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Edible nano-bio-composite film cargo device for food packaging applications

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ABSTRACT

This work is meant to design newer nano-bio-composite films for food packaging applications. Polylactide nanoparticles non-covalent interaction in chitosan matrix was carefully studied and used further to develop uniform nano-bio-composite films. Environmentally benign materials and processes were applied throughout for an intended application in packaging of edibles. Nanoparticles array laden in polysaccharide films served as cargo loaders for active molecules. Quercetin, a bioflavonoid, ubiquitous in many plant species was used as model cargo molecule. Sustained quercetin release imparted a synchronized anti-microbial and antioxidant properties in finished packaging films. Microstructures when examined in FESEM and AFM, suggested nanoparticles homogenous dispersion throughout the film matrix. Film surface RMS roughness in tapping mode AFM experiment was recorded at 1.63 ± 0.23 nm which typically represented conditions for microbial deterrence. Control chitosan film radical scavenging capacity was 5.8% in DPPH assay while that was recorded at 23.5% in new active packaging films.

1. Introduction

Primary packaging materials for food, water and health products mostly originate from the fossil derived polymers. Packaging plastics such as polyethylenes, polypropylene, or the polystyrenes are convenient, but pose imminent health hazards due to migration of toxic additives into the consumables. Recycling of plastics increases leaching of additives and results in adverse biological interactions. Potential carcinogens like bisphenol A, diffusing from polymer wastes into the water and environment, are quite well known (Fasano, Bono-Blay, Cirillo, Montuori, & Lacorte, 2012). Sustainable biopolymers such as chitosan, guar gum and starch are experimented as compatible and safe alternatives for packaging of edibles (Danga and Yoksan, 2015; Mikkonen et al., 2007). Most sustainable materials however failed to serve stand alone due to constrains in filming and barrier properties. Water swell-able starch films and water insoluble guar gum films are known, but both hinders significantly in the moisture and oxygen passage (Das, Ara, Dutta, & Mukherjee, 2011). This work is meant to develop newer nano-bio-composite films using poly-lactides (PLAs) interactions in chitosan for safe packaging design.

Polymer nanotechnology is a vibrant area which attempts to develop materials loaded with specialized particulates in nano-scale (Rhim, Park, & Ha, 2013). Biopolymer nano-bio-hybrids were studied extensively earlier for food packaging applications (Kochumalayil et al., 2013). Chitosan films laden with cellulose nanocrystals improved film permeation properties. Nano-bio-composites are newer class of biopolymer matrices which apply polymer nanoparticle physico-chemical interactions for superior materials design. High surface area of incorporated particulates helps in improvement of biopolymer thermal and barrier properties (Konwar, Gogoi, Majumdar, & Chowdhurya, 2015). Non-covalent polymer functional interactions in nanoscale are some of the predictable techniques for remarkable property enhancement.

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Chitosan exhibits good film present-ability, safety, edibility and inherent antimicrobial properties. The cationic polysaccharide is obtained from the exoskeletons of crustaceans like crabs and shrimps. The compound is however hydrophilic and a poor barrier for moistures. Somewhat dormant antimicrobial property of chitosan is reported, but the means and mechanisms are not well understood. Chitosan therefore expresses properties akin to a food packaging materials if only some of its fundamental characteristics can be enhanced. PLAs are safe biopolymers originating from catalyzed polymerization of lactic acid monomers. Unlike chitosan, PLAs are more hydrophobic at the surface and carry anionic charges. Quercetin (Qr), is a bio-flavonoid available abundantly in foods and vegetables such as onion, broccoli and grapes. Qr posses strong DNA gyrase inhibitory property and is a proven limiting agent against microbial growth. Furthermore, Qr finds use as a powerful anti-oxidant in dairy products, packaged cereals, and processed foods (Harwood et al., 2007). The bioflavonoid is, however, unstable when exposed to pH variations, chemical environment and light (Scalia & Mezzena, 2009). We postulated that Qr when entrapped in PLA nanoparticles may express enhanced bioactivity and stability. Furthermore, Qr cargo nanoparticles interactions in the chitosan film matrix can be applied favourably for active films design.

This work is aimed at Qr cargo PLA nanoparticles synthesis and homogeneous embedding in chitosan matrix. Biocompatible surfactant Pluronic F127 was used for nanoparticles stabilizer in synthesis and filming. Qr served as a molecular cargo loader. Low ebb Qr release over a prolonged period was considered to contribute in antimicrobial and antioxidant film active surface properties. The nano-bio-composite film is proposed as a safe alternative for packaging of edibles.

2. Experimental

2.1. Materials

Poly-Lactide (PLA) (Resomer® L210S) was received as a gift from Evonik Industries, Germany) and the medium molecular weight, 75–85% deacetylated chitosan was purchased from Sigma-Aldrich, (Bangalore, India). Pluronic F127 surfactant, bioactive compound quercetin and glycerol, were purchased from Sigma-Aldrich (Bangalore, India). Glacial acetic acid, fused calcium chloride, solvents and HPLC grade water were procured from Spectrochem Pvt. Ltd., (Mumbai, India). The microbial media constituents such as agar-agar, beef extract and peptone were from Himedia Laboratories (Mumbai, India).

2.2. Synthesis of poly-lactide nanoparticles

Poly-lactide nanoparticles were prepared following oil-in-water emulsion evaporation technique (Das et al., 2014). Briefly, PLA (10 mg) and Qr (2 mg) were dissolved together in 1 mL of methylene chloride and was added into 10 mL of 1% w/v aqueous Pluronic F-127 solution. The mixture was sonicated under probe sonicator (Sonic, USA) for an emulsion. The emulsion was further diluted to 20 mL in water and kept stirring for 3 h over magnetic stirrer at 25 °C. The final Qr loaded nanoparticles (Pln), were separated by centrifugation at 16,000 rpm for 45 min at 4 °C, washed twice with water, re-centrifuged and preserved in desiccators.

2.3. Chitosan nano-bio-composite films

Chitosan films with or without the nanoparticles were prepared following solvent casting technique. Chitosan (1.5% w/v) was dissolved in 0.5% (v/v) aqueous acetic acid solution under magnetic stirring and 0.03 g of glycerol for each 10 g of biopolymer was added as plasticizer. Nano-bio-composite films were simultaneously prepared after homogeneous dispersion of Plns. Solutions were degassed under reduced pressure and poured onto polypropylene Petri-dishes for drying at 60 ± 2 °C for 3 h in air circulating oven. Final films were removed easily from the Petri-dishes. The films were conditioned for 48 h at 23 ± 2 °C, 70 ± 2% relative humidity (RH) and used for further studies.

2.4. Quercetin quantification

All quantifications for Qr were carried out in reverse phase HPLC system, Waters dual pump 515 (Waters, USA) using acetonitrile: water (40:60, v/v) at a flow rate of 1 mL min^{-1}. The analysis was carried out in C18 column (Phenomenex, USA) 250 × 4.6 mm, and PDA detector (2996, Waters, USA) set at 255 nm. A peak area (y) vs. concentration (x) graph, $y = 40367x - 38914$, $R^2 = 0.999$, was first developed from standard injections and used for Qr analysis throughout.

2.5. Characterization of Pln nanoparticles

The particle size, polydisperisty index (PDI) and zeta potential of Plns were determined in a Zetasizer® Nano ZS (Malvern Instruments, UK). Helium–neon laser beam, 4 mW, 633 nm, was applied against back scattering angle of 173°. Batch measurements were performed in triplicate and the results were averaged for comparison. For determination of zeta potentials, Pln suspension was filled in disposable dip cells and electrophoretic mobility was recorded against an applied electrical field. Cargo mass loading was estimated by Qr analysis before and after nanoparticulation in the supernatant. Percent encapsulation efficiency (% EE) and Qr mass loading efficiency (% LE) were calculated from an average of six batch experiments.

$$\%EE = \frac{\text{Qr Mass entrapped in Plns}}{\text{Qr Mass initially taken}} \times 100 \quad (1)$$

$$\%LE = \frac{\text{Qr Mass entrapped in Plns}}{\text{Total weight of Plns}} \times 100 \quad (2)$$

Qr release from Plns was estimated using dialysis bags, having molecular weight cut off 12,400 (Sigma, USA). Typically, 0.0107 g of Plns were weighed accurately, (Sartorius MSE3.6P-000-DM, Sartorius AG, Germany) dispersed in 1 mL of 100 mM, pH 7.4 phosphate buffer and transferred into end-tied dialysis bags. Individual bags were placed in glass vials containing 35 mL of phosphate buffer added with 10% v/v ethanol (Licciardello, Wittenauer, Saengerlaub, Reinelt, & Stramm, 2015). Glass vials were put to shaking at 50 rpm in shaker incubators maintained at 25 ± 2 °C. Dissolution samples were withdrawn from the vials at predetermined time intervals and were replaced with same 5 mL portion of fresh medium to maintain sink conditions. Qr release at each time point was estimated from 20 μL aliquot injections into HPLC set up (2.4). Cumulative percentage release over time was calculated from six batch experiments and the data was averaged for x-y plots.

2.6. Nano-bio-composite film characterization

Film thicknesses were estimated using a 0–25 mm dial thickness gauge with ±0.01 mm accuracy. Thickness at six positions for each of six film samples was recorded and the average value was used for calculation of opacity and water vapour permeability. The film opacity was estimated from the absorbance