Material Properties

Boron Nitride reinforced polylactic acid composites film for packaging: Preparation and properties

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ABSTRACT

Biopolymer composites obtained from renewable resources based polymers and inorganic materials are of potential interest owing to bioactivity, biodegradability and other superior properties. In the present study polylactic acid (PLA) samples containing 0-4 wt% of ultrasonically exfoliated Boron Nitride (BN) were prepared by solvent casting method. To have an insight into the structure of the PLA/BN composites, phase morphologies were studied using Scanning Electron Microscopy (SEM). SEM images showed aggregation of BN at 4 wt% of loading in the composite. Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) and tensile testing were carried out to characterize the thermal and mechanical properties of the prepared composites. The optimum tensile strength of 28.5 MPa was obtained for 2 wt% of PLA/BN composite. This corresponds to an increase of about 132% as compared to PLA.

1. Introduction

In recent years, the demand for sustainable and eco-friendly polymeric materials derived from renewable source is growing at a rapid rate. Biopolymers are an alternative to petroleum based polymers. Among the various biopolymers known, polylactic acid (PLA) has gained particular significance and attracts research organizations and industries due to its biodegradability, biocompatibility and renewability. PLA, thermoplastic aliphatic polyester obtained from wheat, corn and sugar based resources like starch, sugarcane, cellulose, etc features high strength, high modulus, biocompatibility, heat resistance, low toxicity, transparency, good barrier properties, and good processability [1–3]. It is widely applicable in numerous medical domains as scaffolds for urinary bladder, drug delivery systems, porous meshes, implants, automotives, and packaging [4–8]. However, its poor thermal stability, rigidity, intrinsic brittleness, low crystallization rate and high cost, limits their large-scale applications [9]. The favourable biodegradability and mechanical properties led to considerable investigations on the development of this material. Several efforts have been devoted to the modification of PLA by incorporating various fillers inorder to improve its properties. Literature reports that reinforcements of nanoclay [10], cellulose nanocrystals [11], natural fibers [12–14], carbon nanotubes [15] [16], graphene nanosheets [17] with the motive of enhancing various properties for suitable applications.

The physical and mechanical properties of PLA can be altered by incorporating nanoparticles. Boron Nitride (BN) appears to be a potential reinforcement inorganic material for polymers due to its superior thermal conductivity and mechanical properties. The introduction of BN as a reinforcement in PLA may significantly improve their properties, making them more suitable for packaging electronic products. From the literature, it was observed that there are no detailed investigations on PLA/BN composites. Hence it is interesting to investigate whether the incorporation of BN could enhance the properties of PLA. This study aims at exploring the thermal and pivotal mechanical properties of PLA/BN composites. The composites were prepared with BN loadings at four different concentrations 1 wt%, 2 wt%, 3 wt% and 4 wt%, named PLA/BN1, PLA/BN2, PLA/BN3 and PLA/BN4. The effects of BN loading on the impact strengths, stress-strain, crystallization temperature, glass transition temperature and morphology were investigated.

2. Experimental method

2.1. Materials

Polylacticacid (PLA) resin grade (Ingeo-4043D) Supplied by Nature work LLC was used in this work. The Molecular weight of PLA is 1.5×10^5 g/mol. The density of the polymer was 1.24 g/cc according to ASTM- D 1505. It had a melt flow of 3.498 g/10 min according to ASTM-D 1238 and melting temperature T_m of 145-160 °C. BN powder

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was purchased from Sigma Aldrich (molecular weight = 24.82 g/mol, particle size ~ 1 μm, density = 2.29 g/mL at 25 °C), Dimethyl formamide (DMF) and Chloroform (CHCl$_3$) supplied by Merck Specialities, India, were used in this work.

2.2. Exfoliation of BN sheets

A required quantity of BN was mixed with DMF and stirred well. This was then subjected to mild bath sonication for about 6 h to get uniform dispersion. The resultant solution was then centrifuged at 6000 rpm for 10 min in order to remove the heavier unexfoliated BN particles from the dispersion. After centrifugation, the supernatant was filtered, washed with deionized water and dried in an oven at 60 °C for a day. The BN thus prepared was further used for preparing composites.

2.3. Preparation of PLA/BN films

PLA and PLA/BN composite films were prepared by the solvent casting method. The PLA resin was preconditioned in drying oven at 80 °C for 48 h to reduce moisture content prior to use. The required amount of BN was then dispersed with chloroform using ultrasonicator at 12$^\phi$ and 5:5 pulsation for 30 min employing a water bath and the volume was made 20 ml post homogenisation. This suspension was then mixed with solvated PLA in RB flask and stirred for another 15 min. Subsequently, the solution was cast on a level surface and left to evaporate. The cast films were dried at room temperature and then peeled off from the glass plate.

2.4. Characterization

Tensile properties of PLA and PLA/BN composites were performed out using INSTRON universal testing machine 6025 UK within 200-N load cell according to ASTMD 882. All the specimens were of 15 mm wide, 0.15 mm thickness and 15 cm length respectively. The grip separation distance is 50 mm. Test speed was 100 mm/min. The results were taken as the average of five specimens of each sample. Thermogravimetric analyses of PLA and composites were performed using TA Q50, TA Instruments, USA. Tests were done under nitrogen at a scan rate of 10 °C/min in a programmed temperature range of ambient to 600 °C. ASTM E 1131 standard was followed. Samples of about 7 mg were used for each run. The weight change was recorded as a function of temperature. Derivative peak temperature (T_{max}) was taken as the maximum temperature acquired from the differentiation of the weight change as a function of time. DSC analyses were carried out under N$_2$ atmosphere using TA Q20, TA Instruments, USA. First, the samples (ASTM D 3418) were heated to 210 °C with a heating rate of 10 °C/min, followed by isothermal step for 5 min, and then cooled to 30 °C at the rate of 10 °C/min. The second heating scans were monitored between 30 and 210 °C at a heating rate of 5 °C/min to determine the glass transition temperature (T_g), cold crystallization temperature (T_{cc}), crystallization temperature (T_c) and melting temperature (T_m). The samples were then cooled at the rate of 5 °C/min to characterize crystallization behavior. Morphological studies of film surface were observed by Scanning Electron Microscopy (SEM), JEOL Model: JSM-6390 LV. The dried samples were sputter coated with gold for 30 s using a Cressington sputter coater 108 auto under an argon atmosphere. After sputter coating, the samples were placed in aluminium stubs inside the SEM chamber for viewing surface morphology. An accelerating voltage of 10 kV was used for imaging.

3. Results and Discussion

3.1. Prepared composite films

The prepared films (Fig. 1) were peeled off manually from the casted surface. On visual examination, it was seen that the PLA and PLA/BN composite films exhibited smooth surfaces with good homogeneity. Neither cracks nor bubbles were seen in the films.

3.2. Morphology

Fig. 2(a-e) represents SEM micrographs (magnification 5000×) of PLA and PLA/BN composites. It was observed from Fig. 2 (a) that the PLA had a smooth surface [18]. On the other hand, irregular morphology was observed for the BN added PLA composites. A good dispersion was noticed for 2 wt% of BN incorporated composites. Aggregation of BN can be observed for 4 wt% of BN added PLA composites (Fig. 2 (e)).

3.3. Tensile Analysis

The mechanical parameters of PLA and PLA/BN composites were listed in Table 1. The error bars for the calculated values of tensile strength, elongation at break and modulus of elasticity for all the prepared samples were reported in Fig. 3. Tensile strength and elongation at break of PLA was evaluated to be 12.3 MPa and 67.7% respectively. The variation of tensile strength with BN content is shown in Fig. 4(a). All BN added composites showed an increase in tensile strength when compared to PLA. The impressive increase in the tensile strength of PLA/BN films shows an effective interaction between BN and PLA. The optimum tensile strength occurred for PLA/BN2 and the interfacial properties were improved for this concentration. It was further observed that as the concentration increased beyond 2 wt%, there is a decrease in the tensile strength, however this value is still larger than PLA. The increase in tensile strength was attributed to proper dispersion and hence better reinforcement of BN in the composite film when compared with PLA. A decline in the tensile strength for higher BN concentrations was due to the latter's agglomeration leading to non-homogeneity of composite films, which induces cracks in the composites [19] and hence reduced stress transfer between PLA and BN. Similar behavior of increase in tensile strength for 3 wt% of nanocrystalline cellulose (NCC) added PLA and futher decline of tensile strength beyond 3 wt% NCC incorporated PLA composites were reported earlier [20]. It was also observed that there was a decrease in elongation at break for all BN added composites as compared to PLA. It was also seen that the elastic moduli for all BN added composites was higher than PLA. The elastic moduli reached an optimum value of 786 MPa for PLA/BN2. The variation of modulus of elasticity with BN content is shown in Fig. 4(b). The tensile strength and modulus of elasticity for all the BN compositions on comparison with PLA were connected with restriction on the mobility and deformability of PLA imposed by the reinforcing effect of BN. Also out of all BN added composites, promising tensile results were obtained for PLA/BN2 composite. Hence, this composite material is suitable for packaging in industries. The tensile properties of PLA and PLA/BN composites were presented through the stress strain curve as in Fig. 4(c). It was seen that PLA/BN composites showed linear behavior followed by a non linear part which denotes plastic deformations.

3.4. Thermal Analysis

3.4.1. Thermogravimetric analysis

Thermograms of PLA and composites were presented in Fig. 5(a). The onset degradation temperature of PLA was 327.57 °C. The incorporation of BN in the PLA matrix showed a modest decrease in the onset degradation temperature. The lower decomposition temperature of the PLA/BN composites could be indicating a reduction in the thermal stability of the composites when compared to PLA. The variation in degradation temperature with BN content is shown in Fig. 5(b). The degradation temperature of PLA lies between 327 °C and 384 °C and it was noticed that almost the whole of polymer phase has been thermally degraded. PLA/BN composites exhibited overall lower onset