



Correlations between structural, barrier, thermal and mechanical properties of plasticized gelatin films

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ABSTRACT

The aims of this work were to develop gelatin films using glycerol as plasticizer (0–100% based on protein mass) and to establish relationships between glycerol content and structural, barrier, thermal and mechanical film properties. These correlations were established since WVP exhibited a minimum for films containing 20 g glycerol/100 g gelatin, while flexibility increased from 2.2% to 180.9% and T_g shifted from 137.5 to 21.3 °C, for films without glycerol and plasticized films with 80 g glycerol/100 g gelatin, respectively. Furthermore, a satisfactory fit between T_g experimental data and predicted values by Couchman and Karasz's equation was found, with glycerol ranging from 0 to 60 g/100 g gelatin. T_g values correlated inversely with film moisture content, and both mechanical and thermal properties showed a strong dependence since elastic modulus and T_g followed a similar trend. Films exhibited similar X-ray patterns regardless of the glycerol concentration, showing a displacement in the position of the peak located at around $2\theta = 8^\circ$, which shifted towards lower 2θ values with glycerol content. The abovementioned correlations between film physical properties and glycerol content, would allow to select the optimum conditions to develop, process and manage gelatin films according to specific requirements.

Industrial relevance: The methodology used in this work is of considerable importance for the film development and could be used in industrial applications. The management of film formulations and the function that each component plays could allow to obtain tailor-made films. A series of relationships between film properties based on gelatin was found, as well as between these properties and glycerol content of the films. An inflexion point in the behavior and microstructure of these materials was established due to glycerol concentration. The addition of higher quantities of glycerol than that corresponds to the abovementioned point, would not be recommendable since the properties are not modified and moreover, it is not profitable. These results would allow better management of film formulations and an appropriate selection of plasticizer concentration in accordance with the specific requirements of potential users.

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1. Introduction

Gelatin is a protein of animal origin, obtained by the thermal denaturation of collagen, which has a triple-helix structure stabilized mainly by the formation of inter-chain hydrogen bonds between carbonyl and amines groups. After the denaturation process the triple helix is broken and polypeptide chains adopt a random configuration. Then, these chains can interact to form a partial collagen-like triple helix called renatured or structural gelatin (Dai, Chen, & Liu, 2006).

Gelatin is successfully used as a gelling agent of food dispersion systems, drug encapsulation, pharmaceutical and cosmetic products, and mainly in the formulation of biodegradable packaging (Arvanitoyannis, Nakayama, & Aiba, 1998a; Cao, Yang, & Fu, 2009; Johnston-Banks, 1990; Langmaier, Mokrejs, Kolomaznik, & Mladek, 2008).

In general, gelatin films are brittle and susceptible to crack due to the strong cohesive energy density of the polymer (Arvanitoyannis et al.,

1998a). There are a large number of articles describing the effects of plasticizers on the physical, chemical and functional properties of biodegradable films (Cao et al., 2009; Thomazine, Carvalho, & Sobral, 2005; Vanin, Sobral, Menegalli, Carvalho, & Habitante, 2005). Since water is the most ubiquitous plasticizer of hydrophilic polymers, it is important to analyze its state and amounts in polymeric matrix in order to evaluate its effects on film properties. Furthermore, in the case of gelatin, water is necessary to allow the rebuilding of the collagen triple-helix structure (Patil, Marka, Apostolovb, Vassilevab, & Fakirovb, 2000).

The addition of plasticizers helps to decrease inherent brittleness of gelatin films by reducing intermolecular forces, increasing the mobility of polymeric chains, and improving their flexibility (Mendieta-Taboada, Sobral, Carvalho, & Habitante, 2008; Sothornvit, & Krochta, 2001; Thomazine et al., 2005). As a processing aid, plasticizers decrease the process temperature, reduce sticking in molds and enhance wetting. As a final product modifier, plasticizers increase the temperature range of treatment, increase toughness, and lower the glass transition temperature (Irissin-Mangata, Bauduin, Boutevin, & Gontard, 2001; Sothornvit & Krochta, 2005). Polyols are often cited as good plasticizers for protein

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based materials, among them glycerol is the most widely used (Audic & Chaufer, 2005).

Knowledge of film microstructure is of great importance given that it determines their physicochemical, barrier and mechanical properties, and also conditions film applications. Likewise, film properties depend on the polymer state (glassy or rubbery), it is therefore necessary to determine film glass transition temperature (T_g). This is a critical parameter for both the selection of film processing and storage conditions as well as many industrial applications (Langmaier et al., 2008; Mendieta-Taboada et al., 2008).

Several methods have been employed to study semi-crystalline materials, among them, differential scanning calorimetry (DSC) and spectroscopic X-ray diffraction (XRD); DSC is extensively used to determine glass transition temperature of materials. Patil et al. (2000) described the strong decreasing of T_g in gelatin films upon water uptake; this phenomenon has also been observed in films based on different plasticized biopolymers such as Nile-tilapia protein (Sobral, Monterrey-Q., & Habitante, 2002), methycellulose and chemically crosslinked methycellulose (Park & Ruckenstein, 2001), wheat gluten protein (Irissin-Mangata et al., 2001), hydroxypropyl starch and gelatin (Arvanitoyannis et al., 1998a), chitosan and gelatin (Arvanitoyannis, Nakayama, & Aiba, 1998b; Rivero, García, & Pinotti, 2009), gelatin (Sobral, Menegalli, Hubinger, & Roques, 2001), and myofibrillar proteins (Cuq, Gontard, Cuq, & Guilbert, 1997).

Most of the cited literature about plasticized gelatin films describes the effects of glycerol addition in low and middle concentrations, about 0–50% (Cuq et al., 1997; Langmaier et al., 2008; Thomazine et al., 2005; Vanin et al., 2005), however a few studies have been undertaken on films with higher glycerol content (Audic & Chaufer, 2005).

The purposes of this work were to develop gelatin films using glycerol as plasticizer ranging from 0% to 100% based on protein mass and to establish relationships between glycerol content and structural, barrier, thermal and mechanical film properties.

2. Materials and methods

2.1. Reagents

Gelatin of animal source, bovine gelatin type B provided by Gelico (Belo Horizonte, Brazil), was used.

Glycerol (analytical grade) was added as a plasticizer and was provided by J.T. Baker, (Xalostoc, México).

2.2. Film-forming solution preparation

Gelatin solution was prepared, using a concentration of 7.5% (w/v) by hydrating gelatin powder with distilled water for 8 h, then samples were heated at 60 °C until complete dissolution. After that glycerol was added; the plasticizer concentrations tested were 10, 20, 30, 40, 60, 80 and 100 g per 100 g of gelatin.

2.3. Film preparation

Plasticized and unplasticized gelatin films were prepared by casting of 20 g filmogenic solutions into Petri dishes (9 cm in diameter) and drying at 37 °C in an oven until constant weight (approximately 16 h). The obtained films were removed from the dish and stored before the determinations of barrier, thermal and mechanical properties. Films were conditioned in desiccators over NaNO₂ saturated salt solution at 20 °C and 65% of relative humidity (RH) in a controlled room.

2.4. Physicochemical film characterization

2.4.1. Thickness measurement

Film thickness was determined using a coating thickness gauge Check Line DCN-900 (New York, USA) for non-conductive materials

on non-ferrous substrates. The informed values correspond to the average of at least fifteen measurements at different positions for each specimen.

2.4.2. Moisture content

Film moisture contents were determined by measuring their weight loss, upon drying in an oven at 105 ± 1 °C until constant weight (dry sample weight). Samples were analyzed at least in triplicate and results were expressed as grams of water per 100 g of sample.

2.5. X-ray diffraction

Plasticized and unplasticized gelatin films were analyzed by X-ray diffraction in an X'Pert Pro P Analytical Model PW 3040/60 (The Netherlands). The Cu K α radiation (1.542 Å), operating at room temperature, was generated at 40 kV and 30 mA, and the relative intensity was recorded in scattering over an angular range (2θ) of 3–60° with step size 0.02.

2.6. Differential scanning calorimetry (DSC)

Thermal properties of gelatin films with and without plasticizer were determined using a DSC model Q100 controlled by a TA 5000 module (TA Instruments, New Castle, Delaware, USA), with a quench-cooling accessory, under a N₂ atmosphere (20 ml/min).

Film samples of 6–7 mg were weighed in aluminum pans and were hermetically sealed; an empty pan was used as reference. Samples were analyzed between –80 °C and 220 °C, at a heating rate of 10 °C/min.

After the first scan was completed, the sample was cooled until –80 °C and then a second scan was recorded. Finally, the pans were punctured and dried until constant weight at 105 ± 1 °C to obtain the dry weight of the sample.

From the thermograms the following information was obtained: T_m , the peak melting temperature (°C), ΔH , the enthalpy (J/g, dry basis) and T_g , the glass transition temperature (°C) using the Universal Analysis V1.7F software (TA Instruments, New Castle, USA).

2.7. Water vapor barrier properties

Water vapor permeability (WVP, g m⁻¹ s⁻¹ Pa⁻¹) tests were performed using a modified ASTM method E96 (1995) as described in a previous work using a specially designed cell (Rivero et al., 2009).

Each film sample was sealed over a permeation cell with a 0.00181 m² area which was maintained at 20 °C. A driving force of 1753.55 Pa, corresponding to a 75% RH gradient across the film was used. After steady state conditions were reached, eight weight measurements were performed. The reported values correspond to the average of at least three determinations.

2.8. Mechanical properties

2.8.1. Tensile test

Tensile strength (TS) and elongation at break (EB) of the films were determined using a texturometer TA.XT2i – Stable Micro Systems (Surrey, England) equipped with a tension grip system A/TG, according to the standard testing method ASTM D638-01 (2001). The measurements were made at 20 °C and 65% RH in a controlled room. Film probes of 6 cm length and 0.7 cm width were used, a minimum of five probes were prepared from each film. The initial grip separation and velocity were fixed at 50 mm and 1 mm/s, respectively. The curves of force (N) as a function of deformation (mm) were recorded by the Texture Expert Exceed software. Tensile properties were calculated from the plot of stress (tensile force/initial cross-sectional area) versus strain (extension as a fraction of the original length), (Perez-Gago & Krochta, 2001). Tensile strength was calculated by dividing the required force for film rupture by the area of the transverse section (ASTM D638-01, 2001) and

elongation at break was calculated from the ratio of the increase in length to the original length, expressed in percentage. The reported values correspond at least to five determinations.

2.8.2. Tear-propagation resistance

Tear-propagation resistance of the films was determined using the texturometer TA.XT2i – Stable Micro Systems with the tension grip system A/TG, previously mentioned, according to the standard testing method ASTM D1938-02 (2002). Film probes of 7.5 cm length and 2.5 cm width were used; a minimum of five probes were assayed from each film formulation. Besides, with comparative purposes synthetic films of low density polyethylene and polypropylene films were evaluated. In each probe a tear was performed in the middle of the probe width cutting it up to 2/3 of its length. The initial force to continue the propagation of the tear (N) and the extension at maximum force (mm) were determined from the force–deformation curves. A minimum of five tear-propagation force determinations were assayed.

2.9. Statistical analysis

All experiments were performed at least in duplicates, with individually prepared and casted films as replicated experimental units as described previously in each determination. Systat-software (SYSTAT, Inc., Evanston, IL, USA) version 10.0 was used for multifactor analysis of variance and non-linear regression. Differences in the properties of the films were determined by Fisher's least significant difference (LSD) mean discrimination test, using $P < 0.05$ as level of significance.

3. Results and discussion

3.1. Physicochemical film characterization

Gelatin films with different glycerol concentrations were uniform, homogeneous, thin, and easy to handle in all concentrations assayed. The films were removed without difficult from the acrylic plates. They had thickness values between 70 and 100 μm . Glycerol was not released from the film matrix in spite of the use of high concentrations (up to 100% based on protein mass) under the storage conditions (20 °C and 65% RH). The obtained results indicated the good miscibility and compatibility between glycerol and gelatin matrix.

Fig. 1 shows that moisture content of films increased from 10.3 to 44.6% with the plasticizer concentration. In view of these results it could be assumed that water is not only associated with the film matrix but also is retained due to the glycerol hydrophilic nature. Similar results were found by Vanin et al. (2005) for plasticized gelatin films.

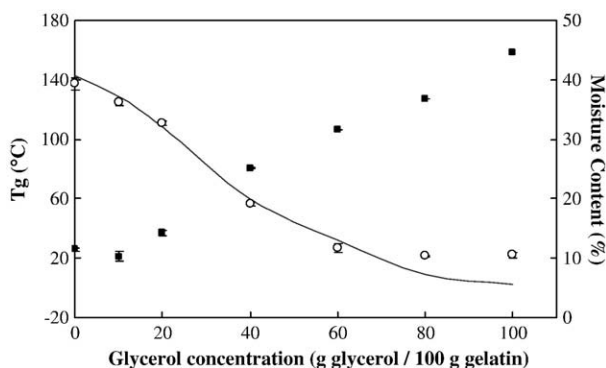


Fig. 1. Experimental data (○) and predicted (—) glass transition temperature (T_g) values and moisture content (■) of gelatin films as a function of glycerol concentration.

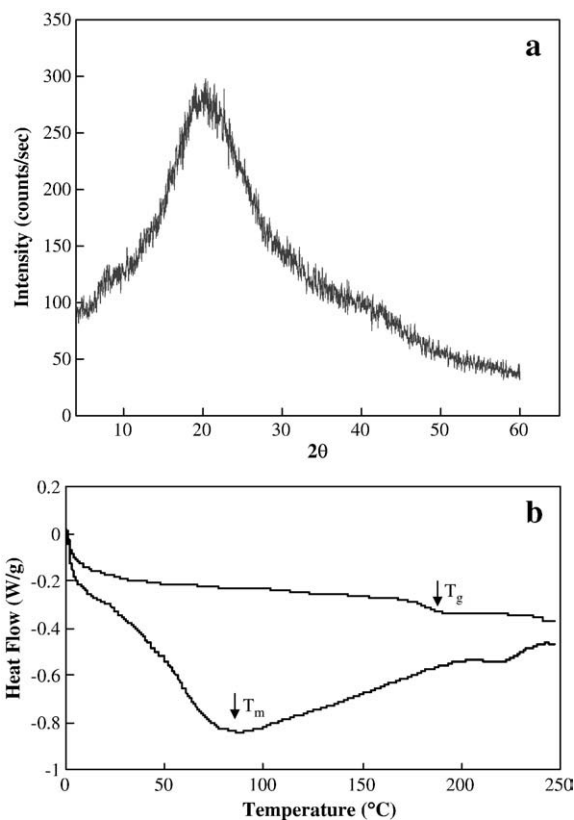


Fig. 2. a) X-ray diffractogram and b) DSC thermograms of first and second scans of gelatin powder conditioned at 20 °C and 65% RH.

3.2. X-ray diffraction

Gelatin type B powder used in this work presented an X-ray diffraction pattern characteristic of a partially crystalline material with a broad peak located at $2\theta = 20^\circ$ (Fig. 2a). Diffractograms of gelatin-based films can be seen in Fig. 3. Unplasticized films exhibited the aforementioned broad peak observed in the powder, within the range $20.5\text{--}21.5^\circ$ (d_{101} spacing, 4.40–4.21 Å) and a peak located in the region of $2\theta = 8.0^\circ$ (d_{101} spacing, 11.08 Å) appeared. According to Tanioka, Miyasaka, and Ishikawa (1996) these peaks indicate the reconstitution of the collagen-like triple-helix structure. Besides, Bigi, Panzavolta, and Rubini (2004) working on gelatin films stressed that the peak at 2θ around 8° is related

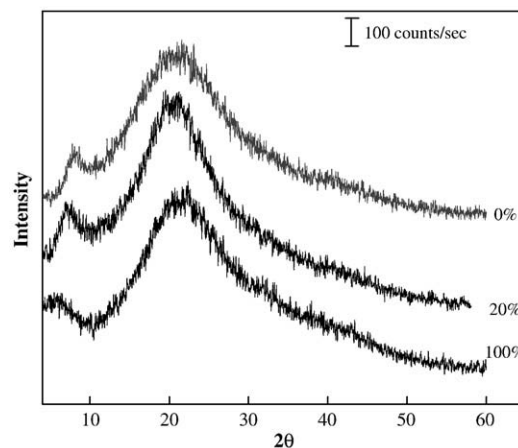


Fig. 3. X-ray diffractograms of unplasticized and plasticized gelatin films with 20 and 100 g glycerol/100 g protein.

Table 1

Glycerol concentration effect on X-ray diffraction, thermal and mechanical properties of gelatin films conditioned at 20 °C and 65% RH.

Glycerol content (g/100 g gelatin)	Displacement of the first peak X-ray pattern (%) ^a	Peak melting temperature (T_m)	Experimental T_g data (°C)	Predicted T_g values (°C)	Mechanical properties		
					Tear-propagation resistance		Tensile test
					Initial tensile strength (MPa)	Deformation (mm)	
0	0	87.9 ± 1.8	137.5 ± 2.1	142.81	na ^b	na	19.62 ± 2.37
10	6.0	90.1 ± 1.9	125.1 ± 2.3	128.61	na	na	11.58 ± 0.27
20	7.3	112.6 ± 0.9	111.0 ± 1.4	108.59	0.94 ± 0.05	52.295 ± 6.08	6.80 ± 0.83
40	8.8	125.5 ± 1.5	56.5 ± 1.3	59.76	0.59 ± 0.03	85.60 ± 2.04	0.63 ± 0.05
60	15.3	128.4 ± 1.8	270 ± 1.2	32.38	0.47 ± 0.02	102.20 ± 2.48	0.15 ± 0.03
80	18.0	134.3 ± 1.6	21.3 ± 0.3	9.12	0.45 ± 0.03	105.83 ± 7.15	0.034 ± 0.002
100	19.3	132.4 ± 0.5	22.0 ± 1.0	1.99	0.47 ± 0.02	114.15 ± 5.42	0.035 ± 0.004

^a Relative to unplasticized gelatin film first peak location.^b na: not applicable.

to the diameter of the triple helix and its intensity would be associated with the triple-helix content of the films.

The obtained patterns of plasticized films were similar to each other for all concentrations assayed even when they showed a displacement in the position of the first peak related to glycerol content (Fig. 3). As can be observed in Table 1, percentage displacement of the mentioned peak (relative to unplasticized films) presented a break point in the range of 40–60 g glycerol/100 g gelatin.

According to Langmaier et al. (2008) this structural change could be attributed to glycerol properties, both its high water affinity as well as its interference in polymer interaction.

3.3. Water vapor barrier properties

Fig. 4 shows the WVP values obtained for plasticized and unplasticized gelatin films. Up to 40 g glycerol/100 g protein WVP values of plasticized films were significantly lower ($P < 0.05$) than those of unplasticized films. However, increasing glycerol content above 40 g/100 g, WVP values increased from 3.21×10^{-10} to $3.87 \times 10^{-10} \text{ g s}^{-1} \text{ m}^{-1} \text{ Pa}^{-1}$. In spite of the fact that glycerol is an effective plasticizer and its efficiency is determined by its low molecular weight, its high capacity to interact with water facilitates the solubilization and permeation through the film (Cuq et al., 1997). Non-significant differences ($P > 0.05$) were found between WVP values of films with glycerol contents higher than 60 g/100 g protein. Regardless of the moisture content of gelatin films that increased with glycerol concentration (Fig. 1) at high glycerol contents WVP values did not vary. These results could be attributed to the water saturation of the plasticized matrix which leads to a practically constant flux of water vapor. In the same way Cho and Rhee (2002) and Cao, Fu and He (2007) proposed that high glycerol concentrations added absorbed more moisture due to its overwhelming hydrophilicity.

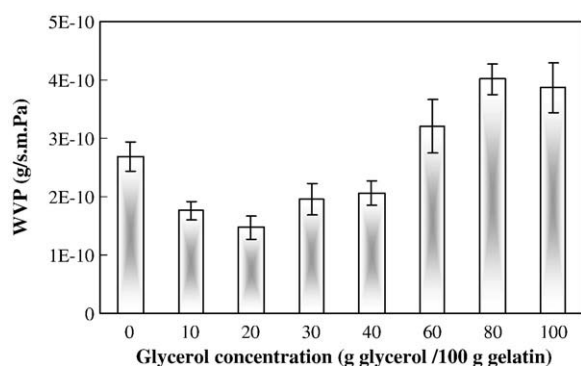


Fig. 4. Water vapor permeability (WVP) of gelatin films as a function of glycerol concentration.

3.4. Thermal properties

Fig. 2b shows the typical thermogram of gelatin powder (first and second scans). The first scan was characterized by the presence of an endothermic peak attributed to the melting of triple-helix crystalline structure, whereas T_g was evaluated from the second scan. T_g value of gelatin powder was found around 183.5 °C; Patil et al. (2000) reported a value of 217 °C for dry gelatin.

Thermograms of films with and without plasticizer are exhibited in Fig. 5. Unplasticized films presented a wide endothermic peak with a minimum at around 87 °C and a high enthalpy value associated (540 J/g). Several authors attribute this endothermic peak to the overlapping of different process such as water evaporation, melting and recrystallization of small and/or imperfect gelatin crystallites, and association of the glass transition of α -amino acid blocks in the polypeptide chain (Dai et al., 2006; Langmaier et al., 2008; Patil et al., 2000). Peak temperature, and moreover enthalpy of this endothermic process are strongly related to film drying conditions. This effect has been studied by some authors, among them Dai et al. (2006) and Chiou et al. (2008).

Thermograms of plasticized films progressively changed with glycerol addition; endothermic peak suffered an unfolding into several peaks, although the enthalpy associated to the whole process remained approximately constant (Fig. 5). This unfolding was also observed by Rahman, Al-Saidi and Guizani (2008) studying the effect of water content on gelatin films. Temperature of the main peak shifted towards higher melting values by increasing glycerol concentration up to 60 g/100 g gelatin, remaining almost invariable at higher plasticizer contents (80 and 100%), Table 1.

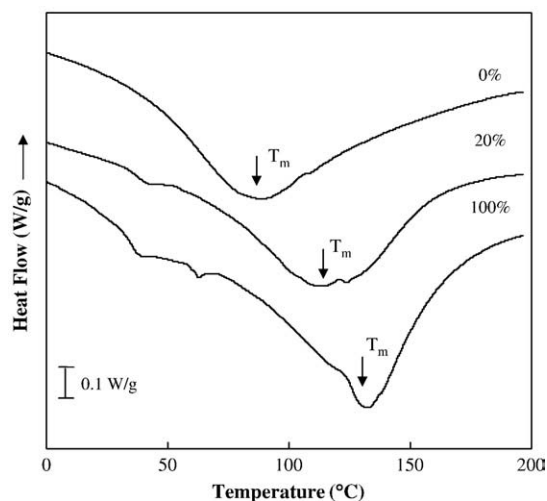


Fig. 5. DSC thermograms (1st scan) of gelatin films without glycerol and plasticized films with 20 and 100 g glycerol/100 g protein.

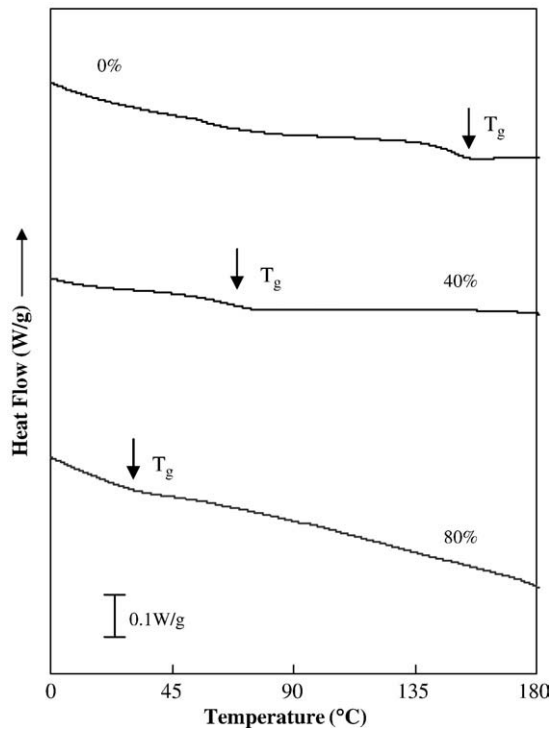


Fig. 6. DSC thermograms (2nd scan) of plasticized gelatin films. The glycerol concentration (g/100 g protein) is indicated in each curve.

The glass transition temperature (Table 1) was visualized more clearly in the second scan of heat flow curves, since after the first scan a completely amorphous material was obtained, (Fig. 6). The effect of plasticizer addition on T_g values can be observed in Figs. 1 and 6. As was expected, T_g of plasticized films decreased with glycerol concentration.

Several experimental models were used to predict T_g ; for binary systems Gordon–Taylor’s equation has been widely used. For the plasticized films formulated in this work, which were ternary systems, the use of the model proposed by Couchman and Karasz was more appropriated (Ghanbarzadeh & Oromiehi, 2009). The corresponding equation used is the following:

$$T_g(\text{blend}) = \frac{X_1 \Delta C_{p1} T_{g1} + X_2 \Delta C_{p2} T_{g2} + X_3 \Delta C_{p3} T_{g3}}{X_1 \Delta C_{p1} + X_2 \Delta C_{p2} + X_3 \Delta C_{p3}} \quad (1)$$

In Eq. (1), the expression $X_1 \Delta C_{p1} T_{g1}$ is related to water, $X_2 \Delta C_{p2} T_{g2}$ to gelatin and $X_3 \Delta C_{p3} T_{g3}$ to glycerol. X represents the weight fraction of each component of ternary system, ΔC_p is the change in heat capacity, being ΔC_{p1} corresponding to water (1.94 J/g°C), ΔC_{p2} that of gelatin (1.69 J/g°C) and ΔC_{p3} the heat capacity of glycerol (0.91 J/g°C). The T_g values of the pure components used were -135 °C, 183.5 °C and -85.6 °C for water, gelatin and glycerol, respectively.

Fig. 1 and Table 1 show the experimental T_g data and those predicted by Couchman and Karasz’s equation (Eq. (1)). Statistical analysis indicates that a good agreement was obtained for films containing up to 60 g glycerol/100 g gelatin ($r^2 > 0.998$). Ghanbarzadeh and Oromiehi (2009) also reported a satisfactory fit between experimental and predicted values for zein and whey protein plasticized with 23 and 33% glycerol, respectively.

Increasing glycerol concentrations over 60%, the differences between experimental and predicted T_g values became more marked (Fig. 1). This result could be attributed to the saturation of the protein matrix and consequently the slight decreasing of miscibility between glycerol and gelatin.

On the other hand, the obtained T_g values correlated inversely with moisture content of plasticized gelatin films (Fig. 1). As was described

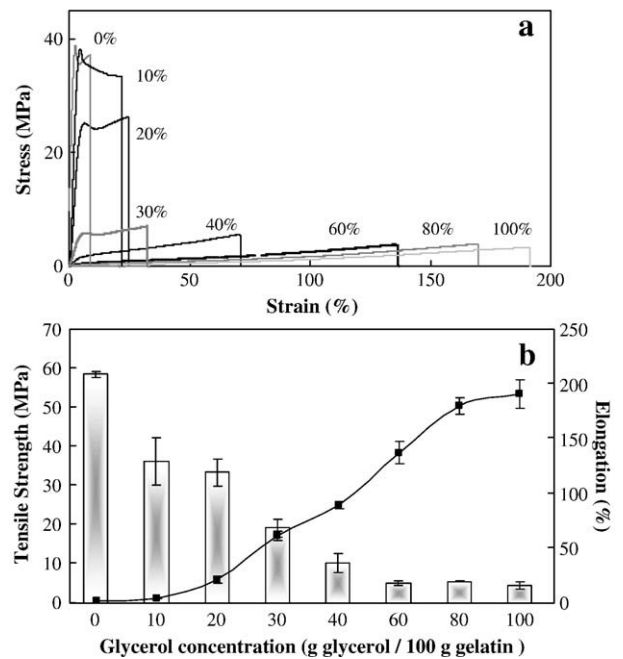


Fig. 7. Mechanical properties of gelatin films as a function of glycerol concentration: a) typical stress–strain curves; b) tensile strength and elongation at break.

previously, moisture increased with plasticizer concentration while T_g decreased. According to Dai et al. (2006), free water plasticizes the amorphous phase of the matrix, contributing to a depression of T_g .

3.5. Mechanical properties

Mechanical properties of films were studied through tensile strength, elongation, elastic modulus and tear-propagation resistance. The mechanical behavior of unplasticized gelatin films shows the typical characteristics of brittle and rigid materials, since they exhibited high values of stress and low values of strain at break (Fig. 7a). A similar trend was reported by Cao et al. (2009) working on gelatin type B films. The aforementioned behavior of unplasticized gelatin films was also observed in the case of other hydrophilic films such as those formulated with hydroxypropyl starch–gelatin and sodium caseinate–starch blends (Arvanitoyannis et al., 1998a; Arvanitoyannis & Biliaderis, 1998).

When glycerol was added up to 30 g/100 g gelatin strain increased and stress at break decreased compared to unplasticized films (Fig. 7a and b) although the material kept its rigid character. Films with glycerol contents of 10 and 20 g/100 g gelatin exhibited elongation values ranging between 4.7 and 21.4%.

At higher plasticizer concentrations the mechanical pattern changed to those corresponding to a ductile and flexible material (Fig. 7a). Thus, in films with 60 g glycerol/100 g protein tensile strength decreased 11 times while elongation increased 61 times compared to unplasticized samples (Fig. 7b). A similar trend was observed by Thomazine et al. (2005) for plasticized gelatin films. In these ductile materials, the stress increased continuously until a maximum to a yield point and then decreased until the sample was broken (Fig. 7a).

In addition, it must be stressed that film elastic modulus (EM) followed a similar trend to that of tensile strength.

Comparing with synthetic materials, tensile strength and elongation at break of gelatin films with 40 g glycerol/100 g were within the range of those corresponding to low density polyethylene (LDPE) films (Smith, 1986).

The mechanical properties of samples with 60, 80 and 100 g glycerol per 100 g gelatin were not significantly different ($P > 0.05$) with regard to tensile strength (Fig. 7b). The higher glycerol concentrations led to an elongation value of around 190%. This could be indicative of the plasticizer

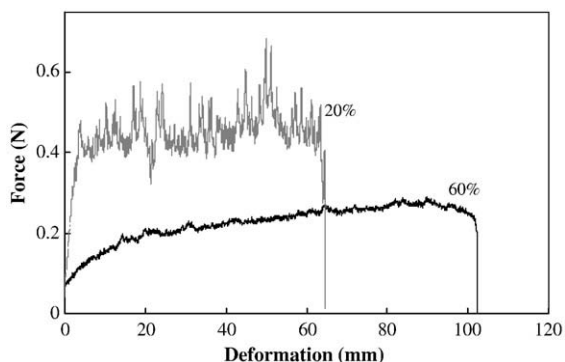


Fig. 8. Tear-propagation resistance pattern of plasticized gelatin films. The glycerol concentration (g/100 g protein) is indicated in each curve.

saturation of the network, and it was also described by Audic and Chaufer (2005) for sodium caseinate plasticized films.

To link the structural modifications induced by glycerol addition with the mechanical properties of gelatin films, EM and T_g were analyzed together as a function of glycerol content. Table 1 shows that mechanical and thermal properties are strongly related, since both EM as well as T_g followed a similar trend. Again, two well defined zones can be observed: up to approximately 40 g glycerol/100 g gelatin, the higher T_g values the higher EM. With higher glycerol concentrations EM decreased, and finally this parameter reached a plateau of around 0.034 MPa, at 80 g glycerol/100 g gelatin, while T_g values remained close to ambient temperature (Table 1). Besides, Yakimets et al. (2005) working on films formulated with gelatin bovine skin type B stressed that mechanical pattern and T_g are determined by their water content. These authors described different zones of water disposition for a binary water–gelatin system. In our case, working with a ternary system, where both glycerol and water act as plasticizers, the aforementioned two zones of mechanical behavior are in agreement with regions II and III described by Yakimets et al. (2005).

On the other hand, tear-propagation resistance was also evaluated for plasticized gelatin films. Films without and plasticized with 10 g glycerol/100 g gelatin were not tested since this method is not applicable for brittle sheeting materials. The tear-propagation resistance pattern suffered a change at approximately the same glycerol concentration that those of tensile tests. Thus, Fig. 8 shows the typical force versus deformation curves obtained for glycerol content of 20 and 60 g/100 g protein. Gelatin films with glycerol addition up to 40 g/100 g could be considered as a low-extensible material, while those with higher concentrations were associated to extensible films. Table 1 shows the values of initial tensile strength and deformation that define the tear resistance of the tested material. Increasing glycerol concentration the necessary strength to propagate the tear of films decreased, and their extensibility increased from 52.3 to 114.1%.

With regard to synthetic films, LDPE, which is an extensible material, exhibited higher media force (0.54 N) and elongation (138.6%) than those of gelatin films with 60 g/100 g protein (Fig. 8). While polypropylene, a low-extensible material, presented lower media force (0.14 N) and higher elongation (72.2%) compared to gelatin films with 20 g/100 g protein (Fig. 8).

4. Conclusions

Correlations between film microstructures and their barrier, thermal and mechanical properties were established, as well as between these ones and glycerol content. Likewise, in films containing above 60 g glycerol/100 g gelatin, an inflexion point in the studied properties was observed. In support of these mentioned findings, X-ray and DSC analysis showed that films presented a structural change with glycerol addition, and accordingly WVP, mechanical properties and T_g showed a

similar trend, remaining their values practically constant for glycerol concentration higher than 60 g/g gelatin.

Films exhibited similar X-ray patterns regardless of the glycerol concentrations tested. However they showed a displacement in the position of the peak located at around $2\theta = 8^\circ$ related to glycerol content; the lower the peak position the higher the glycerol concentration.

In the same way, T_g experimental data were fitted satisfactorily to Couchman and Karasz's equation with glycerol content up to 60 g/100 g gelatin. T_g values correlated inversely with film moisture content, but they showed a direct dependence with the elastic modulus.

In conclusion, it was possible to establish relationships between physical properties and glycerol content of the films, which would permit to select the optimum conditions to develop and manage the films according to the process requirements and storage conditions as well as specific film applications.

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