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J. Mater. Sci. Technol., 2014, 30(8), 791−795

JMST

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Thermal and Oxygen Barrier Properties of Chitosan Bionanocomposites by Reinforcement of Calcium Carbonate Nanopowder

Sarat K. Swain[1,2)*], *Satyabrata Dash*[2)], *Sudhir K. Kisku*[2)], *Rajesh K. Singh*[2)]

1) Department of Chemistry, Veer Surendra Sai University of Technology, Burla, Sambalpur 768018, India

2) Department of Chemistry, North Orissa University, Takatpur, Baripada 757003, India

[Manuscript received August 24, 2013, in revised form September 29, 2013, Available online 8 January 2014]

Chitosan and calcium carbonate nanopowder (chitosan/$CaCO_3$) bionanocomposites were prepared by solution method. Interaction between chitosan and $CaCO_3$ was studied by Fourier transform infrared spectroscopy (FT-IR). Structure and surface morphology of chitosan/$CaCO_3$ bionanocomposites were investigated by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM), respectively. The energy dispersive X-ray spectroscopy (EDS) of chitosan/$CaCO_3$ bionanocomposites was studied in order to establish the elements of composition. Thermal stability of prepared bionanocomposites was studied by thermogravimetric analysis (TGA) and a substantial increase of thermal stability of virgin chitosan was noticed due to incorporation of $CaCO_3$ nanopowder. The oxygen permeability was reduced by three times as compared to the raw chitosan due to the dispersion of nano $CaCO_3$ filler. Biodegradability and resistance towards dilute acid and alkali of the prepared bionanocomposite were investigated. The bionanocomposite having gas barrier and thermal stable property may be suitable for packaging and biomedical applications.

KEY WORDS: Chitosan; Nanocomposites; Thermal properties; Oxygen permeability

1. Introduction

Ever since mankind felt the need of suitable packaging to preserve materials for future use, there have been constant and continuous efforts to devise various methods and means of packaging: from ancient stranded straw bowls for food grains to to-day's small covering of a medicine. Past century contributed various synthetic polymeric materials to the society in various forms, such as plastics, fibres and synthetic rubber which are widely used in variety of fields including packaging, construction materials, agriculture and medical devices. No doubt, these synthetic materials having non-renewable resource origin perform very important roles in our day to day life. On the other hand, due to fast developing society the use of these materials has increased manifold, thereby posing grave concern and danger of pollution to soil, air, water and in fact, to the whole environment due to their non-biodegradability and toxicity[1]. However, to resolve this problem, the modification, development and use of biodegradable polymer of renewable resources are considered as the most advantageous method. Since the last decade of twentieth century the bio based polymers are carefully studied for developing biodegradable polymeric materials to compete with the conventional non-degradable one. A variety of biodegradable polymeric materials have been synthesized and a lot of them have already been industrialized[2−4].

Among the biopolymers, chitosan has shown great potential as biodegradable packaging material as well as in biomedical applications. It is a linear polysaccharide composed of randomly di-substituted β-linked D-glucosamine and N-acetyl-D-glucosamine, and is a fully or partially deacetylated product of chitin, the second most abundant natural resource next to cellulose[5]. As chitosan is biodegradable, biocompatible and almost non-toxic material, it has been widely used in biomedical field and as packaging material. It has reactive amino hydroxyl groups, which offer possibilities of modifications, graft reactions and acid interactions. It possesses a unique cationic nature relative to other neutral or negatively charged polysaccharides[6].

Due to the novel properties of chitosan, researchers investigated this biopolymer for various applications, such as in waste water treatment[7], drug delivery system[8], cell culture[9], antimicrobial agent in textile chemicals[10], biomaterials in cartilage tissue[11], and superabsorbent materials[12]. For several decades investigations have been continuing on chitosan for molecular

* Corresponding author. Prof., Ph.D.; Tel.: +91 9937082348; Fax: +91 663 2430204; E-mail address: swainsk2@yahoo.co.in (S.K. Swain).

http://dx.doi.org/10.1016/j.jmst.2013.12.017

separation, food packaging films, artificial skins, bone substitutes, water engineering and solubility in aqueous medium. However, its mechanical properties are not sufficient enough to meet this wide range of applications. In the literature nanostructured materials are reported for bone tissue engineering[13] and repairing large gaps in severed nerves[14]. A lot of advances on chitosan based nanocomposites have been made to test the best of its uses[15−18]. Biodegradable chitosan/hydroxyapatite nanocomposites were prepared through *in situ* hybridization and reported as a potential material for internal fixation of bone fractures. It was also suggested that the mechanical properties of the composites were increased remarkably and the material was stronger than other bone replacement materials such as methylmethacrylate (PMMA) and bone cement[19]. The chitosan/multiwalled carbon nanotubes (MWNTs) composites show significant improvement of mechanical properties compared with those of neat chitosan as reported by Wang et al.[20]. The chitosan/SiO_2 hybrid composites were prepared and the enhancement of thermal stability with increasing SiO_2 concentration was reported[21]. Some literature[22,23] reported the preparation of chitosan/gold nanocomposites and their application for biosensors and cell culture. In our previous work, chitosan/boron nitride composites were synthesized and the enhancement of thermal and barrier property was reported, suggesting its application in packaging industry[24].

In plastic industries, inorganic fillers are used to improve mechanical properties, such as hardness, toughness, stiffness, mould shrinkage and heat distortion temperature. Enhancement of mechanical properties has been obtained by incorporation of nano sized filler rather than micron-sized one[25,26]. But the physical properties, such as surface smoothness and barrier properties, cannot be achieved by using conventional micron-sized particles. Among the inorganic fillers, calcium carbonate is one of the most abundant biomaterials which can be grown easily under laboratory conditions[27,28]. It is one of the most commonly used inorganic filler for thermoplastics, such as poly (vinyl chloride) and polypropylene (PP)[29]. Efforts have been devoted to surface modified $CaCO_3$ particles to increase the polymer−filler interactions and the enhancement of mechanical properties was reported[30]. Cgan et al.[31] synthesized polypropylene/calcium carbonate nanocomposites and the increase in mechanical properties of polypropylene was reported. John et al.[32] successfully synthesized and characterized cellulose acetate-calcium carbonate hybrid nanocomposites. The poly (methyl methacrylate)/nano calcium carbonate composite was prepared by *in situ* emulsion polymerization and the higher grafting efficiency of the composite was reported[33].

There are series of works on chitosan based composites, but the work related to the composites of chitosan reinforced by $CaCO_3$ nanopowder for study of thermal, oxygen barrier, biodegradable and chemical resistance properties is scarce in literature. In this study the chitosan/$CaCO_3$ bionanocomposites were prepared with variable percentage of nano $CaCO_3$. The uniform dispersion of $CaCO_3$ in chitosan matrix was achieved in order to enhance the thermal and oxygen barrier properties. The biodegradable and chemical resistant properties were also investigated.

2. Experimental

2.1. Materials

Chitosan powder with deacetylation degree of 90% was a product of the Thermo Fisher Scientific, Mumbai, India. Calcium carbonate nanopowder of average particle size of 80 nm was obtained from Sisco Research Laboratories Mumbai, India. Other chemicals were of analytical grade and used as such. All solutions were prepared by using double distilled water.

2.2. Preparations of chitosan/$CaCO_3$ bionanocomposites

Chitosan/$CaCO_3$ bionanocomposites were prepared by solution method taking variable percentage of calcium carbonate. Chitosan was dissolved in 2% aqueous acetic acid solution to produce 2 wt% chitosan solutions. Required amount of prepared chitosan solution was taken in a conical flask. The calcium carbonate nanopowder emulsion with different percentage was prepared by dispersing it in double distilled water by stirring for 30 min at 50 °C and sonication for 30 min (120 W/60 kHz)[34]. After ultrasound treatment the calcium carbonate solutions with different percentage was added to prepare 2 wt% solution of chitosan and stirred for 2 h at 50 °C. Then a prepared 2 wt% sodium hydroxide solution was added dropwise while stirring to get the precipitate. The precipitate was filtered and washed repeatedly to wash off excess alkali. Residues were dried in an oven at 50 °C for 24 h. The prepared dry samples of chitosan/$CaCO_3$ bionanocomposites were powdered and coded as in Table 1. These were preserved for characterization and study of their properties.

2.3. Characterization of chitosan/$CaCO_3$ bionanocomposites

Fourier transform infrared spectroscopy (FT-IR) spectra of the prepared samples were recorded by using a Shimadzu IR Affinity-1 Fourier transform infrared spectrophotometer in the range of 4000 to 400 cm^{-1}. X-ray diffraction (XRD) patterns were obtained by using a Rigaku X-ray machine operating at 40 kV and 150 mA. The surface morphology of the composites was studied with the help of field emission scanning electron microscopy (FESEM, 5200, Jeol Ltd., Japan). The thermogravimetric analysis (TGA) of the prepared samples was performed using a TGA apparatus (DTG-60, Shimadzu, Japan). The sample was heated under nitrogen purge with heating rate of 10 °C/min. Oxygen permeability of the bionanocomposites was measured with STM F 316-86 by using oxygen permeation analyzer (PMI instrument, GP-201-A, Texas, NY, USA). For testing oxygen permeability the synthesized powdered bionanocomposites were converted into films of 5 mm thickness with the help of a polymer press at a pressure of 88260 Pa. The results were recorded as average of the values obtained from five same samples. The biodegradability of the bionanocomposites was studied for six months using sludge water. Resistance towards normal chemicals like dilute HCl and NaOH was investigated for 60 days.

Table 1 Formulation table of chitosan/CaCO3 bionanocomposites at different concentrations of chitosan and calcium carbonate nanopowder

Sample code	Chitosan (w/v, %)	Nano $CaCO_3$ (w/w, %)
CCC 0	5	0
CCC 1	5	1
CCC 2	5	2
CCC 5	5	5
CCC 8	5	8
CCC 10	5	10