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Cellulose nanobiocomposites with reinforcement of boron nitride: Study of thermal, oxygen barrier and chemical resistant properties

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ABSTRACT

A series of cellulose based nanobiocomposites (cellulose/BN) were prepared with incorporation of various percentage of nano boron nitride (BN). The interaction between cellulose and boron nitride was studied by Fourier transform infrared spectroscopy (FTIR). The structure of cellulose/BN nanobiocomposites was investigated by XRD, FESEM, and HRTEM. It was observed that the boron nitride nanoparticles were dispersed within cellulose matrix due to intercalation and partial exfoliation. The quantitative identification of nanobiocomposites was investigated by selected area electron diffraction (SAED). Thermal stabilities of the prepared nanobiocomposites were measured by thermo gravimetric analysis (TGA) and it was found that thermal stability of the nanobiocomposites was higher than the virgin cellulose. The oxygen barrier property of cellulose/BN nanobiocomposites was measured using a gas permeameter and a substantial reduction in oxygen permeability due to increase in boron nitride loading was observed. Further it was noticed that the chemical resistance of the nanobiocomposites was more than the virgin cellulose. Hence, the prepared nanobiocomposite may be widely used for insulating and temperature resistant packaging materials.

1. Introduction

Composite materials, which are in use for different purposes since the inception of human civilization, have expanded its ranges of application to almost all spheres. Nonrenewable based polymeric composites which are used extensively have created a lot of environmental problems. For last two decades more attention has been focused on renewable biobased composite materials, called as bio-hybrid materials (Dujardin & Mann, 2002; Ruiz-Hitzky, Darder, & Aranda, 2005). Recent developments on nanotechnology have contributed for the fabrication of bio-nanohybrid materials or bionanocomposites, by utilizing the interdisciplinary approach. These materials are of great interest due to their versatile applications in important areas as diverse as regenerative medicine and new materials with improved functional and structural properties (Darder, Aranda, & Ruiz-Hitzky, 2007; Fahmy, 2007; Fahmy & Mobarak, 2008a, 2008b; Fahmy & Mobarak, 2011a, 2011b; Fahmy, Mobarak, Fahmy, Fadl, & El-Sakhay, 2006). Nanobiocomposites represent an ecological alternative to conventional polymer nanocomposites, as the materials produced are environmentally friendly and renewable. Nanocomposites obtained from the combination of polysaccharides, such as starch, cellulose or polylactic acid (PLA) with nanoparticulated solids is also called as green nanocomposites or bioplastics (Pandey et al., 2005; Ray & Bousmina, 2005). The properties of nanobiocomposites obtained by assembling inorganic solids such as transition metals, carbon particles, metal oxides, metal hydroxides, silica, silicates, carbonates, phosphates and nitrides with biological species are of diverse nature.

Cellulose which is an organic compound with formula $(C_6H_{10}O_5)_n$, is a polysaccharide consisting of a linear chain of several hundred to over ten thousand β (1→4) linked D-glucose units, is an almost inexhaustible biopolymer with outstanding properties (Klemm, Heublen, Fink, & Bohn, 2005; Nishiyama, Langan, & Chanzy, 2002; Updegraff, 1969). For many years it has been an important raw material used in the form of intact wood for construction purposes, natural textile fibers and papers.

Cellulose derivatives have been used as optical films, coatings, controlled released systems, biodegradable plastics, biomedical materials and composites (Bledzki & Gassan, 1999). In recent years a lot of work has been devoted on nanocomposites having cellulose as a matrix with fillers such as SiO_2 (Pinto, Marques, Barros-Timmons, Trindade, & Pascoal Neto, 2008), TiO_2 (Sequeira, Evtugulin, Portugal, & Esculeas, 2007), gold (Pinto,

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Marques, Martins, Pascoal Neto, & Trinidade, 2007) and kaolin particles (Fahmy & Mobarak, 2008a, 2008b). All these composite materials show improved mechanical, optical and thermal properties due to the combination of organic and inorganic components in the final material. Vilela et al. (2010) synthesized and characterized cellulose/calcium carbonate nanocomposites and reported the improved mechanical properties as compared to virgin cellulose. Pranger and Tannenbaum (2008) prepared biobased nanocomposites of furfuryl alcohol with cellulose whisker and montmorillonite clay and reported their high thermal resistance. Cellulose acetate/organoclay nanocomposites were successfully prepared and studied their mechanical properties (Park, Mishra, Drzal, & Mohanty, 2004). Cerruti et al. (2008) prepared the cellulose/montmorillonite nanocomposites and investigated the increase in thermo-oxidative stability as compared to the cellulose.

Boron nitride bears many specific novel properties, like high melting and decomposition temperature, thermal conductivity, high thermal stability, chemically inertness, oxidation resistance, limited surface activity, nonwettability and lubricating effect. It can be hot pressed, coated and intercalated to synthesize different composites, where it plays an important role. The composite materials made of boron nitride coating/mixing/incorporating have a lot of applications, such as raw material for super abrasives, cosmetic applications, in thermal management, functional coating in the automotive industry and releasing agent in glass industry (Kisku & Swain, 2012). The cooling effect of boron nitride in cosmetics was reported in the literature (Esposito, 2002). The boron nitride composites have also been suggested for high temperature applications (Eichler & Lesnaik, 2008). The addition of boron nitride to alumina and silicon nitride improved the thermal shock resistance of the materials (Trice & Halloran, 1999). Chen et al. (2009) reported the non-cytotoxicity of boron nitride to human beings. Further, a series of works on non biodegradable polymers such as polyaniline, polystyrene and copolymer of vinylidene chloride and acrylonitrile composites were performed with reinforcement of boron nitride, in which the role of BN was justified in terms of thermal, mechanical and optical properties (Zhi, Bando, Tang, Honda, & Kuwahara, 2005; Zhi et al., 2006). A lot of works on boron nitride filled materials were reported, however the investigation of thermal and chemical resistant cellulose composites with substantial reduction in gas permeation property was scanty in the literature.

In the present study we investigated the formation of cellulose nanobiocomposites by solution method where boron nitride was intercalated with cellulose matrix. The dispersion of boron nitride and formation of nanobiocomposite has been evidenced by substantial reduction in oxygen permeability and appreciable improvement of thermal and chemical resistant property.

2. Experimental

2.1. Materials

Cellulose powder was obtained from HiMedia Laboratories Pvt. Ltd., Mumbai, India. Boron nitride nano powder (average particle size 70 nm) was obtained from Sisco Research Laboratories Pvt. Ltd., Mumbai, India, and used without any further purification. The other chemicals were of analytical grade and used as such. All solutions were prepared using double distilled water.

2.2. Preparation of cellulose/BN nanobiocomposites

Cellulose/BN nanobiocomposites were successfully prepared by solution method using variable percentage of boron nitride concentrations. Cellulose was dispersed in distilled water by stirring for 30 min at 60 °C and sonication for 30 min (Lapshin, Swain, & Isayev, 2008; Mohanty & Swain, 2010; Swain & Isayev, 2009). The different wt% solutions of boron nitride were prepared in distilled water by stirring for 30 min at 60 °C and sonication for 30 min using the same instrument. The resulting suspensions of cellulose and boron nitride were mixed and continued stirring for 3 h at 60 °C to get a viscous solution. It was kept overnight and filtered. The residue obtained thereof was dried in an oven for 24 h at 50 °C.

The dried samples were powdered and coded as CBN0, CBN1, CBN2, CBN5, CBN8 and CBN10 for 0, 1, 2, 5, 8 and 10 wt% of boron nitride concentration respectively.

2.3. Characterization of cellulose/BN nanobiocomposites

The formation of composites was studied by Fourier transform infrared (FTIR) spectrophotometer using a Shimadzu IR Affinity-1 instrument in the range of 4000–400 cm^{-1}. X-ray diffraction (XRD) patterns of the composites and the raw materials were obtained by using Rigaku X-ray machine operating at 40 kV and 150 mA. The dispersion of boron nitride nanopowder in the cellulose matrix was studied using Tec-nai 12, Phillips high resolution transmission electron microscope (HRTEM) operating at 20 kV. The surface morphology of the composites was studied with the help of field emission scanning electron microscope (FESEM) from Jeol Ltd., Japan (model 5200 with magnification of 30,000×).

The thermogravimetric analysis (TGA) of the prepared samples was performed using a TGA apparatus model DTG-60 by Shimadzu Corporation, Japan. The sample was heated under nitrogen purge and heating cycle was 10 °C/min. Oxygen permeability of the nanobiocomposites was measured with ASTM F 316-86 by using Oxygen permeation analyzer (PMI instrument, model GP-201-A, Texas, NY, USA). For testing oxygen permeability the synthesized powdered nanobiocomposites were converted into films of 5 mm thickness with the help of a polymer press at a pressure of 9 tons at a temperature of 220 °C. The results were recorded as average of the values obtained from five same samples. The biodegradability of the cellulose/BN nanobiocomposites was studied for 180 days using sludge water. Resistance of the composite toward dilute acid and alkali was measured for 60 days.

3. Results and discussion

3.1. FTIR analysis of cellulose/BN nanobiocomposites

The FTIR spectra of cellulose, boron nitride and cellulose/BN nanobiocomposites were studied to identify the functionalized groups present for the interaction as shown in Fig. 1. The FTIR spectrum of boron nitride has a strong absorption band at 812 cm^{-1} corresponding to B—N bond, which is also present around the same position in the spectra of cellulose/BN nanobiocomposites of all percentages. Further, the broad peak around 3290–3550 cm^{-1} is due to stretching vibration of —OH group of cellulose where as the peak at 2910 cm^{-1} assigned to stretching vibration of —CH, $—CH_2$ or $—CH_3$. The absorption peak at 1670 cm^{-1} corresponds to the C=O stretching mode of ester group of cellulose. The symmetric $—CH_2$ or asymmetric $—CH_3$ stretching mode band was observed at 1440 cm^{-1}. The broad peak at 1065 cm^{-1} is due to pyranose ring C—O—C and asymmetric ring stretching mode. Similar results have been reported in earlier literature (He, Chang, Peng, & Zhang, 2012; Moran, Alvarez, Cyras, & Vazquez, 2008; Vilela et al., 2010). In the synthesized nanobiocomposites all these characteristic peaks of cellulose and boron nitride were seen about the same region indicating the formation of composites.

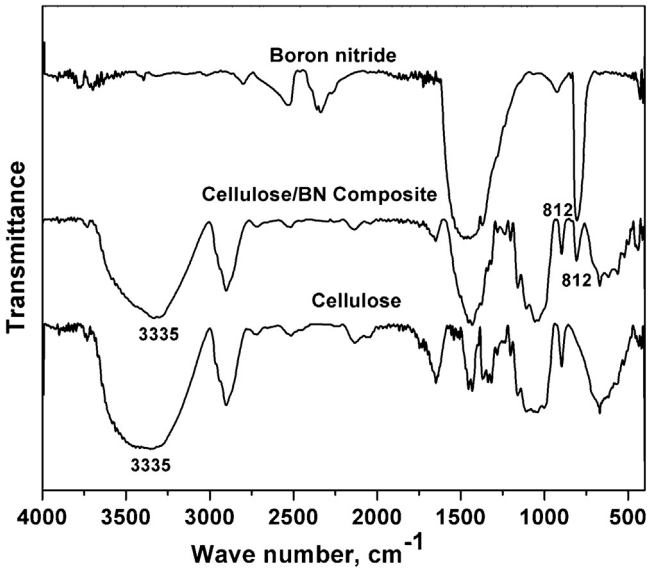

Fig. 1. FTIR spectra of boron nitride (BN), cellulose and cellulose/BN nanobiocomposites.

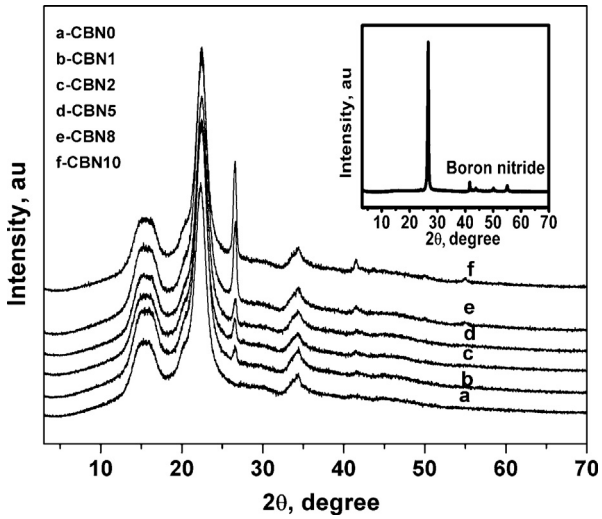

Fig. 2. XRD of boron nitride (inset) cellulose and cellulose/BN nanobiocomposites.

3.2. XRD analysis of cellulose/BN nanobiocomposites

The XRD patterns of cellulose and nanobiocomposites with various wt% of BN are shown in Fig. 2 and that of boron nitride was shown in Fig. 2 (inset). The sharp peak of BN at 2θ value of 26.7° was due to crystalline peak of boron nitride. The three crystal peaks at 2θ value of 15.7°, 22° and 34.5° were assigned to crystal plane of cellulose. In the case of nanobiocomposites the peaks of boron nitride are less intense to the virgin boron nitride. This was due to the interaction between the backbone of cellulose and boron nitride. The crystal peaks of cellulose and boron nitride are present about same position indicating formation of nanobiocomposites. The intensity of these characteristic peaks in the synthesized nanobiocomposites was less intense due to interaction between matrix and filler, hence the formation of the composite. The analysis of FESEM (Fig. 3a) results is also in agreement with the formation of composites.

3.3. Microscopic analysis of cellulose/BN nanobiocomposites

The morphology of cellulose/BN nanobiocomposites was studied by FESEM as in Fig. 3a. It was noticed that the BN nanoparticles were dispersed and distributed within the cellulose matrix to form a layered structure. The BN layers were delaminated with cellulose matrix due to intercalation and partial exfoliation structures. Further, high resolution transmission electron microscopy was used to analyze the BN structures. Though, the BNs were covered by cellulose, they still retain a perfect crystalline structure. The coverage in the image indicated the strong interaction between boron nitride and cellulose. Due to ultimately thin shape the BNs were entirely transparent to an electron beam as shown in Fig. 3b. The black spots in the HRTEM image of the nanobiocomposites may be due to local agglomeration of nano boron nitride. The selected area diffraction technique was used to identify the BN phase in the composites (Chen et al., 2004). The quantitative d-spacing of BN layers were calculated as given in Fig. 3c. The corresponding SAED pattern explained the crystallinity nature of nanobiocomposite which is in agreement with the results of XRD.

3.4. TGA analysis of cellulose/BN nanobiocomposites

To study the effect of boron nitride on the thermal property of cellulose, TGA was carried out under nitrogen atmosphere in the temperature range from 30 °C to 800 °C as shown in Fig. 4. The initial weight loss was observed at 100 °C due to the loss of water on the surface of cellulose. Cellulose shows thermal decomposition at 350 °C due to decomposition of hydroxyl group of cellulose. From TGA analysis, it was observed that cellulose decomposed completely where as a residue was observed in case of cellulose/BN nanobiocomposites. In case of boron nitride no weight loss was observed during this temperature range due to its high thermal stability. The interaction of boron nitride with the cellulose increased the thermal resistance of the composites and consequently the thermal decomposition temperature of nanobiocomposites.

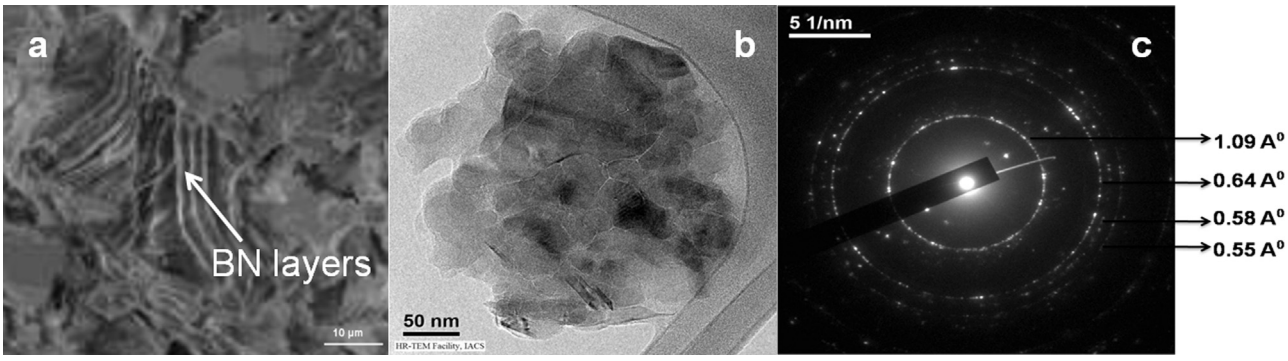

Fig. 3. (a) FESEM, (b) HRTEM and (c) SAED of cellulose/BN nanobiocomposites with 5 wt% of BN.

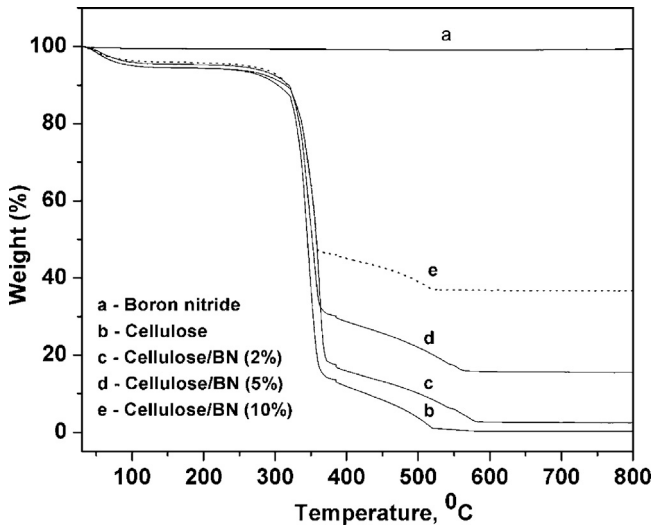

Fig. 4. The TGA of boron nitride, cellulose and cellulose/BN nanobiocomposites.

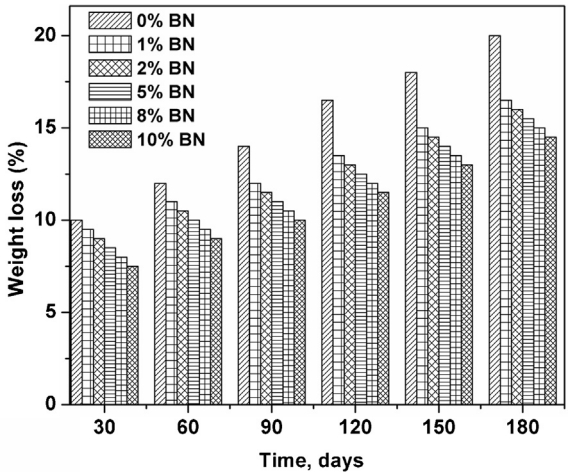

Fig. 6. The weight loss of cellulose and cellulose/BN nanobiocomposites due to biodegradation in activated sludge at different interval of time.

3.5. Oxygen permeability of cellulose/BN nanobiocomposites

Polymer based composites with reduced gas permeation property is being studied for use of packaging industries. Nanobiocomposites are the class of reinforced biodegradable polymeric materials suitable for manufacturing packaging films. The dispersion of boron nitride in cellulose matrix provides the huddles for oxygen entrance whereas; virgin cellulose may have voids for oxygen permeation. Oxygen permeability of the synthesized cellulose/BN nanobiocomposites was conducted to measure the effect of boron nitride concentrations on oxygen barrier properties of the cellulose matrix. The oxygen flow rate through all the nanobiocomposites was observed to be less in comparison to the virgin cellulose at constant pressures of 2 psi (Fig. 5a). It was found that the flow rate was decreased with increase in percentage of boron nitride loading. The remarkable reduction in oxygen permeability was due to nanostructure dispersion of boron nitride within the cellulose matrix at difference pressure up to 2 psi (Fig. 5b).

3.6. Biodegradation study

The biodegradation of cellulose/BN nanobiocomposites was compared with virgin cellulose in a study for 180 days in an interval of 30 days. The degradation was studied in order to calculate percentage weight loss of materials in an activated sludge (Fig. 6). It was noticed that the percentage weight loss in nanobiocomposites was decreased with increase in percentage of boron nitride loading. However biodegradation of nanobiocomposites as well as virgin cellulose were increased with increase in time duration with the sludge water. The weight loss of cellulose after 30 days was found to be double in weight loss of nanobiocomposites after 180 days. The decrease in biodegradation of composite as compared to virgin cellulose was due to active participation and well dispersion of BN with cellulose matrix. However, the properties of thermal resistance and gas permeability have been compromised with the less biodegradable properties of nanobiocomposites (Dash, Kisku, & Swain, 2012).

3.7. Resistance to chemicals

In order to study the effect of acid and base on the synthesized nanobiocomposite, the synthesized materials were treated with dilute hydrochloric acid (2 N) and dilute sodium hydroxide (2 N) for 60 days. The % weight loss of the nanobiocomposites was measured in an interval of 10 days (Fig. 7). The virgin cellulose was resistant to these chemicals however the resistance was more in the case of cellulose/BN nanobiocomposites. Further the resistance was remarkably increased by increasing the boron nitride nanofiller loading. The higher resistance of the synthesized nanobiocomposites may be due to superior properties and inertness of boron nitride.

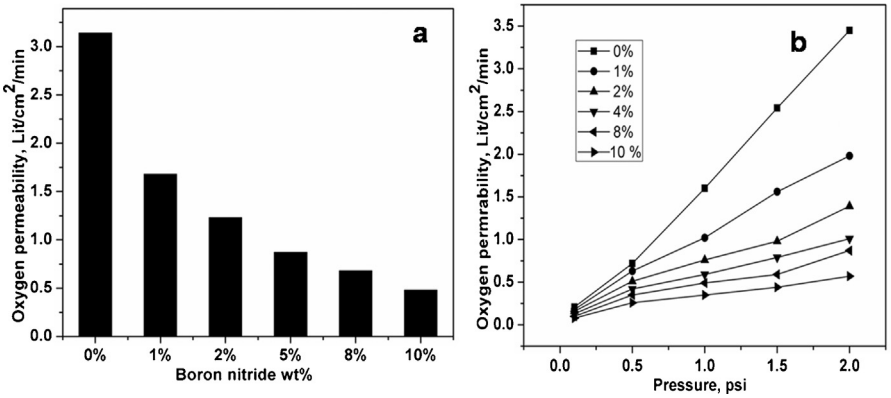

Fig. 5. (a) The oxygen permeability of cellulose/BN nanobiocomposites with various loading of BN at constant pressure of 2 psi and (b) the oxygen permeability of cellulose/BN nanobiocomposites with various loading of BN at difference pressure.

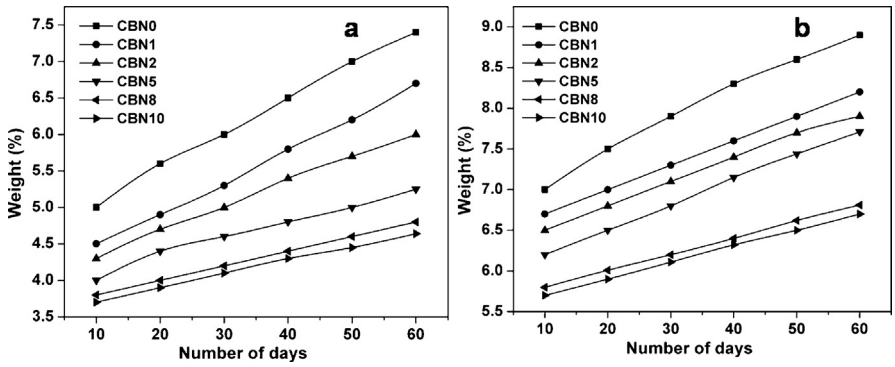

Fig. 7. The weight loss (%) of cellulose and cellulose/BN nanobiocomposites due to treatment of (a) HCl and (b) NaOH at different interval of time.

4. Conclusions

Cellulose/BN nanobiocomposites were synthesized by low cost green technique where water was used as the solvent. The dispersion of BN nanoparticles was achieved which has been evidenced by FESEM and HRTEM. The nanobiocomposite was found to be crystalline from the study of XRD and SAED pattern. The thermal stability of nanobiocomposites was improved as compared to virgin cellulose without compromising the oxygen barrier property. The synthesized nanobiocomposites were resistant to mineral acid and alkali with little scarification of biodegradability. The chemical resistant nanobiocomposites having enhanced thermal stability with substantial reduction in oxygen permeability may enable for usages as covering and protective materials.

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References

Bledzki, A. K., & Gassan, J. (1999). Composites reinforced with cellulose based fibers. *Progress in Polymer Science*, *24*, 221–274.

Cerruti, P., Ambrogi, V., Postiglione, A., Rychly, J., Rychla, L. M., & Carfagna, C. (2008). Morphological and thermal properties of cellulose–montmorillonite nanocomposites. *Biomacromolecules*, *9*(11), 3004–3013.

Chen, L., Huang, M., Luo, T., Gu, Y., Shi, L., Yang, Z., et al. (2004). A low temperature route to nanocrystalline boron nitride whiskers. *Materials Letter*, *58*, 3634–3636.

Chen, X., Wu, P., Rousseas, M., Okawa, D., Gartner, Z., & Zettl, A. (2009). Boron nitride nanotubes are noncytotoxic and can be functionalized for interaction with proteins and cells. *Journal of American Chemical Society Communication*, *131*, 890–901.

Darder, M., Aranda, P., & Ruiz-Hitzky, E. (2007). Bionanocomposites: A new concept of ecological bioinspired and functional hybrid materials. *Advanced Materials*, *19*, 1309–1319.

Dash, S., Kisku, S. K., & Swain, S. K. (2012). Effect of nanoclay on morphological, thermal and barrier properties of albumin bovine. *Polymer Composites*, *33*(12), 2201–2206.

Dujardin, E., & Mann, S. (2002). Insightful review of biomineralization from a molecular biological perspective. *Advanced Materials*, *14*, 775–788.

Eichler, J., & Lesnaik, C. (2008). Boron nitride (BN) and BN composites for high temperature applications. *Journal of European Ceramic Society*, *28*(5), 1105–1109.

Esposito, M. (2002). The cooling effect of boron nitride in cosmetic formulations, cosmetics and toiletries. *Manufacture Worldwide*, *1*, 36–39.

Fahmy, T. Y. A. (2007). Introducing molasses as a new additive in papermaking. *TAPPI Journal*, *6*(8), 23–25.

Fahmy, T. Y. A., & Mobarak, F. (2008a). Vaccination of biological cellulose fibers with glucose: A gateway to novel nanocomposites. *International Journal of Biological Macromolecules*, *42*(1), 52–54.

Fahmy, T. Y. A., & Mobarak, F. (2008b). Nanocomposites from natural cellulose fibers filled with kaolin in presence of sucrose. *Carbohydrate Polymers*, *72*(4), 751–755.

Fahmy, T. Y. A., & Mobarak, F. (2011a). Advanced nano-based manipulations of molasses in the cellulose and paper discipline: Introducing a master cheap environmentally safe retention aid and strength promoter in papermaking. *Carbohydrate Polymers*, *77*(2), 316–319.

Fahmy, T. Y. A., & Mobarak, F. (2011b). Green nanotechnology: A short cut to beneficiation of natural fibers. *International Journal of Biological Macromolecules*, *48*(1), 134–136.

Fahmy, T. Y. A., Mobarak, F., Fahmy, Y., Fadl, M. H., & El-Sakhay, M. (2006). Nanocomposites from natural cellulose fibers incorporated with sucrose. *Wood Science and Technology*, *40*, 77–86.

He, M., Chang, C., Peng, N., & Zhang, L. (2012). Structure and property of hydroxyapatite/cellulose nanocomposite film. *Carbohydrate Polymers*, *87*, 2512–2518.

Kisku, S. K., & Swain, S. K. (2012). Synthesis and characterization of chitosan/boron nitride composites. *Journal of the American Ceramic Society*, *95*(9), 2753–2757.

Klemm, D., Heublen, B., Fink, H. P., & Bohn, A. (2005). Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition*, *44*(22), 3358–3393.

Lapshin, S., Swain, S. K., & Isayev, A. I. (2008). Ultrasound added extrusion process for preparation of polyolefin–clay nanocomposites. *Polymer Engineering and Science*, *48*(8), 1584–1591.

Mohanty, A., & Swain, S. K. (2010). Ultrasonic and viscometric investigation of albumin proteins in aqueous solution. *Journal of Indian Chemical Society*, *87*, 461–464.

Moran, J. I., Alvarez, V. A., Cyras, V. P., & Vazquez, A. (2008). Extraction of cellulose and preparation of nanocellulose from sisal fibers. *Cellulose*, *15*, 149–159.

Nishiyama, Y., Langan, P., & Chanzy, H. (2002). Crystal structure and hydrogen-bonding system in cellulose IB from synchrotron X-ray and neutron fiber diffraction. *Journal of American Chemical Society*, *124*(31), 9074–9082.

Pandey, J. K., Kumar, A. P., Mishra, M., Mohanty, A. K., Drzal, L. T., & Palingh, R. (2005). Recent advances in biodegradable nanocomposites. *Journal of Nanoscience and Nanotechnology*, *5*, 497–526.

Park, H. M., Mishra, M., Drzal, L. T., & Mohanty, A. K. (2004). Green nanocomposites from cellulose acetate bioplastic and clay: Effect of eco friendly triethyl citrate plasticizer. *Biomacromolecules*, *5*(6), 2281–2288.

Pinto, R. J. B., Marques, P. A. A. P., Barros-Timmons, A. M., Trindade, T., & Pascoal Neto, C. (2008). Novel SiO_2/cellulose nanocomposites obtained by in situ synthesis and via polyelectrolytes assembly. *Composite Science and Technology*, *68*, 1088–1093.

Pinto, R. J. B., Marques, P. A. A. P., Martins, M. A., Pascoal Neto, C., & Trinidade, T. (2007). Electrostatic assembly and growth of gold nanoparticles in cellulosic fibers. *Journal of Colloid and Interface Science*, *312*, 506–512.

Pranger, L., & Tannenbaum, R. (2008). Biobased nanocomposites prepared by in situ polymerization of furfuryl alcohol with cellulose whiskers on montmorillonite clay. *Macromolecules*, *41*, 8682–8687.

Ray, S. S., & Bousmina, M. (2005). Biodegradable polymers and their layered silicate nanocomposites: In greening the 21st century materials world. *Progress in Materials Science*, *50*, 962–1079.

Ruiz-Hitzky, E., Darder, M., & Aranda, P. (2005). Functional hybrid materials. *Journal of Materials Chemistry*, *15*, 3650–3662.

Sequeira, S., Evtugulin, D. V., Portugal, I., & Esculeas, A. P. (2007). Synthesis and characterization of cellulose/silica hybrids obtained by heteropoly acid catalysed sol–gel process. *Materials Science and Engineering*, *27*, 172–179.

Swain, S. K., & Isayev, A. I. (2009). PA_6/clay nanocomposites by continuous sonication process. *Journal of Applied Polymer Science*, *114*, 2378–2387.

Trice, R. W., & Halloran, J. W. (1999). Investigation of physical and mechanical properties of hot-pressed boron nitride/oxide ceramic composites. *Journal of the American Ceramic Society*, *82*(9), 2563–2565.

Updegraff, D. M. (1969). Semimicro determination of cellulose in biological materials. *Analytical Biochemistry*, *32*(3), 420–424.

Vilela, C., Freire, C. S. R., Marques, P. A. A. P., Trinadade, T., Pascoal Neto, C., & Fardim, P. (2010). Synthesis and characterization of new $CaCO_3$/cellulose nanocomposites prepared by controlled hydrolysis of dimethylcarbonate. *Carbohydrate Polymers*, *79*, 1150–1156.

Zhi, C., Bando, Y., Tang, C., Honda, S., & Kuwahara, H. (2005). Characterization of boron nitride nanotube–polyaniline composites. *Angew Chemistry*, *44*, 7929–7932.

Zhi, C., Bando, Y., Tang, C., Honda, S., Kuwahara, H., & Golberg, D. (2006). Boron nitride nano tubes/polystyrene composites. *Journal of Materials Research*, *21*(11), 2794–2800.