Effect of zirconium oxide nanopowder on the thermal, chemical and gas barrier properties of starch

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ABSTRACT

Starch/zirconium oxide (Starch/ZrO$_2$) bionanocomposites were prepared using various percentages of nano-ZrO$_2$ by a solution technique. The interaction of ZrO$_2$ nanocomposites with starch was studied by Fourier transform infrared spectroscopy (FTIR) and their structural behavior was investigated by X-ray diffraction (XRD). The dispersion of ZrO$_2$ within virgin starch was investigated by a field emission scanning electron microscope (FESEM), a high resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED). Thermal properties of starch/ZrO$_2$ bionanocomposites were studied by thermogravimetric analysis (TGA). An increase in thermal stability was observed with increase in filler loading. The conductivity of starch/ZrO$_2$ bionanocomposites was measured and an increase in conductivity was observed due to the increase in ZrO$_2$ concentration. Starch/ZrO$_2$ bionanocomposites were more resistant towards chemicals like dilute acid and alkali. The oxygen barrier property of composites was studied and a substantial reduction in permeability was observed. Further, the biodegradability of starch/ZrO$_2$ bionanocomposites was reduced. Thermally stable, chemical resistant, and gas barrier starch bionanocomposites with conducting property may enable the materials for manufacturing packaging materials and semiconducting devices.

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1. Introduction

Nanocomposites are the byword of modern science that holds vast possibilities of eco-friendly high performance materials exhibiting unusual properties due to combinations and unique designing. Because of high growth in demand for engineering polymers, there is tremendous potential for nanocomposite materials, as they have proven to be useful in several applications ranging from packaging to biomedical. Literature survey has reported that at a nanoscale (1–100 nm), the material's property can change dramatically [1–4]. With only reduction in size and no change in the substance, nanocomposites can exhibit new properties, such as electrical conductivity, insulating quality, elasticity, greater strength, different colors and more reactivity. The application of new configuration concept to nanocomposites leads to a significant improvement in strength and moderate fracture toughness [5]. The microstructure of nanocomposites is designed by uniform dispersion of nano-size filler particles that produce ultra-large interfacial area per unit volume between nanofillers and the polymer matrix. This interfacial area and nanoscopic dimensions of particles assist in the formation of a hybrid structure, which vitally differentiates polymer nanocomposites from regularly filled plastics [6–9]. Thermal property mismatch between the matrix and filler particles produces a remarkable improvement in mechanical properties such as fracture strength, fracture toughness, creep resistance, thermal shock resistance and wear resistance [10].

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Conducting fillers including carbon black, graphite and metal powder to set up electrically conducting composites have engrossed vast interest for decades [11,12]. Conductivity of nanocomposites depends upon the loading of conducting fillers. At present nanocomposites have large scale industry use and market prospects.

Over the past decades, attempts have been made on blending plastic materials with cheap, non-toxic, environ-ment-friendly and biodegradable natural biopolymers, such as starch, cellulose and chitin, to create new materials with desired properties [13–27]. The biopolymer, especially starch, is abundant, inexpensive, renewable, and fully biodegradable. It contains two microstructures, e.g. linear (amylose) and branched (amylopectin). Amylose has a linear structure of α-1,4 linked glucose units with a molecular weight of 105–106 and amylopectin is a highly branched structure of short α-1,4 chains linked by α-1,6 bonds with a molecular weight of 107–109 [28]. However, in addition to being susceptible to water absorption, blends of this biopolymer exhibit inferior mechan-ical properties because of the hydrophilic character of starch which leads to poor adhesion with the hydrophobic polymer. Ali et al. studied the nanostructure, molecular conformations and interactions in the multicomponent nanocomposites of starch/polyvinyl alcohol/sodium montmorillonite films [29]. Recent advances in starch, polyvinyl based polymer blends and nanocomposites were reviewed by Tang and Alavi [30]. In our earlier works, we had reported the preparation and characterization of starch/SiC and starch/f-MWCNT nanocom-posites in order to study their thermal and gas barrier properties [31,32].

Nanostructured metal oxides, owing to their small size, exhibit most interesting chemical, physical, and electronic properties that are different from those of bulk materials and can be used to design novel and improved sensing devices, in particular, electrochemical sensors and biosen-sors [33,34]. High hardness, low wear resistance, low coefficient of friction, high elastic modulus, chemical inertness, good ionic conductivity, low thermal conductiv-ity and high melting temperature are common properties of nanostructured metal oxides [35,36]. They are found in varnishes for electronic items, in inkjet printers and other products. Zirconia is a semiconducting material with extensive toughness and strength. Various properties of zirconia, i.e. light absorption, emission characteristics along with other are significantly modified at the nanodi-mension range for which nanozirconia reinforced polymer composites can be used as semiconductor processing materials [37,38]. Semiconductor based nanocomposite materials have been engaged in multiple applications including light emitting devices, optical switches and memory device applications in the electronic industry [39,40]. A large number of nanostructured metal oxides such as Cerium oxide (CeO_2), Iron oxide (Fe_3O_4), Nickel oxide (NiO), Tin oxide (SnO_2), Zinc oxide (ZnO) and Zirconium oxide (ZrO_2) have been explored for application in electrochemical biosensors [41–43]. Among these, ZrO_2 has attracted much attention because of its thermal stability, chemical inertness, biocompatibility, and affinity towards the groups containing oxygen [44,45].

Although a number of works are present on polymer based nanocomposites reinforced by ZrO_2, but the works related to the bionanocomposite based on starch/ZrO_2 materials are few and far between. The objective of the present work is to synthesize thermal and chemical resistant gas barrier starch bionanocomposite with the reinforcement of ZrO_2 nanopowder. The prepared starch/ZrO_2 bionanocomposites are thermally more stable than the virgin starch. Further, the synthesized bionanocompo-sites are more resistance towards acid and alkali. The gas barrier nature of the bionanocomposites is less than raw starch. The conductivity of the prepared bionanocompo-sites is also investigated in order to find out the suitability of the material for application in packaging and semicon-ducting devices.

2. Experimental

2.1. Materials

Starch soluble extra pure was obtained from Merck Specialities Private Limited, Mumbai, India and used as such. ZrO_2 nanopowder (average particle size of 45 nm) was purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai, India and used without any further modification. The other chemicals used were of analytical grade and used without any further purification. All solutions were prepared using double distilled water.

2.2. Preparation of starch/ZrO_2 bionanocomposites

Series of starch/ZrO_2 bionanocomposites were pre-pared with variable wt% of ZrO_2 by the solution technique. ZrO_2 was dispersed in double distilled water by continuous stirring at 60 °C for 30 min and then sonication with ultrasound was performed (120 W/180 kHz) for 30 min [46–48].The starch solution prepared in distilled water was then added to different wt% ZrO_2 solutions. Similar to our earlier work $CuSO_4$/glycine chelate complex as a catalyst [49,50] was added to the above mixture and stirred continuously for 3 h at room temperature. The emulsion obtained was cooled and 6 ml of acetone was added as a non-solvent and kept overnight [51,52]. The viscous product obtained was filtered and washed with double distilled water. The bionanocomposites obtained were dried in an oven for 24 h at a temperature of 50 °C. The dried samples were powdered and marked as S/ZrO 0, S/ZrO 1, S/ZrO 2, S/ZrO 5, S/ZrO 8, and S/ZrO 10 for loading of 0, 1, 2, 5, 8, and 10 wt% of ZrO_2 nanopowder, respectively for characterization and study of their properties.

2.3. Characterization of starch/ZrO_2 bionanocomposites

FTIR spectra of prepared samples (in the form of KBr pallets) were recorded using a Shimadzu IR Affinity-1 Fourier infrared spectrophotometer in the range of 4000–400 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 bionano-composites was studied with the help of a field emission scanning electron microscope (FESEM) from Jeol Ltd., Japan (model 5200 with magnification of 30000 ×). The dispersion of ZrO_2 nanopowder in the starch matrix