Effects of Boron Nitride Nanopowder on Thermal, Chemical and Gas Barrier Properties of Starch

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Abstract Starch/boron nitride (starch/BN) bionanocomposites were prepared with the reinforcement of boron nitride nanopowder by solution technique. The dispersion of BN in the starch was achieved by a continuous sonication process. The interaction between starch and boron nitride nanopowder was investigated by Fourier transform infrared (FTIR) spectroscopy. The structural properties of starch/BN bionanocomposites was studied by X-ray diffraction (XRD). The high resolution transmission electron microscopy (HRTEM) was used for the study of dispersion of boron nitride in starch matrix and diffraction patterns were studied by selected area electron diffraction (SAED). Thermal stability of the starch was increased with rising concentrations of boron nitride due to incorporation of rigid nano BN with starch matrix. The substantial reduction in oxygen permeability was obtained by increasing the concentration of BN. The biodegradability of synthesized bionanocomposites was measured by using activated sludge water. Further, it was noticed that, starch/BN bionanocomposites are resistant towards inorganic acids and bases. The tensile strength of starch/BN bionanocomposites was increased whereas; the water resistance property of the materials was decreased with increasing BN loading.

Keywords: Starch; Boron nitride; Bionanocomposites; Oxygen permeability.

INTRODUCTION

Shortage of non-renewable petroleum-based products has aroused a great deal of interest in materials, based on biopolymers and inorganic nanoparticles. A strong built increase in environmental pollution has been caused by covering a large area use of non-biodegradable materials\textsuperscript{[1]}. On the other hand biopolymers such as starch, protein and cellulose have been considered as unconventional materials to petroleum based plastics as they are renewable, inexpensive, plentiful, eco-friendly and non-toxic to animal kingdom\textsuperscript{[2]}. Bionanocomposites can be prepared from these biopolymers using nano sized fillers. They are applied in the production of biomedical and packaging materials as they have superior physical, thermal and easy processing characteristics\textsuperscript{[3]}.

Among the natural biopolymers, starch is one of the most popular, cheap, nontoxic, environmental friendly, abundant and fully biodegradable polymers stored as granules in plants\textsuperscript{[4]}. It is composed of two microstructures consisting of linear water soluble amylose and branched insoluble amylopectin\textsuperscript{[5]}. Starch is hydrophilic and has been proven as a conventional composite with kaolinite\textsuperscript{[6-8]}. It is a promising raw material because of its annual availability from many plants and its low cost\textsuperscript{[9]}. Natural biopolymers and bio-fibres are used in engineering fields because of three factors. They include low compatibility with hydrophobic polymer matrices, thermal sensitivity at the temperature of compounding processes and flammability which struggles with safety requirements\textsuperscript{[10]}. Avella et al. studied the preparation and characterisation of compatibilized polycaprolactone/starch composites\textsuperscript{[11]}. In our earlier works, we have studied the preparation of starch/f-MWCNT nanocomposites

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and reported on improvement of their thermal, chemical and gas barrier properties\cite{12}.

Hexagonal boron nitride (h-BN) appears very similar to that of graphite having layer like structure in nature with strong bonding in the planner, fused, six-membered rings and weak van-der Waals bonding in between layers\cite{13, 14}. It has low elastic modulus, excellent thermal shock resistance, chemical inertness, limited surface activity, non-wet ability, corrosion resistance and lubricating effect\cite{15}. Boron nitride can be hot pressed, layered and interposed to prepare different composites where boron nitride plays vital role. The substances made up of boron nitride have several uses in cosmetic application, functional coating in the automotive and glass industry\cite{16}. Some researchers studied on polymer-boron nitride composites with nonbiodegradable polymers like polyaniline, polystyrene, copolymer of vinylidene chloride and acrylonitrile, justifying the key role of boron nitride in terms of better thermal, chemical resistant and mechanical properties\cite{17, 18}. The non-cytotoxicity of boron nitride to human body was studied by Chen et al\cite{19}.

In the present work, the nano BN has been incorporated into starch matrix to study the improvement of thermal, chemical and gas barrier properties along with mechanical properties, chemical and water resistant properties of starch/BN bionanocomposites in comparison with those of the starch matrix. It was found that, these properties of the bionanocomposites are substantially improved as compared to starch with little scarification of biodegradable properties.

EXPERIMENTAL

Materials
Starch, soluble was purchased from Fisher Scientific, Mumbai, India of analytical grade and it was used as such. Boron nitride nano powder of average particle size of 70 nm was obtained from Sisco Research Laboratories Pvt. Ltd., Mumbai, India which was of 99.9% purity. The other chemicals used were of analytical grade and used without any further purification. All solutions were prepared using double distilled water.

Preparation of Starch /BN Bionanocomposites
The series of starch/BN bionanocomposites were prepared by simple solution technique with variable percentage of boron nitride. The different wt% of boron nitride was dispersed in double distilled water by continuous stirring for 30 min at 50 °C and then sonication with ultrasound (120 W/180 kHz) for 30 min\cite{20-24}. The starch solution prepared in distilled water was then added to different wt% boron nitride solutions. Thereafter the prepared CuSO\textsubscript{4}/glycine solution was added to the above mixture and stirred constantly for 3 h at room temperature\cite{25}. The product was cooled and 6 ml of acetone was added to it as a non solvent and kept overnight\cite{26, 27}. The viscous product obtained was filtered and washed time and again with double distilled water. The bionanocomposites obtained were dried in an oven for 24 h at a temperature of 50 °C. Then the dried samples were powdered and coded as SBN 0, SBN 2, SBN 3, SBN 5, SBN 8, and SBN 10 for loading of 0 wt%, 2 wt%, 3 wt%, 5 wt%, 8 wt%, 10 wt% of boron nitride nanopowder respectively for characterization and study of their properties.

Characterization of Starch/BN Bionanocomposites
The formation of composites was studied by Fourier transform infrared (FTIR) spectrophotometer using a Shimadzu IR Affinity-1 instrument in the range of 4000 cm\textsuperscript{-1} to 400 cm\textsuperscript{-1}. X-ray diffraction (XRD) patterns of the nanocomposites and the raw material were obtained by using a Rigaku X-ray machine operating at 40 kV and 150 mA. The dispersion of the nano boron nitride in the starch matrix was studied using a Tec-nai 12, Phillips high resolution transmission electron microscope (HRTEM) operating at 20 kV.

The thermogravimetric analysis (TGA) of the prepared samples was carried out using a TGA apparatus of model DTG-60 by Shimadzu Corporation, Japan. The sample was heated under nitrogen purge with a heating rate of 10 K/min. Oxygen permeability of the bionanocomposites was measured with ASTM F 316-86 by using an Oxygen Permeation Analyzer (PMI instrument, model GP-201-A, Texas, NY, USA). For testing oxygen permeability, the prepared powdered bionanocomposites were changed into films of 5 mm thickness with the help of a polymer press at a pressure of 9 tons and at a temperature of 200 °C. The results were recorded as