Mechanical properties of poly(propylene fumarate)/nanotube composites: experimental results and theoretical predictions

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Abstract. Biopolymers such as synthetic poly(propylene fumarate) (PPF) are widely used in the biomedical field. In order to be used as orthopaedic scaffolds, their stiffness and strength have to be improved. Inorganic boron nitride nanotube (BNNT) 1D nanomaterials have recently attracted a lot of interest as reinforcing fillers of polymers due to their outstanding physical properties. This article deals with the preparation and mechanical characterization of PPF/BNNT composites with nanotube concentrations in the range of 0.1-5 wt%. Results demonstrate that the composites exhibit rigidity enough to be used for tissue engineering applications.

1. Introduction

The metastable allotropic form of hexagonal boron nitride nanotubes was first proposed by Rubio et al. [1] in 1994 based on the analogies between the lattice structure of graphite and hexagonal boron nitride (Figure 1, left). They are structural analogs of carbon nanotubes (CNTs) but with boron and nitrogen atoms instead of carbon atoms. BNNTs can be visualized as a rolled up hexagonal boron nitride layer, and have different chiralities [2]. The chiral vector that can be expressed as: \( C_b = n \mathbf{a}_1 + m \mathbf{a}_2 \approx (n,m) \), where integers \( n \) and \( m \) represent the chiral indices. According to this, three types of single-walled BNNTs have been described (Figure 1, right): (a) zigzag \( (m=0) \); (b) armchair \( (m=n) \); (c) chiral \( (m \neq 0) \). The B–N bonds have somewhat ionic character since the electron density of B is attracted to the N atoms owed to their higher electronegativity. This provokes a large band gap between the valence and conduction bands of \( \sim 5.5 \) eV, hence they are electrically insulating.

BNNTs can be synthesized by a variety of techniques. The first works on BNNTs employed techniques similar to those used for the synthesis of CNTs such as arc-discharge, laser heating and vaporization, chemical vapor deposition (CVD) and high temperature ball milling. Complete reviews on the synthesis approaches of BNNTs can be found elsewhere [3,4]. Among different paths employing the CVD approach, it should be highlighted those reported by Tang et al. [5], who employed metal oxides like MgO, FeO and Li2O as precursors to synthesize reactive boron oxide (BxOy) vapour that reacted under an NH3 atmosphere in an induction heating chamber at 1300 °C to produce the BNNTs. This approach has been further improved by Zhi et al. [6] to produce high purity BNNTs. This procedure was successful for synthesizing BNNTs in a lab, although commercialization and practical use of BNNTs in industry is hampered by their low production rate and the necessity for tailored chamber design.
Using an analogous method, Lee et al. [7] reported the preparation high-purity and high-quality BNNTs at 1200 ºC in a traditional tube furnace. The fundamental characteristic of this technique is the use of a quartz tube closed at the end to entrap the vapours for the growth of the BNNTs. This method is denominated the growth vapour trapping (GVT) approach, and can be tailored via using catalytic nanoparticles coated on Si substrates. The raw BNNTs produced by this CVD/GVT method are vertically-aligned and display super-hydrophobicity due to their high surface roughness and reduced surface energy. BNNTs can be synthesized by a variety of techniques. The first works on BNNTs employed techniques similar to those used for the synthesis of CNTs such as arc-discharge, laser heating and vaporization, chemical vapor deposition (CVD) and high temperature ball milling. Complete reviews on the synthesis approaches of BNNTs can be found elsewhere [3,4]. Among different paths employing the CVD approach, it should be highlighted those reported by Tang et al. [5], who employed metal oxides like MgO, FeO and Li2O as precursors to synthesize reactive boron oxide (BxOy) vapour that reacted under an NH3 atmosphere in an induction heating chamber at 1300 ºC to produce the BNNTs. This approach has been further improved by Zhi et al. [6] to produce high purity BNNTs. This procedure was successful for synthesizing BNNTs in a lab, although commercialization and practical use of BNNTs in industry is hampered by their low production rate and the necessity for tailored chamber design. Using an analogous method, Lee et al. [7] reported the preparation high-purity and high-quality BNNTs at 1200 ºC in a traditional tube furnace. The fundamental characteristic of this technique is the use of a quartz tube closed at the end to entrap the vapours for the growth of the BNNTs. This method is denominated the growth vapour trapping (GVT) approach, and can be tailored via using catalytic nanoparticles coated on Si substrates. The raw BNNTs produced by this CVD/GVT method are vertically-aligned and display super-hydrophobicity due to their high surface roughness and reduced surface energy.

On the other hand, polyesters based on fumaric acid, a constituent of the Krebs cycle, have involved a lot of attention for biomedical uses due to their superior biocompatibility and biodegradability [8]. Amongst them, the most extensively investigated is poly(propylene fumarate) (PPF), an linear polyester incorporating two ester bonds and one unsaturated carbon-carbon double bond (Figure 2) that allows cross-linking either by free radical polymerization with monomers of methyl methacrylate (MMA) or N-vinyl pyrrolidinone (NVP) or by means of photoinitiation in the presence of photoinitiators like bisacrylphosphine oxide (BAPO) [9]. Cross-linked PPF can suit a number of medical requirements such as biocompatibility, osteoconductivity, sterilizability, and handling characteristics. PPF degrades by simple hydrolysis of the ester bonds and the degradation time depends on polymer characteristics such as molecular weight, type of cross-linkers, and cross-linking density. The degradation products are non-toxic fumaric acid and propylene glycol.

**Figure 1.** Left: Lattice structure of hexagonal boron nitride; Right: Atomic models of BNNTs: (a) zigzag; (b) armchair; (c) chiral.
PPF is an amorphous polymer with a glass transition temperature ($T_g$) ranging between -30 and 32 ºC depending on the molecular weight, thermal decomposition temperature of 345 ºC, density of 0.998 g/cm$^3$ and melt viscosity in the range of $10^2$–$10^4$ Pa·s. It is an injectable polymer that can be crosslinked in situ through chemical reaction or UV laser. Its mechanical properties are dependent on the molecular weight and degree of crosslinking [10]. In previous studies, polyethylene-glycol (PEG)-grafted boron nitride nanotubes (PEG-g-BNNTs) were incorporated into a PPF matrix [11,12]. The present article deals with the reinforcement of a PPF matrix with raw BNNTs, and focuses on the mechanical characterization of the resulting composites.

2. Preparation of PPF/BNNT composites

The inorganic nanotubes were synthesized by CVD following an alternative of the process reported previously [13]. Amorphous boron, NH$_4$NO$_3$ and Fe$_2$O$_3$ powders (15:15:1 mass ratio) were mixed in an alumina boat and heated to 650 ºC. The temperature was increased to 1200 ºC under a nitrogen flow and kept constant for 3 h. The nanotubes were purified by washing with concentrated HCl solution and finally washed with deionized water and dried overnight. The nanotubes were uniform, showing a characteristic bamboo-like structure and outer diameters of 40–100 nm, with a mean value of 82 nm, and length $\geq$5 μm, as revealed by scanning electron microscopy SEM (Figure 3).

PPF composites incorporating different amounts (0.1–5.0 wt%) of the inorganic nanotubes were prepared via ultrasonication and curing. Firstly, the nanomaterial was dispersed in chloroform by ultrasonication for 15 min. Separately, PPF and the cross-linker, N-vinyl-pyrrolidone (NVP), were mixed (1:1 w/w) and afterward the corresponding amount of the nanotube dispersion was added. The mixture was then ultrasonicated for another 15 min, and the free radical initiator, benzoyl peroxide (BP), was added to the mixture to begin the polymerization. The mixture was finally casted onto Teflon molds and cured under reduced pressure at 80 ºC for one day. The dispersion of the inorganic nanotubes within the matrix was visualized by SEM. Homogenous distribution was found for all the nanotube concentrations investigated, with randomly oriented and curled tubes, as shown in Figure 3.

3. Mechanical properties of PPF/BNNT composites
The study of the mechanical properties of composite biomaterials is crucial for their applications; an adequate balance between flexibility and strength is required. The tensile properties of PPF/BNNT composites were investigated on a 4204 mechanical tester at 23ºC and 50% RH, with a speed of 1 mm/min, following the UNE-EN ISO 527-1 standard, and the results are shown in Figure 4.

**Figure 4.** Young’s modulus (E) and tensile strength (σ_y) of PPF/BNNT nanocomposites as a function of the nanotube content. The dashed red lines represent the predictions by the Krenchel’s rule of mixtures for discontinuous reinforcement.

PPF has a Young’s modulus value close to 1 GPa, which increases gradually with increasing nanofiller content, leading to a 4.4 fold-increase for the composite with 5.0 wt% BNNTs. This exceptional rise should be ascribed to the homogenous filler dispersion and strong PPF-BNNT interfacial adhesion via hydrogen bonding and Van der Waals interactions along with the high elastic modulus of BNNTs [14]. Remarkably, the reinforcement effect attained herein is even higher than reported for the addition of similar amounts of other nanofillers such as single-walled carbon nanotubes (SWCNTs) to PPF [15], despite the carbon based nanotubes present higher modulus, demonstrating the importance of the strong interfacial adhesion to attain an effective stress transfer from the matrix to the filler. Similar trend is found for the tensile strength, resulting in 1.4-fold rise at 5.0 wt% BNNT. Regarding the ductility of the composites, a significant decrease was found on increasing nanotube concentration, particularly at loadings ≥2.5 wt%, and the nanocomposite with 5.0 wt% exhibits around 50% drop in ductility. This behaviour is expected to be associated with the intense PPF-BNNT H-bonding interactions. With regard to the toughness of the composites measured as the area under the tensile curve, a slight decrease was at the highest loadings tested.

The modulus (and strength) of the composites can be evaluated by the Krenchel’s rule of mixtures (Equation 1) for discontinuous reinforcement [16]:

\[
Y_c = (n_o n_l Y_f - Y_m) V_f + Y_m
\]

where \(n_o\) is the orientation factor, \(n_l\) the length efficiency factor, \(Y_f\) the filler modulus, \(Y_m\) the matrix modulus and \(V_f\) the filler volume fraction. \(n_l\) approaches to 1 for \(l/D > 10\), and \(n_o = 1/5\) for randomly oriented fillers. Taking reported data for the modulus (750 GPa) and strength (10 GPa) of BNNTs [14], it was possible to estimate the theoretical values for the concentration range studied (see red dashed lines in Figure 4). Experimental Young’s modulus of composites containing nanotube loadings ≤2.5 wt% are in good agreement with the predictions (differences <10%), whereas the value of the composite with higher loading is well below the predictions (about 55% lower). Similar trend is found for the tensile strength. Notice that the model assumes perfect nanotube dispersion and tube-matrix interfacial adhesion. Dispersion is probably the most crucial issue. To attain a uniform stress distribution and minimize the presence of stress concentration centers, BNNTs have to be uniformly dispersed to the level of isolated tubes individually coated with the biopolymer. However, the
nanotubes still remain gathered in small bundles, as revealed by SEM micrograph (Figure 3), and it may occur shear slippage of individual nanotubes within the bundle, which limits the stress transfer; this could explain the discrepancies between the experimental and the theoretical values for the composite with 5.0 wt% BNNTs.

4. Conclusions

Inorganic boron nitride nanotubes were synthesized by CVD and incorporated via ultrasonication and curing into a biocompatible PPF matrix at loadings of 0.1-5.0 wt%. Scanning electron microscopy images revealed a random and homogenous distribution of the inorganic nanotubes within PPF. The nanotubes led to an extraordinary increase in the stiffness and strength of the polymer, ascribed to the strong PPF-BNNT interfacial adhesion via hydrogen bonding and Van der Waals interactions. Experimental Young’s modulus and tensile strength of composites containing nanotube loadings ≤2.5 wt% were consistent with the predictions, while the values of the composite with 5.0 wt% were considerably below the predictions. These composites are suitable to be used as orthopaedic scaffolds in particular for the replacement of soft tissues like muscles, tendons, ligaments, etc.

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