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Effects of glycerol and nanoclay on physiochemical properties of camelina gum-based films

Guangyan Qi[a], Ningbo Li[b], Xiuzhi Susan Sun[a], Yong-chen Shi[a], Donghai Wang[c,*]

[a] Department of Grain Science and Industry, Kansas State University, Manhattan, KS 66506, United States
[b] Sunhai Bioadhesive Technologies LLC, Manhattan, KS 66502, United States
[c] Department of Biological and Agricultural Engineering, Kansas State University, Manhattan, KS 66506, United States

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ABSTRACT

Film-forming properties of camelina gum (CG) were evaluated, including film appearance and morphological, mechanical, water/light barrier, and thermal properties. With 4% nanoclay, tensile strength of film increased from 43.2 MPa to 54.6 MPa without change elongation property. The formation of physically cross-linked networks in the film increased interfacial affinity between the CG matrix and intercalated nanoclay, as proved by FTIR and X-ray diffraction (XRD) data, which contributed to the mechanical strength of film. The increased nanoclay level (6%–10%) resulted in limited mechanical strength improvement due to poor dispersion and the appearance of agglomerates of nanoclay in the film matrix, as shown in morphological study. The compact structure of CG/nanoclay film could reduce the free volume of film matrix and obstruct the diffusion of water, thereby decreasing the water vapor permeability. The ultraviolet (UV) light transmittance of CG film decreased by 40% with 10% nanoclay.

1. Introduction

Health and environmental concerns as well as high demand for extended shelf life have motivated the development of edible films, thin layers that can be served as barriers between food components or between food and the surrounding environment, or function as carriers for food additives, antioxidants, antimicrobial agents, and nutrients (Talens, Chiralt, & Fabra, 2010). Appropriate materials for making edible films include polysaccharides, proteins, lipids, and the combinations of those materials (Sothornvit & Krochta, 2000). The use of polysaccharides, such as starches and their derivatives, cellulose, and gums for edible films has been increasing because of their abundantness and properties that may be improved by chemical modifications (Phan et al., 2002). Polysaccharide-based film forms when gum solutions are casted on a surface and then dried at a certain temperature and humidity level, consequently demonstrating plasticity, tensile strength (TS), and clarity characteristics. Film properties vary depending upon gum properties. In previous studies, linear polysaccharides, such as agar, curdlan, hydroxypropyl methylcellulose (HPMC), and gellan-based films, which all have methyl, hydroxypropyl, acyl, or acetyl substituents covalently attached to their individual sugar molecules, showed optimum film-forming property with good mechanical strength (Labropoulos, Niesz, Danforth, & Kevrekidis, 2002; Murray, 2000). As opposed to linear polysaccharides, branched polysaccharides, however, have very large molecular weights with globular conformation, but this molecular structure does not allow the formation of micelles consisting of intimately associated polymer chains, resulting in poor film-forming properties as evidenced by gum arabic, gum ghatti, and gum karaya-based films (Embuscado & Huber, 2009, chp 1).

Properties of polysaccharide-based films can be manipulated through plasticization or physicochemical modification. Plasticizers with low molecular weight are widely used to soften the rigid structure and improve the processing, mechanical, barrier, and physical properties of films. Most-favored plasticizers are compatible with film-forming polymers and can reduce intermolecular forces and increase the free volume or mobility of polymer chains by reducing hydrogen bonding between polymer chains. Examples of such plasticizers include glycerol, sorbitol, and polyethylene glycol (Gontard, Guilbert, & Cuq, 1993). Efforts also have been made to improve the physical properties of polysaccharide film by reinforcing the polymer matrix with layered clay minerals, such as environmentally friendly, nontoxic, abundant montmorillonite (MMT) (Alexandre & Dubois, 2000). Nanoscale distribution of nanoclay with high aspect ratio and high surface-to-volume ratio in the gum matrix (agar, carrageenan, arga/carrageenan/konjac glucomannan, carrageenan/locust bean) improved the mechanical,

* Corresponding author.
E-mail address: dwang@ksu.edu (D. Wang).

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thermal, and barrier properties of films with low filler content (less than 5% of gums by weight) (Martins et al., 2013; Rhim & Wang, 2013, 2014; Rhim & Hong, 2011). Therefore, nanoclays significantly improve the feasibility of gum-based films in food packaging application.

CG extracted from camelina seed has shown excellent viscoelastic property and has the potential for use as a thickener, suspending agent, and stabilizer (Li, Qi, Sun, & Wang, 2016). We speculate that those properties of CG may attribute its film forming properties. Little to no research information is available regarding to CG-based films. Therefore, the objective of this research was to investigate CG film-forming properties as affected by plasticizer (glycerol) and nanoclay. Nano clay can be modified through exchanging of hydrated cations with organic modifiers such as alkylammonium cations etc (Ruiz-Hitzky, Aranda, Darder, Rytwo, 2010). The modified clay known as organo clay with the increased hydrophobicity was used in this study. We expected that the increased hydrophobicity might be better for improving water vapor permeability of gum film besides the mechanical and UV barrier properties etc. The clay modified CG films were characterized using FTIR, XRD, SEM, atomic force microscopy (AFM), and thermal gravimetric analysis (TGA) analysis. Transparency, moisture content, water vapor permeability, thickness, and mechanical properties of films were also evaluated.

2. Materials and methods

2.1. Materials

CG consisting of polysaccharides (75.1%) and protein (12.3%) (Li et al., 2016) was provided by Sunhai Bioadhesive Technologies LLC (Manhattan, Kansas, United States). Nanoclay of MMT organoclay modified by quanternary ammonium salts (methyl dihydroxyethyl hydrogenated tallow) and glycerol (99.5%) were purchased from Sigma Aldrich (St. Louis, Missouri, United States).

2.2. Film preparation

CG film was prepared using a solution-casting method. A 0.5% CG gum solution was prepared by adding 0.35 g of camelina powder (<0.25 mm) to 70 ml distilled water with 30%–70% glycerol (w/w, dry basis) as a plasticizer. The mixture was stirred vigorously with a magnetic stirrer for approximately 30 min at 25 °C and then casted evenly onto leveled polystyrene petri dishes (15 mm diameter) and dried for 17 h at 50 °C.

CG/nanoclay films were prepared using a solution intercalation method. Nanoclay was used at five levels: 1%, 2%, 4%, 8%, and 10% (w/w, dry basis). The method described by Martins et al. (2013) was used. Nanoclay powder was dispersed into distilled water under magnetic stirring for 24 h for hydration. CG powder was then dissolved into the nanoclay solution after adding glycerol (50% w/w, dry basis). The suspension was sonicated for 30 min using an ultrasonic machine (model AP-1000, Sonic-Mill, Albuquerque, New Mexico, United States) and then heated for 30 min at 70 °C in a water bath. Film-forming solutions were degassed under vacuum to remove dissolved air bubbles, and then 70 ml solution was cast onto the petri dishes (15 mm diameter) and the same procedures were followed as described for CG film preparation. Obtained films were conditioned at 50% relative humidity (RH) and 25 °C for at least 3 days in a controlled environmental chamber (Electro-Tech Systems, Inc., Glenside, Pennsylvania, United States) for further analysis.

2.3. Film morphology

2.3.1. Scanning electron microscopy

A Hitachi S-3500N (Hitachi Science System, Ibaraki, Japan) scanning electron microscopy (SEM) was used to observe the microstructure of the gum films. Films were affixed to an aluminum stub with two-sided adhesive tape, and a sputter coater was used to coat the films with an alloy of 60% gold and 40% palladium (Desk IIS putter/Etch Unit, Moorestown, New Jersey, United States). SEM images of samples were obtained at an operation condition with an accelerating voltage of 5 kV.

2.3.2. Atomic force microscopy

Surface morphology of the films was analyzed using an Innova AFM (Bruker Nano Surfaces Division, Texas, United States). After equilibration at 53% RH for 48 h, samples were cut into thin pieces that fit into the AFM image sample holder; the samples were then affixed to double-sided tape. Film samples were scanned in contact mode using a Burker's sharp nitride lever (SNL) probe, which combines the sharpness of a silicon tip with a low spring constant of 0.12 N/m and a nominal tip radius of approximately 2 nm. Experiments were carried out in air at a scan rate of 2 Hz, and a vertical deflection of 2 V was applied. All AFM images with 512 × 512 pixels were obtained.

2.4. Fourier transform infrared spectroscopy

A PerkinElmer Spectrum 400 FT-IR/FT-NIR spectrophotometer (Shelton, Connecticut, United States) was used to collect FTIR spectra of gum films in the region of 400–4000 cm^{-1}. Transmission spectra of 32 scans of each sample were collected at a resolution of 1 cm^{-1} in the reflectance mode. All samples were tested with duplications.

2.5. XRD analysis

XRD patterns of the film samples were analyzed using an EMPYREAN X-ray diffractometer (PANalytical, Westborough, Massachusetts, United States) operated at 40 kV and 30 mA. Samples were prepared by placing a rectangular film (2 × 3 cm) on a glass slide, and spectra were recorded using Cu-Ka radiation at a wavelength of 0.154 nm. All experiments were carried out from 4° to 50° (2θ range) with a step interval of 0.007°. Interlayer spacing of the films containing the nanoclays was determined by the XRD peak using Bragg's equation ($\lambda = 2d \sin\theta$), where λ corresponds to the wavelength of X-ray radiation (0.154 nm), d corresponds to interlayer spacing between diffraction lattice planes, and θ is the measured diffraction angle of the peak in the XRD pattern.

2.6. Mechanical properties

The TS and percentage of elongation at break (Eb, %) were measured with a tensile tester (TT-1100, ChemInstruments, Fairfield, Ohio, United States) according to ASTM D882-12 (ASTM D882-12, 2012). The films were cut into strips (1.4 × 5 cm) using a dual-blade shear cutter (JDC Precision Cutter 10 in., Thwing-Albert Instrument Company, West Berlin, New Jersey, United States) and conditioned for 3 days (50% RH). Before testing, thickness of the strips was measured with a digital micrometer to the nearest 0.001 mm. Five thickness measurements were taken on each testing sample at various points, and the mean values were used in mechanical and permeability calculations. Force and distance were recorded during the extension of the strips mounted between the grips at 2.5 cm/min. until the sample broke. The results are the averages