



Sodium caseinate-starch-modified montmorillonite based biodegradable film: Laboratory food extruder assisted exfoliation and characterization

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ABSTRACT

The present work aims at using a laboratory food extruder for exfoliating starch-montmorillonite (nanoclay) blend and uses the extrudate for blending with sodium caseinate for developing a bionanocomposite film (OP). Exfoliation of nanoclay was confirmed by TEM and XRD pattern. SEM revealed that surface of OP film was rough. Nanoclay addition had significant effect on tensile strength, elongation at break, water sorption and solubility of the film. Glass transition temperature of OP film was 44 °C. Moisture sorption isotherm was found to be of type-II with a typical sigmoid shape. FTIR spectra revealed that formaldehyde and nanoclay caused minor changes and the film was completely biodegradable within 114 h. Overall migration into *n*-heptane was found to be lowest among all food simulants. It was concluded that laboratory food extruder could be used to achieve exfoliation of nanoclay and develop a bionanocomposite film.

1. Introduction

Packaging industry utilizes significant quantities of plastics for food applications. Worldwide consumption of plastics is estimated to be more than 200 million tons. Synthetic plastics have been increasingly used as packaging materials because of their several advantages. However, they are not completely biodegradable and cause environmental problems such as terrestrial and marine littering. Consequently, awareness and demand for packaging materials that possess both process-friendly and environmental friendly nature is increasing. A number of bio-based materials have been used to develop such materials packaging applications. However, the use of such bio-based polymers is challenging due to their poor properties (Arora & Padua, 2010). The most commonly used methods to improve the properties and increase the performance is by blending with other polymers, coating with suitable barrier materials, utilization of multiple layered films, chemical modification of native materials and producing composite or blended materials with the aid of different fillers (Arora & Padua, 2010; Sorrentino, Gorrasi, & Vittoria, 2007). It has been reported that the performance of bio-based packaging materials could be improved by incorporating suitable additives such as fillers, crosslinking agents, etc. Composite packaging materials consist of continuous (polymer matrix)

and discontinuous phases (filler) (Muller et al., 2017). Additives (mostly reinforcing agents) in their native dimensional state exhibit poor matrix–filler interactions. However, with the reduced dimensions of the filler materials, the properties are improved. The use of such fillers having at least one dimension at nano-scale (generally lower than 5%) results in nanocomposites formation (Sorrentino et al., 2007; Azeredo, 2009). Such composites exhibit increased barrier properties, mechanical strength, dimensional stability, improved heat resistance and modulus compared to their pristine polymers and composites (Ray & Okamoto, 2003; Sorrentino et al., 2007; Schmid, Merzbacher, Brzoska, Muller & Jesdinszki, 2017).

Bionanocomposites also offer additional advantages such as reduced density, increased transparency, flow, improved surface properties, and recyclability (Avella, Errico, & Gentile, 2005; Zhao, Torley, & Halley, 2008; Azeredo, 2009). Therefore, nanocomposites enhance the use of biodegradable films, may aid in reducing the packaging waste and also may support sustainability. As possible additives, several nanoparticles (inorganic and organic) have been recognized to enhance polymer performance. However, the layered inorganic solids like clays and silicates, have gained the industry attention due to their availability in plethora, significant improvement in both mechanical and barrier properties, relatively simple processability and also low cost (Azeredo,

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2009; Sorrentino et al., 2007; Silvestre, Duraccio, & Cimmino, 2011). The most widely used clay reinforcement fillers is the hydrated alumina-silicate layered clay consisting of an edge-shared octahedral sheet of aluminum hydroxide between two silica tetrahedral layers, referred to as montmorillonite (MMT) (Weiss, Takhistov, & McClements, 2006). Although, due to its high aspect ratio (50–1000) and surface area, MMT is considered as effective reinforcement filler (Uddin, 2008; Ghanbarzadeh, Oleyaei, & Almasi, 2015) but due to the hydrophilicity of its surface, it is difficult to disperse in polymers in unmodified or natural state (Kim, Lim, Park, & Lee, 2003). Therefore, clays such as MMT are modified to become organophilic.

Sodium caseinate, a dairy by-product has been found to be an interesting substitution for traditional synthetic polymers, owing to its film forming and thermoplastic properties (Audic, Chaufer, & Daufin, 2003; Audic & Chaufer, 2005; Coltelli et al., 2016). Another biopolymer, starch, a widely available and low cost polymer due to its non-toxicity, biodegradability and environmental compatibility could help in developing a biocomposite packaging material at reasonable cost. Further, organically modified montmorillonite (reinforcing agent) and formaldehyde (cross linking agent) could be used to improve the properties of the resulting film (Zink, Wyrobnik, Prinz, & Schmid, 2016). The molecular interactions involved in the bionanocomposite films could be quantitatively studied by methods such as spectroscopy techniques, X-ray scattering, swelling, solubility, etc. (Hammann & Schmid, 2014). In view of the above, the present work was conducted to develop and characterize a milk protein-starch-nanoclay based biodegradable nanocomposite film for which a laboratory food extruder was used for exfoliation of the nanoclay.

2. Materials and methods

2.1. Materials

Sodium caseinate containing 90% protein (on dry basis) and having crystal white color and bland taste was purchased from M/s Mahaan Proteins Limited, Kosi Kalan, Mathura, India. Corn starch and formaldehyde solution were procured from M/s Hi-Media Laboratories Private Limited, Mumbai. Modified montmorillonite (surface modified with 25–30% methyl dihydroxyethyl hydrogenated tallow ammonium) (OMMT) (Nanomer[®] I.34 TCN), a product of Nanacor[®], (less than 20 micron size) was procured from M/s Sigma-Aldrich (St. Louis, MO, USA). Purified glycerol supplied by M/s S.D. Fine Chemicals Limited, Mumbai, India was used as a plasticizer.

2.2. Preparation of corn starch and nanoclay extrudate solution

Nanomer[®] I.34 TCN (10% w/w of corn starch) was added to distilled water (100 mL) and placed on a magnetic stirrer (Digital Spinot, M/s Tarsons Pvt. Ltd.) at 500 rpm for 24 h for hydration. After 24 h, glycerol (15 g) was added and again mixed for 30 min. Corn starch (100 g) was then added to the mixture and placed in an oven maintained at 60 °C for 4 h for moisture adjustment (14%). The mixture was then extruded through a twin-screw co-rotating extruder (M/s Basic Technology Private Ltd., Kolkata) at 100 rpm and 120 °C. Later, the extrudate was dried at 60 °C. Solution of corn starch and nanoclay extrudate was prepared (4% w/v) by stirring in hot distilled water for 10 min as per the method given by Zhang and Han (2006) with minor modification. Modification included heating of distilled water to 90 °C instead of boiling temperature. After complete dissolution, glycerol (40% w/w of extrudate) was added.

2.3. Preparation of sodium caseinate solution

Sodium caseinate aqueous solution (8% w/v) was prepared as per the method given by Fabra, Perez-Masia, Talens and Chiralt (2011) with minor modification by dissolving it in distilled water followed by

addition of glycerol (30% w/w of sodium caseinate). Prepared solution was continuously stirred with magnetic stirrer (Digital Spinot, M/s Tarsons Pvt. Ltd.) at 60 °C and 450 rpm for 2 h for complete hydration and dissolution, followed by cooling, filtration and degassing.

2.4. Preparation of bionanocomposite film

Sodium caseinate solution and corn starch-nanoclay extrudate solution were vigorously mixed together along with formaldehyde (0.5% w/v) for 30 min at 30 ± 2 °C with a magnetic stirrer (Digital Spinot, M/s Tarsons Pvt. Ltd.) followed by degassing (ROCKYVAC[™] vacuum pump, M/s Tarsons Pvt. Ltd.) for 20 min. The dissolved solution was poured (20 mL) onto a leveled polystyrene petridish (12 cm × 12 cm) and evenly spread. Later, it was allowed to dry (at 38 °C and 53 ± 2% RH) for about 24 h in an incubator. The resultant film was peeled off from the casting petridish and stored at 50 ± 2% RH for about 2 days for further analysis. Since, protein-based films are known to change their properties during the first days up to 2 weeks after production due to crosslinking and post formation of molecular interactions (Schmid, Reichert, Hammann, & Stabler, 2015), all the films have been stored for only 2 days prior to further analysis to nullify the storage-related effect. This bionanocomposite film was considered as “OP” film. Other films such as composite film consisting of blend of 90% sodium caseinate and 10% corn starch casting solutions (control film, CT), control film containing 0.5% formaldehyde only (CF) and control film containing 10% nanoclay (CN) were also prepared.

2.5. Validation of exfoliation of nanoclay due to extrusion

With a view to confirm the exfoliation of nanoclay (Nanomer[®] I.34 TCN) in the present study, the corn starch – nanoclay extrudate was subjected to x-ray diffraction analysis. The d_{001} spacing of the starch-nanoclay samples was measured using the XRD Xpert Pro PAN analytical (Netherlands). For which, Cu K-alpha-1 radiation was generated (45 kV and 40 mA) with a wavelength of 0.15406 nm. With a step size of 0.017°, the diffraction data was collected from 2θ (θ is the angle of incidence of the beam) values in the range of 4°–30°. Later, the d_{001} spacing was calculated from the Bragg's Law ($n\lambda = 2d \sin\theta$), where λ is the wavelength of the incident wave, d is the distance between the d_{001} planes and n is an integer.

2.6. Characterization of bionanocomposite film

2.6.1. Mechanical properties

Film thickness was measured using a digital micrometer (M/s Engineering Corporation, Saharanpur, Uttar Pradesh; 0.01 mm sensitivity) for which, 20 random positions across the film were measured and mean value was calculated for each sample. Texture Analyzer (TA.XT2i, M/s Stable Micro System, UK), fitted with 25 kg load cell, was used to determine the tensile strength and elongation at break (ASTM, 1992). Samples cut into required dimensions (2.54 cm × 10 cm) were acclimatized for 48 h (at room temperature with 50 ± 2% relative humidity) before analysis. For tensile strength, the initial grip separation and crosshead speed were set at 50 mm and 2 mm/sec, respectively. For seal strength, the samples were cut into 2.54 cm × 5.00 cm. Later two strips were joined together and sealed by an impulse heat sealer at a temperature of 110 ± 10 °C and a sealing time of 1–2 s. The unsealed ends of the strips were attached between two jaws of the texture analyzer where the distance between the jaws was set 5 cm apart and a crosshead speed of 2 mm s⁻¹. The tests were repeated with 8 film specimens.

2.6.2. Instrumental color analysis

Instrumental color analysis of the films was carried out using a colorimeter (Color Flex, M/s Hunter Colorlab, USA). Films were cut into circles to cover the base of the glass sample container of the instrument

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