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Physicochemical and thermomechanical characterization of tara gum edible films: Effect of polyols as plasticizers

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ABSTRACT

The aim of this study was to evaluate tara gum as edible film material as well as the influence of polyols as plasticizers on the properties of the films. Thermomechanical, physicochemical and barrier properties were determined as a function of plasticizer type and concentration. Glycerol, sorbitol and PEG 400 were used in the range of 0.075–0.3 g/tara g. Glycerol was the best plasticizer in terms of mechanical properties with the highest elongation (16–44%) and resistance (45–90 MPa). Sorbitol presented the best barrier properties with the lowest hydrophilicity and water vapour permeability (0.24–0.34 g mm m^{-2} h^{-1} kPa^{-1}). Fourier transform infrared (FTIR) spectroscopy showed no significant effect on the structure of the polysaccharide. Dynamic mechanical analysis (DMA) revealed that incorporation of plasticizers increased the mobility of the polymer chains and reduced the glass transition and melting temperature by 30 and 100 °C respectively.

1. Introduction

During the last decade, the serious ecological problems caused by the increasing use of synthetic, non-biodegradable packaging films has led to an increasing interest in the utilization of renewable sources such as hydrocolloids from biological origin in order to replace synthetic packaging. Replacing conventional synthetic packaging with biodegradable polymers can decrease waste through biological recycling to the biosystem (Krochta & De Mulder-Johnston, 1997). This need has created an increasing demand for new materials with film forming abilities. Natural polysaccharides such as galactomannans are an alternative material that can be used for the production of edible films/coatings based on their edibility and biodegradability (Cerqueira, Bourbon, et al., 2011).

Galactomannans are reserve polysaccharides composed of linear chains of (1 → 4)-β-D-mannopyranosyl residues having single side chain units of (1 → 6)-α-D-galactopyranosyl (Dey, 1978). The various galactomannans differ among each other in the mannose to galactose ratio and distribution pattern of galactose residues along the mannan chain (Mikkonen et al., 2007). Galactomannans have a wide use in the food industry as stabilizers, thickeners, emulsifiers and gelling agents due to their high viscosity, water binding capacity and their ability to interact synergistically with other polymers (Cui, Eskin, Biliaderis, & Mazza, 1995; Embuscado & Huber, 2009; Savitha Prashanth et al., 2006; Wu, Cui, Eskin, & Goff, 2009; Wu, Li, Cui, Eskin, & Goff, 2012). Among commercial galactomannans is tara gum which is the ground endosperm of the seeds of tara tree (*Cesalpinia spinosa*). It is comprised of approximately 3:1 mannose to galactose ratio. Tara gum, based on steric hindrance, possesses less galactose substitution compared to other galactomannans such as fenugreek and guar gum so it can produce a stronger film (Embuscado & Huber, 2009).

Most polysaccharides form films that are brittle and crack during handling and storage. For that reason, small non-volatile compounds of low molecular weight are typically added as plasticizers to reduce brittleness and increase flexibility. However, it is well known that addition of most plasticizers may cause significant changes in the barrier properties of the films (Skurtys et al., 2010; Sothornvit & Krochta, 2005). Commonly used plasticizers in polysaccharide-based film formations are polyols (glycerol, sorbitol and polyethylene glycol) because of their resemblance in structure with the polymers and their hydrophilic nature allowing them to attract water in the system (Banker, 1966; Mali, Sakanaka, Yamashita, & Grossmann, 2005; Mikkonen et al., 2007). The efficiency of each plasticizer is related to the molecular size, shape, number of oxygen atoms, spacing of oxygen atoms and water binding ability of each plasticizer (Haq, Hasnain, & Azam, 2014; Sothornvit & Krochta, 2001).

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In the past few years plenty of research has been conducted on the properties of films produced form different galactomannans (Aydinli & Tutas, 2000; Aydinli, Tutas, & Bozdemir, 2004; Cerqueira, Souza, et al., 2011; Cerqueira, Souza, Teixeira, & Vicente, 2012; Chaires-Martínez, Salazar-Montoya, & Ramos-Ramírez, 2008; Haq et al., 2014; Martins et al., 2012; Mikkonen et al., 2007). However, no information has been published on films made with tara gum. Furthermore, there is limited knowledge about the thermomechanical properties of galactomannan films. The aim of this study was to develop and evaluate tara gum films and to investigate the effect of polyols with different molecular weight and number of oxygen atoms as plasticizers.

2. Materials and methods

Tara Gum (TG) was obtained from Dymatic Chemicals Co., Ltd., Guangdong, China with molecular weight ~1000 kDa which was determined by gel permeation chromatography (GPC) (Tosoh Corp., HLC-8320GPC, Japan). All the other chemicals were analytical reagent grade chemicals and were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

2.1. Preparation of solutions for film casting

The TG solutions were prepared using the method described by Martins et al. (2012) with modifications. TG was dissolved in water (1%, w/v) at 35 °C for 2 h until a homogeneous solution was obtained. Film-forming solutions were then centrifuged at 3000 × *g* for 10 min to remove un-dissolved matter and air bubbles. Three polyols of the same shape but with different molecular weight and number of oxygen atoms (Table 1) were added as plasticizers at the same concentrations in the range of 0.075–0.3 g g^{-1} tara gum weight basis. 70 mL of solutions were poured into square plastic petri dishes (10 cm × 10 cm) and dried at 35 °C for 24 h. The obtained films were conditioned at 53 ± 1% RH and 25 ± 1 °C for at least 3 days in a controlled environmental chamber (Shanghai, China).

2.2. Characterization of films

2.2.1. Mechanical properties

A texture analyzer (Stable Micro Systems Ltd., TA.XTPlus, Surrey, UK) was used in order to measure mechanical properties according to ASTM D882 (ASTM, 2001) with some modifications. The films were initially cut into stripes (2 cm × 8 cm) and the average film thickness was calculated by measuring at least 5 different points with a digital micrometer (Shanghai, China). The initial grip separation and crosshead speed used were set at 50 mm and 0.5 mm/s respectively. Tensile strength (TS) and percent elongation-at-break (*E*%) were calculated from the plot of stress (tensile force/initial cross-sectional area) versus strain (extension as a fraction of the original length) using the following Eqs. (1) and (2):

$$\mathrm{TS} = \frac{F}{L \times X} \quad (1)$$

$$E\% = \frac{l - l_1}{l_1} \times 100\% \quad (2)$$

where *F* is the tensile force (N), *L* the width of the film (mm), *X* the thickness (mm), l_1 is the initial length of the film and *l* is the length of the film at breaking point.

2.2.2. Dynamic mechanical analysis (DMA)

DMA was performed (TA Instruments, Q800, New Castle, Del., USA) in order to measure stiffness and damping of the samples which are reported as storage modulus (E'), loss modulus (E'') and $\tan\delta = (E''/E')$. Samples with dimensions 1 cm × 2 cm were analyzed using frequency and temperature sweep tests.

After equilibrating at 25 °C for 5 min, the frequency sweep tests were performed at a frequency range of 0.1–100 Hz at amplitude of 10 μm (within the LVR) and a preload force of 0.01 N.

For the temperature sweep, the samples were heated at a rate 3 °C min^{-1} from −70 to 200 °C. A dynamic deformation was applied on samples at a frequency of 1 Hz under a strain amplitude of 10 μm. Temperatures above 200 °C were used in some samples in order to determine the melting temperature (T_m). The glass transition temperature (T_g) values were measured as the peak temperature of $\tan\delta$ caused by the discontinuity of the specific heat of the sample. All measurements were conducted at least in duplicate.

2.2.3. Water vapor permeability (WVP)

The water vapor transmission rate (WVTR) and water vapor permeability (WVP) were determined according to ASTM E96 (ASTM, 1995) with some modifications. Initially the films were cut in square pieces (4 cm × 4 cm) and the average thickness was measured. The films were sealed in cups containing 10 mL of distilled water and placed in desiccator containing silica gel. The weight of the cups was monitored every 2 h over 24 h. The slope of each line was calculated by linear regression ($R^2 > 0.99$) of weight change vs. time. WVTR and WVP were calculated based on the Eqs. (3) and (4) by Gennadios, Weller, and Gooding (1994) and McHugh, Avena-Bustillos, and Krochta (1993):

$$\mathrm{WVTR} = \frac{\text{slope}}{\text{film area}} \quad (3)$$

$$\mathrm{WVP} = \frac{\mathrm{WVTR} \times L}{PA_1 - PA_2} \quad (4)$$

where PA_1, vapor partial pressure at film outer surface in the cabinet, PA_2, vapor partial pressure at film inner surface in cup and *L*, the average film thickness.

2.2.4. Fourier-transform infrared (FTIR) spectroscopy

The IR spectra of the films were determined using an infrared spectrometer (FTIR) (Thermo Fisher Scientific Inc., Nicolet iS10, USA). The spectrums were obtained in Attenuated Total Reflectance mode (ATR) between 500 and 4000 cm^{-1}, using 16 scans at a resolution of 4 cm^{-1}. Data analysis of each film was performed with OMNIC 8.3 Thermo Fisher Scientific Inc.

2.2.5. Measurement of contact angle

Contact angle (CA) was determined in fresh films with sessile drop method, by depositing a drop of a liquid onto the film surface. 10 μL distilled water was carefully dropped on films through a 2.0 mL micrometer syringe (KDL Corp., Shanghai, China) and contact angles were quickly measured before the swelling started. The measurements were carried out in open air at a relative humidity of 30% RH and at a room temperature of 25 °C. Both sides of each film were measured with underside being the side attached to the casting mold and upper side the one exposed to air. The software belonging to the equipment (DataPhysics Instruments GmbH, OCA15EC, Germany) automatically calculated both left and right contact angles from the digitalized image expressed in degrees. Measurements were taken in triplicate for each type of film.

2.2.6. Water solubility

The percent of solubility of the gum and plasticizers (*S*%) in water was determined based on the method reported by Cuq, Gontard, Cuq, and Guilbert (1996) with a few modifications. It was expressed as percentage of the film dry matter solubilized after 24 h immersion in distilled water. Pre-weighted (W_0) dried sheet films (2 cm × 2 cm) were immersed in 30 mL distilled water

Table 1
Plasticizers selected for study and their properties.

Plasticizer	Molecular weight (g/mol)	Number of oxygen atoms	Formula & shape
Glycerol	92	3	$C_3H_8O_3$, straight chain
Sorbitol	182	6	$C_6H_{14}O_6$, straight chain
Polyethylene glycol 400	400	9	$H(OCH_2CH_2)_nOH$ $_{(n=8.2–9.1)}$, straight chain

Reference: Sothornvit & Krochta (2001).

at 25 ± 1 °C under constant agitation for 24 h followed by centrifugation at 150 × *g* for 10 min. The un-dissolved matter was dried at 105 °C for 24 h until constant weight (W_1). All tests were carried out in tetra-plicate and water solubility (*S*%) was calculated using the following Eq. (5):

$$S\% = \frac{W_0 - W_1}{W_0} \times 100 \quad (5)$$

2.2.7. Moisture content

The moisture content (*M*%) of the films was determined by drying 2 cm × 2 cm pieces at 105 °C for 24 h. The samples were equilibrated at 50% RH for 3 days. They were cooled to room temperature at 0% RH in a desiccator containing silica gel. The percent moisture content was calculated using the following Eq. (6):

$$M\% = \frac{W_0 - W_1}{W_0} \times 100 \quad (6)$$

where W_0 and W_1 are the weight of initial and dried samples respectively.

2.2.8. Statistical analysis

OriginPro 8 SR4 (Version 8.0, Northampton, USA) and SPSS Statistics software (Version 17.0, SPSS Inc. Chicago, IL) were used to analyze the resulting data. Data were initially evaluated by analysis of variance (ANOVA), and significant results were further analyzed using Duncan's multiple range tests ($P < 0.05$) to compare the mean values of films' properties.

3. Results and discussion

3.1. Mechanical properties

Mechanical testing of the films was conducted with a constant increasing strain until film fraction occurred. Tensile strength (TS) and elongation (*E*%) were calculated as a function of plasticizers at various concentrations (Table 2). For each plasticizer, the TS of the film was inversely correlated to the concentration of the plasticizer and *E*% was positively correlated. TG films plasticized with PEG 400 exhibited the lowest TS values compared to sorbitol and glycerol. On the other hand, glycerol presented the highest *E*% values followed by sorbitol and PEG 400. Increasing content of glycerol increased almost linearly the *E*% of the films and sorbitol was effective only for concentrations above 0.225 g g^{-1}. For TG films both TS and *E*% decreased with the increasing molecular mass and number of oxygen atoms. The same result was reported by Mikkonen et al. (2007) for locust bean and guar gum films. This observation was attributed to the molar ratio between plasticizer and polymer which was higher for glycerol compared to sorbitol since glycerol has lower molecular weight and therefore made the film more elastic. At the same time the smaller size of glycerol's molecule allowed it to interact better and more between the polymer chains increasing TS of the films. In our knowledge, galactomannan are the only films which behaved that way compared to films produced from other polysaccharides probably due to structural differences (Gennadios, Weller, Hanna, & Froning, 1996; Srinivasa, Ramesh, & Tharanathan, 2007; Tapia-Blácido, do Amaral Sobral, & Menegalli, 2011; Thomazine, Carvalho, & Sobral, 2005).

PEG 400 had no plasticizing effect on the polymer. This decrement in the mechanical properties must be a result of the inability of PEG 400 to connect with the polymer. It has been previously discussed that plasticizers with big molecular size were unable to insert between the polymer chain of gums (Aydinli et al., 2004; Haq et al., 2014).

Based on criteria by (Han & Gennadios, 2005), TG films showed good mechanical properties and can be classified as good with TS in the range 10–100 MPa and *E*% 10–100%. TG films with addition of glycerol and sorbitol exhibited higher values in both TS and *E* compared to locust bean gum and guar gum films (Mikkonen et al., 2007). This result suggests that a cohesive film structure is not only related to the substitutions of galactose on the mannan backbone chain since locust bean gum is the least substituted with mannose to galactose ratio 4:1 (McCleary, Clark, Dea, & Rees, 1985).

3.2. Solubility and moisture content of the film

Glycerol, due to its hydrophilic nature, helps retain water in the film matrix, therefore, higher concentrations of plasticizer provide higher moisture contents (Table 2). On the other hand, the moisture content for films with sorbitol and PEG 400 did not present a statistically significant difference ($P > 0.05$) when compared to unplasticized films. Similar results were reported by Cerqueira et al. (2012) and Tapia-Blácido et al. (2011) where addition of glycerol increased the moisture content of films compared with other plasticizers. Because of glycerol's small molecular size the number of hydroxyl groups was higher at the same concentration compared to sorbitol and PEG 400. Therefore, the hydrophilicity increased and the attracted water into the polymer matrix created more mobile regions with greater inter-chain distances (Zhang & Han, 2006).

For each plasticizer, the solubility of the film was found to increase with increasing concentration (Table 2). Glycerol and sorbitol had a similar effect on the film solubility despite the fact that glycerol is more hydrophilic producing films with higher moisture contents and more hydrophilic surfaces compared to sorbitol-plasticized films. On the other hand, PEG 400 being the most hydrophilic among the three plasticizers exhibited statistically significant difference in solubility regardless of the low moisture content. This is probably related to the inability of PEG 400 to insert effectively between the polymer chains due to its big molecular size thus leaving gaps (Haq et al., 2014).

3.3. Water vapour permeability (WVP)

It is know that the WVP of hydrocolloid films increases with increasing polymer hydrophilicity (Debeaufort, Martin-Polo, & Voilley, 1993). Therefore addition of plasticizers resulted in a more hydrophilic polymer matrix and eventually more water permeable films (Diab, Biliaderis, Gerasopoulos, & Sfakiotakis, 2001). PEG 400 plasticized films exhibited the highest WVP and were found to increase linearly with concentration (Fig. 1). The same trend occurred with the presence of glycerol but at lower values compared with PEG 400. It has been reported that films plasticized with hydrophilic plasticizers such as glycerol favor the adsorption of water molecules and increase the inter-chain spacing of the polymer resulting in increasing WVP (Aydinli & Tutas, 2000; Gontard,

Table 2
Effect of plasticizer type and concentration on mechanical properties, solubility and moisture content of tara gum film*.

Film type	Plasticizer content (g g^{-1})	Tensile strength (MPa)	Elongation (%)	Solubility (%)	Moisture content (%)
TG	0.0	97.24 ± 7.60^{a}	11.20 ± 4.66^{ef}	12.39 ± 4.81^{d}	12.82 ± 0.54^{cde}
TG + glycerol	0.075	90.60 ± 11.33^{ab}	15.90 ± 5.40^{def}	14.37 ± 6.06^{d}	12.83 ± 0.19^{cde}
TG + glycerol	0.150	78.26 ± 10.91^{bc}	23.05 ± 2.69^{c}	17.98 ± 4.41^{d}	13.91 ± 0.12^{c}
TG + glycerol	0.225	54.00 ± 2.74^{ef}	33.50 ± 2.12^{b}	25.37 ± 3.05^{bc}	16.86 ± 0.17^{b}
TG + glycerol	0.300	45.36 ± 2.26^{f}	44.07 ± 3.81^{a}	32.40 ± 1.45^{a}	18.89 ± 0.76^{a}
TG + sorbitol	0.075	81.95 ± 6.91^{bc}	12.00 ± 2.96^{ef}	13.62 ± 1.03^{d}	12.93 ± 0.07^{cde}
TG + sorbitol	0.150	62.87 ± 8.77^{de}	16.47 ± 3.74^{de}	18.67 ± 3.43^{cd}	12.29 ± 0.18^{e}
TG + sorbitol	0.225	50.11 ± 11.70^{ef}	20.87 ± 1.50^{cd}	25.09 ± 2.96^{bc}	12.44 ± 0.73^{de}
TG + sorbitol	0.300	43.64 ± 1.18^{f}	26.30 ± 0.42^{c}	34.16 ± 1.50^{a}	12.62 ± 0.47^{de}
TG + PEG 400	0.075	69.52 ± 11.29^{cd}	4.60 ± 1.13^{g}	29.72 ± 4.65^{ab}	12.89 ± 0.83^{cde}
TG + PEG 400	0.150	46.75 ± 3.00^{f}	6.10 ± 0.42^{fg}	32.83 ± 5.84^{a}	12.66 ± 0.11^{cde}
TG + PEG 400	0.225	29.29 ± 3.79^{g}	8.47 ± 0.76^{fg}	33.92 ± 4.52^{a}	13.34 ± 0.64^{cde}
TG + PEG 400	0.300	23.86 ± 1.88^{g}	10.20 ± 1.41^{efg}	36.56 ± 1.72^{a}	13.66 ± 0.75^{cd}

* Values are given as mean ± standard deviation. Different letters in the same column indicate a statistically significant difference ($P < 0.05$).

Guilbert, & Cuq, 1993; Yang & Paulson, 2000). Sorbitol showed a profound effect on WVP of the films. At the lowest concentration WVP decreased slightly and then increased with increasing concentration but without significant change. This was probably due to sorbitol's smaller hydrophilic nature compared with the two other plasticizers. A Similar result was reported by Cherian, Gennadios, Weller, and Chinachoti (1995) who reported that addition of sorbitol to wheat gluten films reduced WVP.

3.4. Contact angle

Surface hydrophobicity was evaluated by means of contact angle determination. It is known that the CA will increase with increasing surface hydrophobicity (Ghanbarzadeh et al., 2007). Because of the casting method, it was observed that the two sides of each film were different in texture. The underside, because of the contact with the casting mold, had a more polished and smooth texture compared with the upper side which was exposed to air. For that reason the underside of un-plasticized TG films was more hydrophilic compared to the upper side surface. However, films with plasticizers did not always show the same behavior. The CA for each film sample is shown in Fig. 2. Sorbitol increased the hydrophobicity of the films at all concentrations by increasing the CA almost 30° on the underside. On the upper side the CA remained almost constant and increased slightly with 0.3 g g^{-1} of sorbitol. Addition of glycerol induced significantly only the upper side by increasing its hydrophilicity but had no effect on the underside of the film. Same as WVP, sorbitol compared to glycerol improved the hydrophobicity of the films. Ghasemlou, Khodaiyan, and Oromiehie (2011) reported that the structure of sorbitol-plasticized films was more compact or less favorable to water molecules than the structure of glycerol-plasticized films. PEG 400 changed dramatically the texture of the films. Both sides became much more hydrophilic reducing the CA with increasing plasticizer concentrations especially for the underside. This could have been due to the excess of the plasticizer that was not able to interact with the polymer because of its big molecular size. PEG 400 escaped to the surface of the film giving an oily texture. The free plasticizer was trapped in higher concentration in the underside between the cast and the film making this side much more hydrophilic.

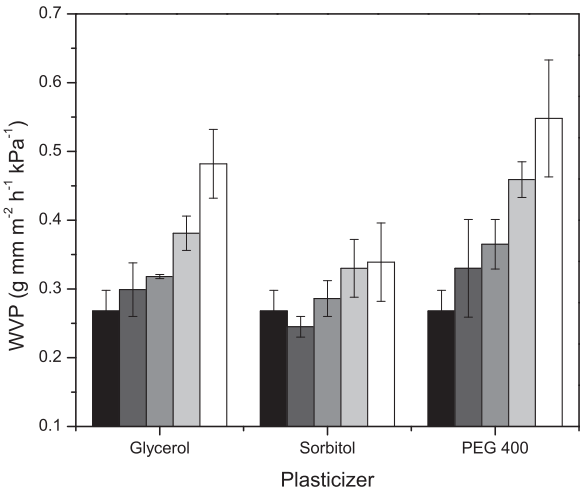

Fig. 1. Effect of plasticizer type and concentration on water vapour permeability of tara gum films. ((■) 0.0 g g^{-1}, (■) 0.075 g g^{-1}, (■) 0.15 g g^{-1}, (■) 0.225 g g^{-1}, (□) 0.3 g g^{-1}).

3.5. FTIR

The FTIR spectra of TG films with addition of glycerol, sorbitol and PEG 400 was measured (Fig. 3). The major peaks in the IR

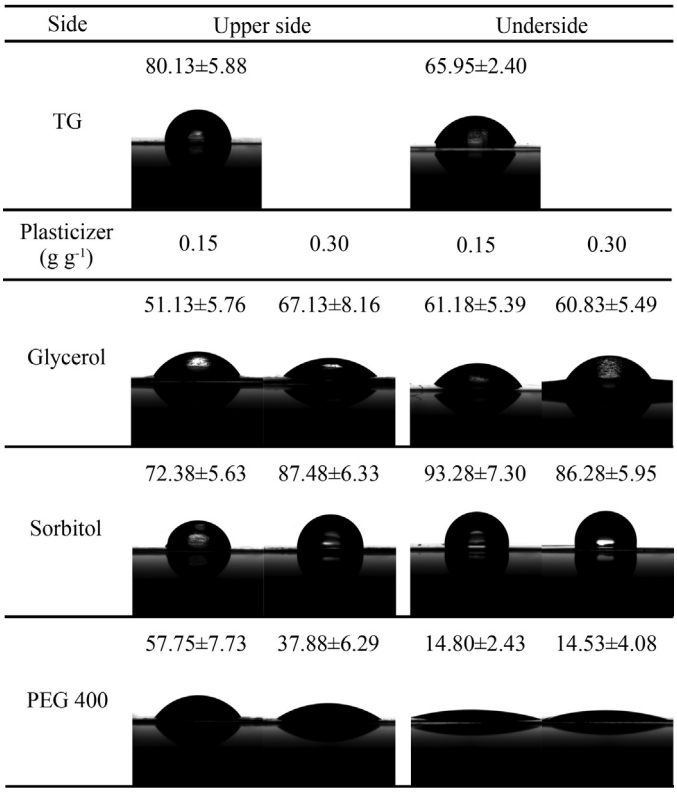

Fig. 2. Contact angles of water sessile drops on both sides of tara gum films with plasticizers at different concentrations.

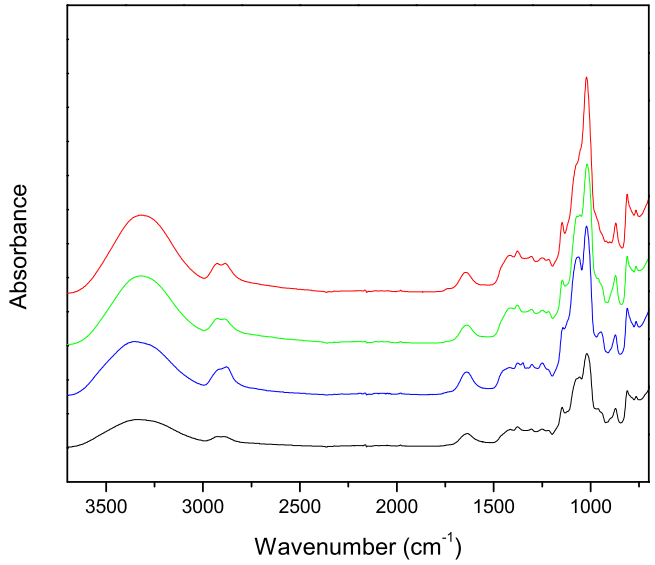

Fig. 3. Effect of plasticizers (0.3 g g^{-1}) on FTIR spectrum of tara gum film. (–unplasticized, (—)glycerol, (—)sorbitol, (—)PEG 400).

spectra appeared in two regions, 3700–2500 cm^{-1} and 1700–700 cm^{-1}. The broad band at 3700–3000 cm^{-1} is a result of O—H stretching vibration associated with free, inter, and intra-molecular bound hydroxyl groups and the peaks in the region 3000–2800 cm^{-1} is a result of C—H stretching (Yuen, Choi, Phillips, & Ma, 2009). Different plasticizers resulted in different magnitudes of absorbance in these regions with the highest from the glycerol-plasticized films. These films had higher moisture contents. Within this region, the wavenumber of highest intensity was also shifted from 3329 to 3357 cm^{-1} by with addition of PEG 400 probably by the weakening of the hydrogen bonding in the film.

The broad band between 1132 and 981 cm^{-1} results from the stretching vibrations of alcoholic C—O in C—O—H bonds (1072 cm^{-1}) and in the asymmetric and symmetric C—O—C bonds (1018 cm^{-1}) (Jamróz et al., 2007). These vibrations are related with the galactomannan's composition and showed small shifts with addition of the plasticizers especially glycerol (Cerqueira, Souza, et al., 2011). The same shifts were reported by Cerqueira et al. (2012) in galactomannan films with increasing concentration of glycerol. With addition of PEG 400 the absorption in these bands was significantly increased indicating the higher interactions between the polymer hydroxyl groups which at high concentrations induced some conformational changes in the polymer (Haq et al., 2014).

The spectra of the TG and plasticized TG films had generally the same shape and with non-significant shifts in the wavenumber of the ether bonds are present in the region 1100–900 cm^{-1}. It has been previously reported that plasticizers had no significant interaction with the polysaccharide (Hegyesi, Sovány, Berkesi, Pintye-Hódi, & Regdon Jr, 2013).

3.6. Thermomechanical properties

DMA measurements were carried out in order to understand the effect of plasticizers on the thermomechanical properties of TG films. As shown in Fig. 4 all the plasticized films showed a dual glass transition temperature whereas the un-plasticized polymer presented a single (Diab et al., 2001). Films with higher plasticizer content, with higher system mobility, exhibited more intense peaks on the tan δ spectrum and the first glass transition temperature T_{g1} could only be detected clearly at the highest concentration

Table 3
Values of glass transition temperatures (T_{g1}, T_{g2}) and melting temperature (T_m) of tara gum films with different plasticizers.

Film	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)
TG	–	95.6	252.2
TG-glycerol 0.15 g g^{-1}	–	88.7	210.4
TG-glycerol 0.30 g g^{-1}	−46.7	69.5	158.2
TG-sorbitol 0.15 g g^{-1}	–	80.5	205.8
TG-sorbitol 0.30 g g^{-1}	6.6	75.7	160.6
TG-PEG 400 0.15 g g^{-1}	–	72.6	–
TG-PEG 400 0.30 g g^{-1}	−24.2	66.3	–

(0.3 g g^{-1}) (Table 3). T_{g1} is detected at temperatures below or close to zero and is probably due to the relaxation associated with the plasticizer-rich fraction of the film (Tapia-Blácido et al., 2011). For instance glycerol's T_g has being reported to be much lower (−75 °C) compared to sorbitol's (0 °C) (Mathew & Dufresne, 2002) explaining the big difference in the T_{g1} between the two films. The effect on T_{g1} for galactomannan films plasticized with glycerol and sorbitol was similarly reported by Mikkonen et al. (2007). The different values of T_g compared with other galactomannans can be attributed to different mannose to galactose ratio (Chaires-Martínez et al., 2008). T_{g2} is related to the polymer-rich fraction and it is detected at higher temperatures (50–100 °C) (Table 3). Higher plasticizer concentrations changed the physical structure of the film by increasing the free volume of the polymer matrix and consequently increased the mobility of the molecules resulting in lower values of T_{g2}. The largest shift occurred when PEG 400 was incorporated as a possible result of the poor mechanical structure of the film obtained by PEG 400. Glycerol decreased T_{g2} more compared to sorbitol which it is probably associated with the moisture content of the films. The higher water content related to the hydrophilic glycerol made it a more effective plasticizer increasing the molecular mobility. The results are in agreement with Diab et al. (2001) and Appelqvist, Cooke, Gidley, and Lane (1993) who reported decrease of T_g by approximately 30 °C with increasing moisture content in pullulan films. Mitsuiki, Yamamoto, Mizuno, and Motoki (1998) reported also that T_g values in polysaccharides are water content dependent and changed according to the quantity of water molecules interacting with the polymer's functional groups. The peak detected at temperatures above 150 °C was the melting peak of the film and was only observed for glycerol and sorbitol at their highest concentration (0.3 g g^{-1}). Same as glass transition temperature, the higher the concentration of the plasticizer the lower the T_m of the film (Table 3). The increase in the mobility of the polymer chains by incorporating plasticizers decreased the intermolecular forces between them and consequently reduced both T_g and T_m.

Fig. 4 shows the storage modulus of plasticized tara gum films compared with plain tara gum films. At low temperatures the water phase of the film froze causing increase of E'. As the temperature increased above the T_{g1} of each plasticized film, the polymer gained its mobility and E' dropped below that of plain tara gum. The greatest change in E' with increasing plasticizer was observed with glycerol since it had the biggest effect on the T_g of the film. Probably due to higher water content of the glycerol-plasticized films. For temperatures above 100 °C the storage modulus increased due to water evaporation and was reduced again with the reduction of water content until reach zero at melting temperature.

The frequency dependence of storage modulus (E'), loss modulus (E'') and tan δ for TG films with addition of plasticizers (0.3 g g^{-1}) was measured with a DMA and results are shown in Fig. 5. The higher E' values compared to E'' and the low dependence on the frequency sweep indicate that the films were in a glassy state for the frequency range tested. Therefore, the temperature was below the glass transition temperature T_g. (Cespi, Bonacucina, Mencarelli, Casettari, & Palmieri, 2011; Perfetti, Jansen, Wildeboer, Van Hee, &

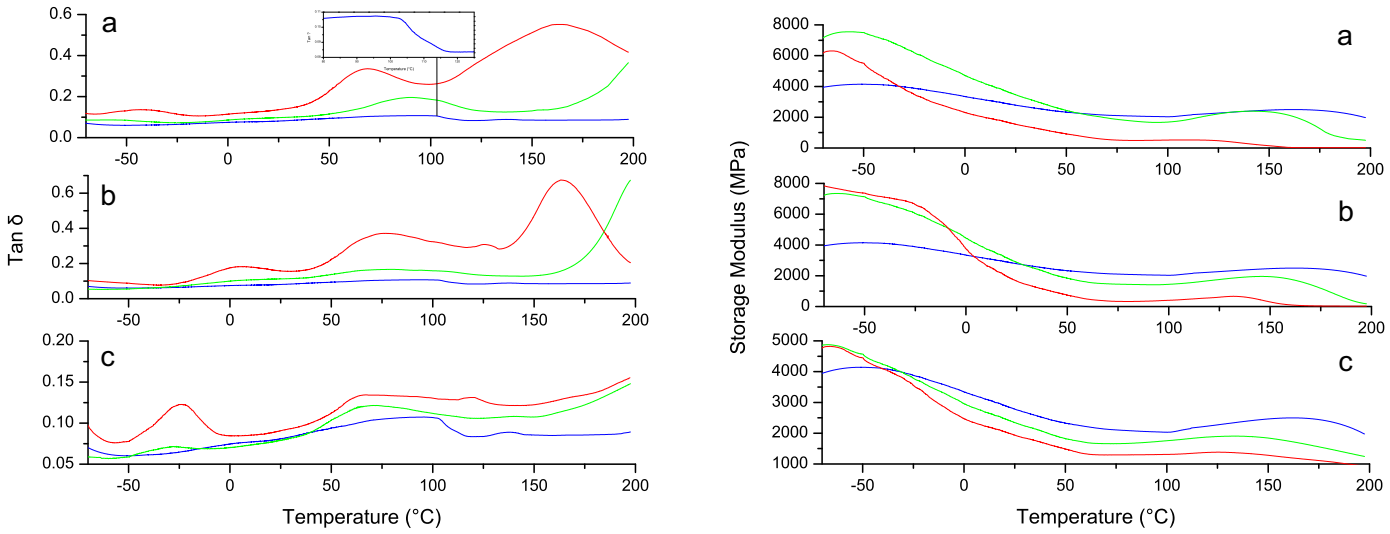

Fig. 4. Effect of (a) glycerol, (b) sorbitol and (c) PEG 400 contents on the film viscoelasticity as a function of temperature. ((_)0.0 g g^{-1}, (_)0.15 g g^{-1}, (_)0.3 g g^{-1}).

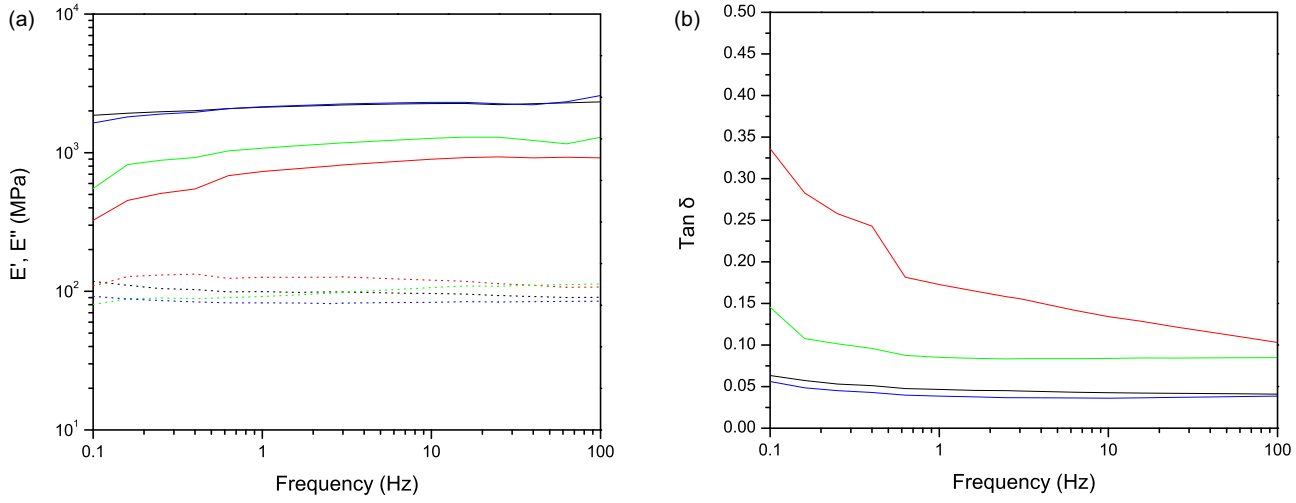

Fig. 5. The influence of applied frequency on the mechanical parameters (a) storage modulus (line), loss modulus (dots) and (b) tan δ of tara gum films. (–un-plasticized, (_)glycerol, (_)sorbitol, (_)PEG 400).

Meesters, 2010). As shown in Fig. 5a, addition of plasticizer had a bigger effect on E' compared to E''. The largest decrease in E' was exerted by glycerol, followed by sorbitol and PEG 400 which had no significant effect. This result correlates with the flexibility of the corresponding films from the tensile tests. The increase in flexibility based on the type of plasticizer is also suggested with the increase of tan δ (Fig. 5b).

4. Conclusions

Tara gum can be used for production of free standing edible films by the casting method and exhibited good mechanical properties. The presence of polyol plasticizers affected the thermomechanical and barrier properties of the films but had no significant interaction with the polysaccharide (FTIR). DMA measurements showed that incorporation of plasticizers increased the mobility of the system by decreasing the intermolecular forces between the polymer chains and therefore reduced both T_g and T_m. TS and E% decreased with the increasing molecular mass and number of oxygen atoms of the plasticizer. For that reason glycerol-plasticized films have good mechanical properties due to glycerol's hydrophilic nature which increased the moisture content of the film. Incorporation of sorbitol presented the best barrier properties in the TG films which exhibited the lowest hydrophilicity and water vapour permeability. PEG 400 on the other hand had no plasticizing effect on TG and diminished all its properties. This study suggests the use of tara gum as a potential biodegradable material for packaging films.

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