4a. Figures 4b-d present the results of uniaxial tensile testing of neat epoxy, BNNF nanocomposites, and PBA–BNNF nanocomposites, including the elastic modulus (Figure 4b), ultimate tensile strength (Figure 4c), and toughness (Figure 4d). The elastic modulus of the PBA–BNNF nanocomposites is compared with theoretical values, calculated by the modified Halpin-Tsai model, which was utilized to predict the modulus of the nanocomposites with nanofillers. To model the elastic modulus of the PBA–BNNF nanocomposites, we assumed that PBA–BNNFs act as an effective rectangular planar sheet (see the Supporting Information).[32,46] For the neat epoxy, the elastic modulus, and ultimate tensile strength are 2.75 GPa and 46.7 MPa, respectively. The addition of PBA–BNNFs effectively enhanced the strength, modulus, and toughness of epoxy nanocomposites as well as the break point of strain. At 0.3 wt% PBA–BNNFs, the elastic modulus and ultimate tensile strength of the nanocomposites are 3.34 GPa and 71.9 MPa, corresponding to the increases of 21% and 54%, respectively. (Figures 4b,c) At the same fraction, the elastic modulus of the BNNF nanocomposites is similar to the value of neat epoxy. The theoretical prediction of the elastic modulus is 3.11 GPa (Figure 4b), which under-predicts the experimental results by ~4%. This could be a consequence of the shape of the PBA–BNNFs, which is different from the rectangular shape of PBA–BNNFs assumed by the model.[32] The toughness (area under stress-strain curve) of neat epoxy and the 0.3 wt% PBA–BNNF nanocomposites are 0.758 MJ/m³ and 1.573 MJ/m³, respectively. The nanocomposite with 0.3 wt% PBA–BNNFs
exhibits a toughening effect as high as 107% as illustrated in Figure 4d. This indicates that an applied mechanical load might effectively be transferred to PBA–BNNFs through the interfacial interactions. PBA molecules interact with BNNFs via π–π interactions and inhibit the restacking and aggregation of BNNFs. This results in a relatively large surface area of BNNFs in the nanocomposite, consequently increases the contact surface between the BNNFs and the epoxy matrix and improves the dispersion state of the BNNFs in these epoxy matrix.33,47,48 The comparison of enhancement ratios to previous researches and control experiment is listed as Table S7 and Table S1. Also, dynamic mechanical analysis (DMA) results give further information of the mechanical properties of PBA–BNNF nanocomposites (Figure S6). The mechanical properties of PBA–BNNF nanocomposites are enhanced by improving the interfacial interaction between PBA–BNNFs and polymer matrix and better dispersion of PBA–BNNFs within a polymer matrix.

Figure 5a shows the creep strain versus time for both the pristine and the 0.3 wt% nanocomposite samples at room temperature. The stress level is 15 MPa, which represents 75% of the yield stress. No necking or significant deformation in the cross-sectional area of the specimen occurred during the test. The smallest creep strain is measured in the PBA–BNNF nanocomposite, which deforms significantly less than the neat epoxy and the BNNF nanocomposite. The strain of the PBA–BNNF nanocomposite at the end of the hold period (after 10 hrs) is 16% smaller than that of the BNNF nanocomposite. The creep compliance of the PBA–BNNF nanocomposite is also reduced in comparison with the BNNF nanocomposite (Figure 5b). The curves shown in Figure 5b are approximated with a power law function of time. The curve is approximated by the function \( \varepsilon(t) \sim t^{-q} \). The exponent \( q \) of the neat epoxy, BNNF, and PBA–BNNF nanocomposite are 2.98, 3.19, and 3.40, respectively. This functional form of the strain-time relationship results from a constitutive equation of the form Equation (1):

\[
\frac{\partial}{\partial t} \left[ \frac{\varepsilon(t)}{\mu_c} \right]^q = \frac{\sigma(t)}{\mu_c}
\]

for the viscoelastic body, where \( \sigma \) is the stress, and \( \mu_c \) and \( p \) are constants.\(^{49}\) The observation that better creep performance is exhibited by the nanocomposite with PBA–BNNFs is in agreement with tensile test results, in which it was shown that the nanocomposite with 0.3 wt% PBA–BNNFs has the higher toughness by noncovalent functionalization.

The SEM images of fracture surfaces of the neat epoxy and epoxy nanocomposites after tensile tests are shown in Figure 6. It can be observed clearly from Figure 6a that river patterns appear on the fracture surface of the neat epoxy. In addition, the fracture surface is very smooth and mirror-like and the structural deformation is brittle failure of a homogeneous material. For nanocomposites containing 0.3 wt% PBA–BNNFs, PBA–BNNFs seem to be more homogeneously dispersed within the matrix without naked BNNF fillers and clusters (Figure 6c). As the loading of the PBA–BNNFs increases, the aggregation begins to occur increasing the average BNF cluster size due to degradation in the dispersion quality causing the reduction of mechanical properties. (Figure 4c and Figures 6d-f). The smaller agglomerates not only decrease the incidence of defects, but also increase the polymer contact area. PBA–BNNFs homogeneously embedded in the epoxy matrix were likely to have covalent bonding with epoxide groups in the epoxy matrix via the carboxylic groups of the PBA, which provides strong interfacial interactions and improves the dispersion state of the BNNFs in these epoxy matrix.

Table 1. Mechanical properties of the pristine epoxy and the nanocomposites.

<table>
<thead>
<tr>
<th>Filler content [wt%]</th>
<th>( E_p ) [GPa](^{46} )</th>
<th>UTS [MPa](^{46} )</th>
<th>( \varepsilon_f ) [%](^{46} )</th>
<th>Toughness [MJ/m(^3)](^{46} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure epoxy</td>
<td>2.749</td>
<td>46.7</td>
<td>2.71</td>
<td>0.758</td>
</tr>
<tr>
<td>0.3 wt% PBA–BNNFs</td>
<td>3.338</td>
<td>71.9</td>
<td>3.45</td>
<td>1.573</td>
</tr>
<tr>
<td>0.3 wt% PBA-RGO</td>
<td>3.295</td>
<td>58.1</td>
<td>2.60</td>
<td>0.870</td>
</tr>
</tbody>
</table>

\(^{46}\)Elastic modulus obtained from the slopes of linear region in stress-strain curves; \(^{46}\)Stress at the fracture point; \(^{46}\)Strain at fracture; \(^{46}\)Calculated by integration stress-strain curves; \(^{46}\)Control experiment PBA functionalized RGO/epoxy nanocomposites prepared by the same fabrication process.
interaction between PBA–BNNFs and the epoxy matrix.\cite{50} In previous reports, surface modification of fillers is effective to increase the strength as well as the toughness by strong affinity between fillers and matrix.\cite{51, 52} The enhancement of the mechanical properties in the whole system of nanocomposites can be ascribed to the local stress efficiently transferred to the PBA–BNNFs through intimate contact with the epoxy matrix.

2.4. Light Transmittance of PBA Functionalized BNNF–Epoxy Nanocomposites

Figure 7 and Figure S5 show the light transmittance of pure epoxy and PBA–BNNF nanocomposites with thickness in the wavelength range of 350–800 nm. The characters underneath the nanocomposites are legible through the specimens as shown in the inset of Figure 7. This suggests that the optical transparency of the composites in a visible wavelength region is achieved in all the fabricated composites. The addition of fillers decreases the light transmittance and greater reductions occur at relatively shorter wavelengths.\cite{53}

![Figure 6. SEM images of fracture surfaces of a) the neat epoxy, and PBA–BNNF nanocomposite with b) 0.3 wt%, c) 0.1 wt%, d) 0.5 wt%, e) 1 wt%, f) 2 wt%.](image)

![Figure 7. Light transmittance of PBA–BNNF nanocomposites.](image)
respectively, and the transmittance reduction of the 0.3 wt% PBA–BNNFs nanocomposites are 37%. In previous report, the transmittance reduction of 0.1 wt% CNT/epoxy composites was 70.3%.[34] This is because PBA–BNNFs are effectively dispersed in polymer matrix without noticeable segregation by PBA functionalization as well as transparency characteristic in visible wavelength range of BN nanoflakes.

3. Conclusion

This study has demonstrated a novel approach to improve the mechanical properties of epoxy nanocomposites filled with BN nanoflakes noncovalently functionalized with PBA molecules. The improvements in mechanical properties for BNNFs and graphene are comparable at low nanofillers loadings, while h-BN provides some unique functionalities such as transparency and electrical insulation that graphene is unable to provide. The BN nanoflakes chemically surface modified by PBA were prohibited from stacking and aggregation, resulted into high stability in solvent and homogeneous dispersion in epoxy matrix with a strong interface interaction. The elastic modulus and ultimate tensile strength of epoxy nanocomposites filled with BN nanoflakes noncovalently functionalized with PBA–BNNFs are efficiently enhanced to 3.34 GPa and 71.9 MPa (increase by 21% and 54%), respectively, compared with neat epoxy and the toughening effect is enhanced by as high as 107%, compared to neat epoxy. The significantly improved mechanical properties are attributed to the large surface area, which increases the contact surface area between the BNNFs and epoxy matrix, as well as enhancement of the interfacial interaction between BNNFs and the epoxy matrix and efficient load transfer at the interface.

4. Experimental Section

Preparation of PBA–BNNFs and Dispersion: PBA-functionalized BNNFs were prepared through exfoliation of h-BN micro-sized particles. In a typical experimental, BN powder (100 mg, KOJUNDO KOREA CO., LTD, used as received) was sonicated for 10 h in 1-pyrenebutric acid (PBA, 100 mg, Aldrich) in isopropyl alcohol (IPA, 500 mL, Merck). The dispersed BN solution was then centrifuged at 3000 rpm for 15 min to remove the unreacted and thick flakes. The supernatant was collected and washed several times with IPA to remove the unreacted PBA and then dried in a vacuum oven at 80 °C for 2 h. The collected PBA–BNNFs were re-dispersed in 30 mL of acetone (Aldrich) with sonication for 3 h. After 2 weeks, absorbance of the suspension was measured after making a baseline with pure acetone.

Preparation of Composites: Epoxy resin (diglycidyl ether of bisphenol A, EPON 862) was dissolved in the PBA–BNNF suspended acetone, and the curing agent (diethyltoluenediamine, SEIKA-S) was added under sonication (36 wt% to epoxy). The homogeneous mixture of PBA–BNNFs with epoxy was casted into a bone-shaped stainless steel mold, and then dried and degassed at 70 °C under the vacuum. Finally, an additional curing process was conducted at 175 °C for 1 h. A series of composites with PBA–BNNFs loading ratio between 0.1 and 2 wt% was prepared. For comparison studies, epoxy composites filled with nonfunctionalized BNNFs were prepared via the same procedure.

Characterization: The morphology of PBA–BNNFs was investigated using atomic force microscopy (AFM, Seiko Instrument Inc.) in tapping-mode under ambient conditions. Transmission electron microscopy (TEM, JEOI JEM-2200FS) analyses were also conducted. AFM and TEM samples were prepared by drying a droplet of the PBA–BNNF suspension on a Si substrate and Lacey carbon grid. Also, field-emission scanning electron microscopy (SEM, Hitachi S4800) was used to study the morphology of the composites. UV-Vis spectra were measured to evaluate the dispersion concentration and functionalization using an UV-3101PC spectrometer. FT-IR spectra (Jasco FT/IR-4100 type-A spectrometer, ATR mode) and photoluminescence spectra (VLV PL measurement system) were recorded. Zeta potentials were collected by an ELS-Z2 (Photol). X-ray photoelectron spectroscopy experiments were performed using a Sigma Probe (Thermo VG Scientific, AlKα). For the thermo-gravimetric analysis (TGA) measurements, a TGA 92-18 device (Setaram) was utilized at temperatures from 20 to 900 °C at a heating rate of 10 °C/min in air. Tensile properties were measured using a universal testing machine (INSTRON 8848 microtester) according to ASTM D638-10 with a crosshead speed of 0.2 mm/min at room temperature. Macroscopic tensile creep tests were conducted in load control using an INSTRON 8848 microtester at room temperature. The strain was measured using optical measuring system. The loading rate is increased immediately (50 MPa s−1) and then stress is held constant. The time at the beginning of the hold period is considered the initial time for creep. The creep strain was recorded for 10 h. Bone-shaped specimens with a length of 25 mm, and a width of 2 mm were used. All tensile surfaces of the specimens were polished.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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