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

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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.

Keywords: Camelina gum, Nanoclay, Film

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 et al., 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 (Murray, 2000; Labropoulos et al., 2002). 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).

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 et al., 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, agar/carrageenan/konjac glucomannan, carrageenan/locust bean) improved the mechanical, thermal, and barrier properties of films with low filler content (less than 5% of gums by weight) (Rhim & Hong, 2011; Martins et al., 2013; Rhim & Wang, 2013; Rhim & Wang, 2014). 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 et al., 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 et al., 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 quaternary 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 Martin 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

Scanning Electron Microscopy

A Hitachi S-3500 N (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.

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 Bruker'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 $400\text{--}4000\text{ cm}^{-1}$. 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 40kV and 30mA. Samples were prepared by placing a rectangular film ($2 \times 3\text{ cm}$) on a glass slide, and spectra were recorded using Cu-K α 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). The films were cut into strips ($1.4 \times 5\text{ cm}$) 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 of the five samples. TS and percentage elongation at the point at which the film broke was calculated

using Eq. 1 and 2.

$$\text{Tensile strength (TS)} = \frac{\text{Max force (N)}}{\text{Thickness (m)} \times \text{Width (m)}} \quad (1)$$

$$E(\%) = 100 \times \frac{dr}{do} \quad (2)$$

where $E(\%)$ is the percentage of Eb, do is the distance onset of gage (cm), and dr is the distance of rupture (cm).

2.7 Water Vapor Permeability

Water vapor permeability (WVP) of the films was measured according to the ASTM E96/96M standard test method (ASTM E96/96M). Glass cups with bottle mouth diameters of 10 mm (depth of 40 mm and internal diameter of 20mm) were preconditioned at 105 °C for 24 h to remove any water. The cups were filled with calcium chloride at half the bottle volume to obtain 0% RH in the interior of the glass cup; the preconditioned films were mounted on the bottles with paraffin as a sealant. The cups were placed in a desiccator containing saturated sodium chloride solutions (75% relative humidity) at 25 °C. Cup weight with 0.0001 g accuracy was recorded at 0, 5, 15, 20, and 24 h. Every measurement were made in triplicate, and WVP was calculated using Eq. 3.

$$WVP = w/t \times x/\Delta p \times A \quad (3)$$

where w/t is calculated by linear regression ($R^2 > 0.99$) from water absorbed by the system when steady state was reached, A is the film area exposed to moisture transfer, x is the mean sample thickness, and Δp (kPa) is the partial pressure difference through the film calculated with Eq. 4.

$$\Delta P = S(R1 - R2) \quad (4)$$

where S is the saturated vapor pressure at 25 °C (3166 kPa) and $R1$ and $R2$ are the RHs in the desiccator (0.75) and in the interior of the bottle (0), respectively, expressed in fractions.

2.8 Light Transmission and Film Transparency

All films were cut into a rectangular shape and placed in a spectrometer (UV-1650PC, Shimadzu Scientific Instruments, Columbia, Maryland, United States), using air as the reference. The light barrier property of the film samples was measured at wavelengths of 280 nm (UV) and 660 nm (visible light) according to the method described by Rhim & Wang (2014). Three replicates of each sample were tested; results were expressed as percentage transmittance.

2.9 Thermal Gravimetric Analysis

TGA of films was conducted with a Perkin-Elmer TGA 7 (Norwalk, Connecticut, United States) in a nitrogen atmosphere. Approximately 5 mg of each sample was weighed into a platinum cup and scanned from 25 °C to 700 °C at a heating rate of 10 °C min⁻¹. Maximum degradation rate was calculated as mass (%) at peak temperature divided by peak temperature.

2.10 Statistical Analysis

Data from the mechanical property evaluation were taken from an average of at least two samples. Data from experiments carried out in duplicate were analyzed using analysis of variance (ANOVA) and least significant difference (LSD) at the 0.05 level according to procedures in the SAS statistical software package (SAS Institute 2005, Cary, North Carolina, United States).

3. Results and Discussion

3.1 Moisture content (MC), appearance, and morphology

Based on preliminary investigation, CG at a concentration of 0.5% was selected to prepare films since any lower concentration could cause complications, such as low and uneven film thickness, and require more energy for water evaporation. A higher concentration of CG could make hydration and homogenization difficult and cause casting issues when making films. At least

30% glycerol was used as a plasticizer since lower glycerol levels resulted in undesirable film brittleness when the film was peeled off the glass. CG films were transparent with a smooth surface via visual measurement, as illustrated in Fig. 1A, and ranged from 0.025 to 0.030 mm in thickness (the thickness of films were the average of 3 measurements with an electronic micrometer with 0.001 mm resolution). MC of the films increased from 18.96% to 28.23% as the glycerol content increased from 30% to 70% (Table 1), which was in agreement with previous studies that showed that glycerol has water-holding capacity, thereby increasing MC in films (Ghasemlou et al., 2011). A similar study reported that when glycerol content was higher than 10%, psyllium hydrocolloid-based films showed increased MC since the formation of glycerol-gum and glycerol-water interactions increased the water-holding capacity of films (Ahmadi et al., 2012).

Increased understanding of the mechanism of CG film formation and visualization of individual components of gum in networks at the molecular level could be advanced by observing film's structures at various length scales. Therefore, in this study, morphology properties of CG and CG films were investigated. Under AFM (Fig. 2), we observed intersecting fibrils, which are believed to be the direct shape of CG, with average diameters of 5 nm and over micrometers length in CG solution. The linear structure of CG was expected to form films with maximum mechanical strength because intermolecular hydrogen bonding causes more compactly aggregate of the polymer chain (Murray, 2000; Labropoulos et al., 2002). The thickness of the films studied in this research was 0.025-0.030 mm, consisting of at least 5000–6000 layers of gum fibrils, with each single fibril of gum having an average diameter of 5 nm. Although CG film showed smooth surfaces under visual estimation, condensed fibrils humps were observed under high resolution microscopy, resulting in rough film surfaces in nanoscale (Fig. 2B).

Film structures with nanoclay were more compact than structures of pure gum films because

nanoclay served as filler in the crossed matrix of gum fibrils (Figs. 2C and 2D). With 10% nanoclay (Fig. 2D), fibril humps were nearly invisible in the film because they were submerged by the nanoclay. The interaction of fibril matrix in gum and nanoclay increased the mechanical strength and barrier properties of the film due to the formation of hydrogen bonds with those fibrils, as discussed in the following sections. Although the nanoclay served as the filler for CG film, it did not improve films' surface smoothness (Figs. 1C and 1D). In fact, films with nanoclay demonstrated rougher surfaces than pure gums films as a result of nanoclay aggregation during the film-making process, leading to accumulated humps and rough film surfaces. This finding was in agreement with previous studies of nanoclay/chitosan, poly/chitosan/nanoclay, or carrageenan/locust bean gum/nano films (Mahdavi et al., 2013; Xu et al., 2006; Martins et al., 2013).

3.2 FTIR analysis

FTIR absorbance patterns of samples are presented in Fig. 3. Nanoclay exhibited typical bands responsible for stretching vibrations of O-H at $3,627\text{ cm}^{-1}$, stretching vibrations of C-H from CH_2 and CH_3 groups $2,900\text{--}2,800\text{ cm}^{-1}$, respectively, bending vibrations of O-H from absorbed water and C-H from CH_2 bending at $1,640\text{ cm}^{-1}$ and $1,480\text{ cm}^{-1}$, respectively, and bending vibrations of Si-O-Si at $800\text{--}1,100\text{ cm}^{-1}$ (Martins et al., 2013; Paluszkiwicz et al., 2011).

A spectra of pure CG powder is also presented (Fig. 3) in order to provide a complete investigation of the gum. A broad and intense band between $3000\text{ and }3600\text{ cm}^{-1}$ was ascribed to –OH stretching, and the broad band was overlapped to the stretching vibration of N-H and C-H bond in $-\text{CH}_2$ (2920 cm^{-1}) and $-\text{CH}_3$ (2875 cm^{-1}) groups, respectively (Silva et al., 2012). CG showed specific bands in the range of $1200\text{--}800\text{ cm}^{-1}$, which was dominated by ring vibrations overlapped with stretching vibrations of C-OH side groups and C-O-C glycosidic bond vibration

(Kacurakova et al., 2000). Peaks observed at 1070 cm^{-1} were assigned to galactose unit: The intensive peak at 1070 cm^{-1} indicated high galactose unit content (Kacurakova et al., 2000). The peaks around 1151 cm^{-1} were ascribed to contributions from glycosidic linkages (C-O-C). Similar observations were described in an earlier report in which galactose units with any link type and position were found at approximately 1155 cm^{-1} , xyloglucan was found at 1153 cm^{-1} , and polysaccharides with mannose, arabinose, and rhamnose constituents were found at low frequencies ($1051\text{--}1039\text{ cm}^{-1}$) (Kacurakova et al., 2000). Although the anomeric region between 800 and 1000 cm^{-1} was complicated due to peak overlapping, this region provided supplemental information to the above descriptions. According to Kacurakova et al. (2000), peaks at 834 cm^{-1} and 898 cm^{-1} were designed for α and β glycosidic linkage types of aldopyranoses and furanoid compounds, respectively. The peak at 898 cm^{-1} was sharper than the peak 834 cm^{-1} , indicating that β glycosidic linkage was dominated in CG. Peaks around 1630 cm^{-1} and 1540 cm^{-1} were dominated by amide I for --C=O stretch and amide II for --N-H bend, respectively (Yu et al., 2005). A sharp peak around 1600 cm^{-1} was detected for CG, which was attributed to carboxylate asymmetrical stretch (Pasqui et al., 2012). Amide I and II uniquely contained C=O, C-N, and N-H from camelina albumin protein (Li et al., 2016). Amide I absorption contained contributions primarily from C=O stretching vibration (80%) with a minor C-N stretching vibration, while amide II absorption was caused by N-H bending vibrations (60%) and C-N stretching vibrations (40%) (Jackson & Mantsch, 1995).

Interactions of gum with glycerol and nanoclay were also investigated. The peak of O-H stretching vibration at 3260 cm^{-1} on gum shifted to 3255 cm^{-1} on film with and without nanoclay, indicating that hydrogen bond interaction occurred between CG and the glycerol. The hydrogen bonds between polysaccharide molecules might be broken, and new hydrogen bonds might be

formed between hydroxyl groups in nanoclay (3627 cm^{-1}) and the O-H stretching vibration in glycerol (3260 cm^{-1}) and the polysaccharide molecules as indicated by previous study (Slavutsky et al., 2012).

3.3 X-ray diffraction

Crystallinity of the film samples was evaluated using XRD analysis (Fig. 4). The broad peaks at $2\theta = 22.13^\circ$ and 16° suggested that CG is an amorphous material. The characteristic diffraction peak of XRD pattern of nano clay was 7.05° (2θ), corresponding to a nanoclay interlayer spacing of 1.25 nm. This peak shifted to lower angle around 4.8° ($d = 1.83\text{ nm}$) after the nanocomposite formed with the CG matrix. The d spacing of nanoclay was not affected by the nanoclay concentration, but the peak intensity (4.8°) increased as the clay amount increased, indicating that the camelina chains entered into the silicate layers and formed intercalated CG/nanoclay nanocomposite instead of the complete exfoliation structure. The interaction between CG and nanoclay was promoted by hydrogen bonding between carbonyl groups in CG and hydroxyl groups at the silicate layer of nanoclay, as shown in Fig. 3. In addition, the peak (22.13°) from CG broadened with the inclusion of nanoclay, indicating reduced crystallinity of CG film and suggesting that the interaction between two polymers further weaken the CG chain primary structure.

3.4 Mechanical property

Mechanical properties of a film determine its durability and ability to be used as a coating to enhance the mechanical integrity of foods. Without plasticizer, CG exhibited poor film-forming ability because it did not show sufficient cohesive strength to remain intact when peeled off the casting glass. Therefore, the data of CG film without plasticizer is not presented in this paper. The effects of glycerol and nanoclay on tensile strength (TS) and elongation at break (Eb) are reported

in Tables 1 and 2, respectively. Glycerol contents had a positive effect on the Eb and negative effect on the TS of films. In particular, Eb values increased from 8.3% to 22.47% and TS values decreased from 56.01 MPa to 25.89 MPa when glycerol content increased from 30% to 70%. Glycerol acted as a plasticizer, decreased the molecular weight of the mixture compared to pure camelina gum, and reduced the intermolecular force and increased the mobility of polymer chains in CG, leading to decreased TS and increased Eb of films. Similar observations of the effects of glycerol on mechanical properties of polysaccharide-based gums have been made in previous studies. TS decreased from 17.75 MPa to 9.44 MPa for chia seed mucilage-based film and Eb values increased from 1.93% to 15.89% when glycerol increased from 25% to 75% as plasticizer (Dick et al., 2015). Moreover, the presence of glycerol at low concentrations (15%) showed high tensile strength for starch-based films because strong hydrogen bonds between starch intermolecular dominated the hydrogen bonds between glycerol and starch. A high concentrations (30 and 45%) of glycerol weakened the intramolecular attraction between the chains in polysaccharides and reinforced the formation of hydrogen bonds between polysaccharides and glycerol, resulting in decreased tensile strength (Sanyang et al., 2015).

Increasing Eb values of plasticized film indicated that glycerol can improve the flexibility and stretchability of films because glycerol enhances the mobility of polymer chains of CG. Because plasticizers disrupt intermolecular hydrogen bonds in CG molecular and cause new hydrogen bonds to form between glycerol and gum, film rigidity was weakened and film deformability and flexibility was strengthened with the addition of glycerol. Film making formula of CG with 50% of glycerol was selected for further nanoclay modification for it showed balanced mechanical strength and flexibility compared to other formulas.

Incorporation of 2%–4% nanoclay can improve the TS of CG film without change of Eb (Table

2). When nanoclay content was higher than 4%, the CG film reached a plateau of TS and Eb values of the films increased only slightly. Based on previous reports, improved TS of film was attributed to the hydrogen bond-induced interaction between the CG matrix and intercalated nanoclay, which was proved by the XRD data (Fig. 4). Moreover, the organic modifier, methyl dihydroxyethyl hydrogenated tallow (quaternary ammonium salts), had two –OH groups, which may also have acted as a bridge connecting CG polymer chains and nanoclay layers (Nayak & Mohanty, 2010). Interfacial affinity between intercalated nanoclay and the CG matrix demonstrated physically cross-linked networks, resulting in significantly improved TS. However, high nanoclay loading levels (6%–10%) dispersed poorly in CG polymer and contained agglomerates (Fig. 1D) due to the high surface energies of nanoclay (Jang et al., 2010; Xu et al., 2006), therefore, the TS of CG film decreased but not significant. therefore, the TS of CG film decreased but not significant. No distinctive change in the Eb value within a range of 13.52%–16.47% was observed for the ductility of CP film. Similar results have been reported regarding agar/nanoclay nanocomposite films (Rhim, 2011; Rhim & Wang, 2013).

CG films have comparable mechanical strength (56.01 MPa) to carrageenan gum films (56.5 MPa) with 30% glycerol (Rhim & Wang, 2014). However, the mechanical strength of CG films was much stronger than that of the films made from other polysaccharides, such as agar gum (46.36 MPa) with 30% glycerol (Rhim & Wang, 2013), guar gum film with 10% glycerol (42.84 MPa) (Kurt & Kahyaoglu, 2014), or salep galactomannan films with 10% glycerol (49.59 MPa) (Kurt & Kahyaoglu, 2014). Compared to other polysaccharide films that form solutions with 1%–2% solid content, a lower CG loading level (0.5%) was sufficient to allow film formation with improved mechanical properties.

3.5 Water vapor permeability (WVP)

Barrier properties of packaging films play a key role in eliminating or reducing the water, oxygen, carbon dioxide, aroma exchange between food components and the environment during storage resulting from food metabolism and microbial respiration. The hydrophilic characteristics of polysaccharides cause them to have high affinity with water, thereby promoting the diffusion of water molecules and causing large WVP values of films. As shown in Table 2, nanoclay decreased the WVP of CG films from 0.405 to 0.325 g.mm/h.m² as the nanoclay loading level increased from 0% to 10%. This decrease can be attributed to the fact that nanocomposite enhanced the tortuosity of the diffusive path for a penetrant molecule (Mirzadeh et al., 2007) or that the layered structure of the nanoclay increased the path length for water moisture diffusion and retarded the transmission of moisture through the film matrix (Park et al., 2003). Moreover, the methyl tallow bis-2-hydroxyethyl ammonium cations contained in organoclay demonstrated increased hydrophobicity (Antoniou et al., 2015) compared to unmodified nanoclay, which also may have contributed to the improved water barrier properties of the nanocomposite film. The MC of CG/nano-based film with 10% nanoclay decreased to 18.55% compared to 22.23% for pure CG gum film. The CG/nano-based films potentially had a more compact structure that allowed less hydroxyl groups of CG chains to connect with water molecules than pure gum-based film.

3.6 Light transmission

UV barrier and transparency properties of the films were evaluated by measuring the transmittance of the films at 280 nm (UV) and 660 nm (visible), as shown in Fig. 5. The transmission of CG films was 19.55% and 39.53% at UV and visible region, respectively. CG typically contains approximately 12% camelina albumin protein (Li et al., 2016). Protein-based films had a high content of aromatic amino acids that absorbed more UV light (Ramos et al., 2013), potentially contributing to the improvement of film's UV barrier properties but also potentially

causing decreased visible light transmission and reduced transparency of CG films. The inclusion of nanoclay into the camelina films reduced the transmission of UV and visible light. With 10% nanoclay, transmittance values decreased to 12.65% and 28.99%, respectively. The decrease in light transmission could be attributed to the prevention of light passage by the nanoclay dispersed in the polymer matrix. This result suggested that nanoclay could be used in film making for packaged food to retard lipid oxidation, discoloration, formation of off-flavor, and loss of nutrients induced by UV light (Ramos et al., 2013). Transparency is also an important physical property of packaging films. CG film with 6% nanoclay or higher had reduced transparency (Fig. 5), potentially due to the opaque appearance and aggregation of nanoclay (Kanmani & Rhim, 2014; Hong & Rhim, 2008).

3.7 Thermal properties

Thermogravimetric analysis was used to evaluate the thermal stability of films in this study. All the films displayed similar behavior with four main stages of thermal degradation in the temperature range of 25–700 °C (Fig. 6). The first stage (50–120 °C) corresponded to the moisture released from the films. The second stage (160–200 °C) was related to the loss of glycerol and structurally bound water (Martin et al., 2012). CG film decomposition was attributed to the third and fourth stage (weight loss of approximately 65%), which occurred at 250–290 °C and 310–350 °C, suggesting two types of chain structures with unique thermal stabilities. The temperatures corresponding to camelina film thermal degradation (T_d) and the temperatures of 50% weight loss (T_{50}) are shown in Table 2. T_d and T_{50} increased from 268 °C to 273 °C and from 275 °C to 282 °C, respectively, as the nanoclay increased from 0% to 8% and then levelled off at 10%. Thermal stability of CG film increased after formation of the nanocomposite with nanoclay. However, nanoclay levels higher than 8% may have the nanoclay aggregation and steric hindrance effects on

the interaction with CG, leading to limited thermal stability enhancement.

4. Conclusions

CG-based films demonstrated mechanical strength comparable to carrageenan gum film and was stronger than other gums, including agar gum, guar gum, and salep galactomannan. A low CG concentration (0.5%) was required in order for CG film to form with good mechanical properties compared to other polysaccharide gums (1%–2%). FTIR and XRD results revealed that the intercalation structure of nanoclay in CG polymer matrix was formed by the hydrogen bonding interaction between CG and nanoclay, contributing improved mechanical and barrier properties of CG/nanoclay based films. Increased nanoclay loading levels (6%–10%) did not significantly improve mechanical strength due to poor dispersion and the presence of agglomerates of nanoclay. Nanoclay improved WVP and UV barrier properties but slightly decreased film transparency. CG/nanoclay showed great potential application as environmentally friendly food packaging materials.

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Table 1. Effects of glycerol contents on mechanical properties of CG-based films.

Glycerol (wt, %)	Moisture content (%)	Tensile strength (MPa)	Elongation at break (%)
30%	18.96a ¹	56.01a ¹	8.30a ¹
40%	22.96b	50.11b	10.67b
50%	22.23c	42.38c	14.07c
60%	28.24d	34.17d	17.60d
70%	28.23d	25.89e	22.47e

¹ Means in the same column followed by different letters are significantly different at $p < 0.05$.

Table 2. Moisture content, water vapor permeability, and mechanical and thermal properties of CG and CG-based films.

Nano-clay (wt, %)	MC (%)	WVP (g.mm/h.m ² .Mpa)	Tensile strength (MPa)	Elongation at break (%)	T ₅₀ (°C) ²	T _d (°C) ³
0%	22.23a ¹	0.405ab ¹	43.23a ¹	14.07a ¹	275.02	268.06
2%	21.18b	0.409a	52.36b	14.01a		
4%	21.32b	0.396bc	54.55b	13.52a	279.26	270.47
6%	19.47c	0.402ac	53.96b	13.98a	281.01	270.08
8%	18.20e	0.337d	51.63b	16.47b	282.84	273.05
10%	18.55d	0.325e	51.50b	16.25b	281.12	273.55

¹ Means in the same column followed by different letters are significantly different at $p < 0.05$.

² The temperature of 50% weight loss of films.

³ The residue at 450 °C and decomposition temperature of films.

FIGURE CAPTION:

Figure 1. SEM images of CG-based films

Figure 2. AFM topography images of CG and CG-based films

Figure 3. FTIR spectra of CG and CG-based films

Figure 4. XRD pattern of CG films

Figure 5. Light transmission of CG-based films

Figure 6. TGA thermograms of CG-based films

A: Gum solution

B: Film with 0% clay

C: Film with 4% clay

D: Film with 10% clay