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Biodegradable hybrid nanocomposites of chitosan/gelatin and silver nanoparticles for active food packaging applications

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ABSTRACT

Due to stringent environmental regulations, packaging industry is exploring economically viable biodegradable packaging materials for food use with desired properties and less impact on the environment. Biopolymers such as chitosan, gelatin have emerged as effective alternatives to plastic packaging materials, with desired packaging functionality and biodegradability. In this present work, we have successfully fabricated hybrid nanocomposite film consisting of chitosan, gelatin, polyethylene glycol and silver nanoparticles (AgNPs) by solution casting method. A series of films was prepared having different contents of AgNPs and chitosan. Nano-Ag addition led to enhanced mechanical properties and decrease in light transmittance in visible light region. However, transparency studies, X-ray Diffraction (XRD) pattern, Scanning Electron Microscopy (SEM) and optical microscopy confirmed transparent and homogenous nature for all newly prepared films indicating the uniform distribution of the components in the developed films. Further studies on packaging of red grapes indicated that the shelf life of the fruit extended for additional two weeks in case of the hybrid film. Therefore, the results of the present study can be further explored to fabricate commercially viable and effective packaging material for food applications.

1. Introduction

Bioplastics have received considerable interest as an alternative packaging materials to plastics, which are made from petroleum by-products (Yang et al., 2015). The bioplastics may degrade under appropriate conditions of moisture, temperature and oxygen availability and do not produce any toxic residue, but at the same time overall environment impact needs further assessment (e.g. life cycle analysis) to validate the above claims. Once validated, bioplastics may find increased use in the food packaging and allied industrial products.

Packaging films for food materials should have desired mechanical and barrier properties for light and mass transfer (O_2, CO_2 and moisture)and therefore, the bioplastic should possess the same. The two common biopolymers, chitosan (CS) and gelatin (GL) are extensively used in food, pharmaceutical and other product applications (Volpe et al., 2015). CS-based films and coatings are reported to exhibit good barrier property against water vapour (Dutta, Tripathi, Mehrotra, & Dutta, 2009). However, the mechanical and antimicrobial properties of pure chitosan film do not satisfy the food packaging needs (Aljawish et al., 2016; Sadeghi & Shahedi, 2016). The other abundantly available biopolymer, GL has also good film forming ability and readily absorb UV-light due to presence of aromatic amino acid in their structures. However, the poor mechanical, thermal and barrier properties in comparison to conventional plastics are the major disadvantages to use gelatin as food packaging material (Vieira, da Silva, dos Santos, & Beppu, 2011). In general, blending of two different biopolymers may optimize the physico-chemical and barrier properties of the gelatin based films for food applications (Malafaya, Silva, & Reis, 2007). Therefore, the composite film fabricated by blending of CS with GL may perform better with respect to physico-chemical properties in comparison to film developed with mono-biopolymer, either CS or GL. Incorporation of nanoscale materials as a filler into such CS-GL composite film generally further enhances the mechanical, thermal, barrier performance of the film (Hosseini, Rezaei, Zandi, & Ghavi, 2013; Jridi et al., 2014). In this respect, silver nanoparticles (nano Ag) appear to be the material of choice due to its antimicrobial activity. (Kumar, Mitra, & Halder, 2017). To make the biopolymer-nanoparticles composite material cheap, non-toxic and environmentally benign, the nanoparticles should be originated out of green protocol (Roopan et al., 2013). One of the promising green synthesis protocols of silver nanoparticle is to use

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extract of plant materials like root, stem, bark, leaf, fruit, etc. as reducing and stabilizing agent (Kumar, Singh, Halder, & Mitra, 2015; Kumar et al., 2017; Roopan et al., 2013). It has been shown that polyphenols, flavonoids, alkaloid, etc., present in extract of various plant part, may act as reducing as well as stabilizing agent during nanoparticles synthesis (Nethravathi et al., 2015).

Mimuosops elengi is an evergreen tree distributed throughout the greater parts of India having enormous medicinal value (Jahan, Ahmed, & Malik, 1995; Mitra, 1981). It has been reported that the fruit extract of *Mimuosops elengi* plant is rich in terpenoids, steroids, steroidal glycosides, flavonoids and alkaloids (Baliga, Pai, Bhat, Palatty, & Baloor, 2011). The objective of this study was to develop CS, GL and AgNPs based nanocomposite films with enhanced microbial protection or enhanced antimicrobial properties to increase the shelf life of red grapes. The present study reports on the fabrication of chitosan and gelatin based packaging film incorporated with nano-Ag. Green synthesis of silver nanoparticles was performed using aqueous fruit extract of *Mimusops elengi*, as the reducing and stabilizing agent. Optical, mechanical, structural, and antimicrobial properties of the films were examined to assess their potential use in food packaging.

2. Materials and methods

2.1. Materials

Silver Nitrate ($AgNO_3$, with more than 99.5% purity) and Chitosan (Low MW, having more than 90% degree of deacetylation) were procured from Sisco Research Laboratories (SRL) Pvt. Ltd., India. Purified Gelatin was purchased from Merck Pvt. Ltd., India. Polyethylene glycol and Acetic acid both were procured from RANKEM RFCL Ltd., India. Fruit of *Mimusops elengi* (Bakul/Maulsiri) was collected from the campus garden of our Institute CIT Kokrajhar, Assam.

2.2. Preparation of aqueous extract of fruit

Fresh fruit was collected from tree of *Mimusops elengi* and washed with double distilled water. It was first dried in shed at room temperature and then at 70 °C for 24 h in a hot air oven (Macro Scientific Pvt. Ltd., MSW-211, Delhi, India). The dried fruits were ground using mixture grinder (Bajaj, Classic-750, India) for 5 min at 6000 rpm and then sieved (200 μm) to separate out the finest powder. Finally, it was stored in the sealed air tight plastic container. Hot water extraction method was used to get aqueous extract of the fruit powder. 100 mL of distilled water was taken into a volumetric flask and 4 g m of fruit powder was added into it. The mixture was heated at 60 °C for 15 min and filtered using filter paper. The filtrate was centrifuged in a cooling centrifuge (REMI, C-24BL, Maharastra, India) at 10,000 rpm for 10 min at 25 °C. The supernatant was collected and termed as an aqueous fruit extract and stored at 6.0 ± 0.5 °C for further use.

2.3. Synthesis of AgNPs

For synthesis of AgNPs, 19 mL of silver nitrate solution (2 mM) was taken in 30 mL glass container. It was heated at 70 °C on a hot plate magnetic stirrer (2MLH, REMI, India) at 500 rpm with continuous stirring. After 5 min heating, the fruit extract was added drop wise into the glasscontainer. Similarly, five different samples were prepared by varying the percentage of fruit extract in the reaction mixture from 1 to 5 (v/v). Additionally, one blank sample was also prepared with 1.0 mL fruit extract in 19 mL of double distilled water. The final volume was made up to 20 mL in each case by adding double distilled water. As heating continued up to 70 min, the colour of the mixture gradually turned from colourless to light yellow to yellowish brown due to formation of silver nanoparticles. To know the completion of reduction process, the UV–vis spectra (spectrophotometer, Perkin Elmer; model λ-35, Massachusetts, USA) of the reaction mixtures were taken at each regular interval of time.

2.4. Characterization of synthesized AgNPs

The UV–vis absorption spectra of reaction mixture was recorded as a function of reaction time and the amount of fruit extract added using UV–vis spectrophotometer (Perkin Elmer; model λ-35, USA) with a quartz cell (1 cm path). Transmission electron microscopy (TEM) analysis of as-synthesized silver nanoparticles was performed at an acceleration voltage of 200 KeV with the microscope (FEI Tecnai, G2 20, USA) available at Sprint Testing Solutions, Mumbai. Carbon coated copper grid of 300 mesh was used to prepare sample for TEM analysis. Sample for TEM analysis was prepared by placing a small drop of colloidal AgNPs on carbon coated copper grid. After 2 min of deposition of the film on TEM grid, the excess solution was removed using a blotting paper and the grid was allowed to dry in room temperature prior to measurement. FTIR analysis was done to identify the phyto-constituents present in the fruit extract of *Mimusops elengi* and the responsible biomolecules in reduction and stabilization of AgNPs. FTIR spectra of the AgNPs powder were analyzed by FTIR spectroscopy (Perkin Elmer, FTIR Spectrum 2, Massachusetts, USA) at Sprint Testing Solutions, Mumbai, India. The FTIR was recorded in the range of 400–4000 cm^{-1}. The XRD analysis of the AgNPs was conducted with an X-ray diffractometer (Shimadzu, Model-7000, Japan) operated at 40 kV and 30 mA with Cu Kα radiation θ–2θ performed at Sprint Testing Solutions, Mumbai, India.

2.5. Preparation of hybrid nanocomposite films

CS-GL-nano Ag (CS-GL-AGNPs) composite films were prepared using the solution casting method as described by Rahman et al. with slight modification (Rahman, Abdul Mujeeb, & Muraleedharan, 2017). Initially, two solutions were prepared namely; Solution-A & Solution-B. Solution-A was prepared by dissolving 2 g of chitosan in 100 mL of 2% (v/v) acetic acid using magnetic stirrer (REMI, India) for 12 h at room temperature. Three different Solutions-namely, B1, B2 & B3 were prepared by dissolving 2 g of gelatin in 100 mL of three different solvents i.e. colloidal silver (1 mM), colloidal silver (2 mM) and water (for control), respectively. The resulting solutions were filtered by using cheese cloth. According to the study made by S. Ahmed et al. the blend film having the concentration of CS:GL (90:10) shows better morphology compared to other composition (Ahmed & Ikram, 2016). Thus, to achieve hybrid nanocomposite, 90 mL of solution-A was taken in each of three different beakers and 10 mL of each of three different solutions- B1, B2 and B3 was added into it, separately. The mixtures were placed on the magnetic stirrer with continuous stirring at 500 rpm without heating. After 30 min, 0.5 g (25% of total dry solid) of polyethylene glycol (as a plasticizer) was added in each beaker and it was further stirrered for 2 h. Finally, the film forming solution (FFS) was obtained. The films were fabricated by pouring 15 mL of these FFS solutions into Petridishes (100 mm diameter) followed by evaporation of solvent under high air speed fan at ambient temperature and 60 ± 5% relative humidity overnight. The films were then peeled off from petri-dishes and kept in air tight polythene bags for further analysis and applications.

2.6. Characterization of hybrid films

2.6.1. Color and opacity

The color and opacity of the pure CS-GL and CS-GL-AgNPs hybrid films were evaluated using a Chroma Meter (D25LT, HunterLab, USA). Lightness (L*) and chromaticity parameters a* (red-green) and b* (yellow-blue) were used to characterize the film color in the Hunter Lab scale (CIE Lab scale). A white standard color plate (L* = 91.33, a* = −1.12 and b* = −2.05) was used as background for color measurements. Total color difference (ΔE) was calculated using the