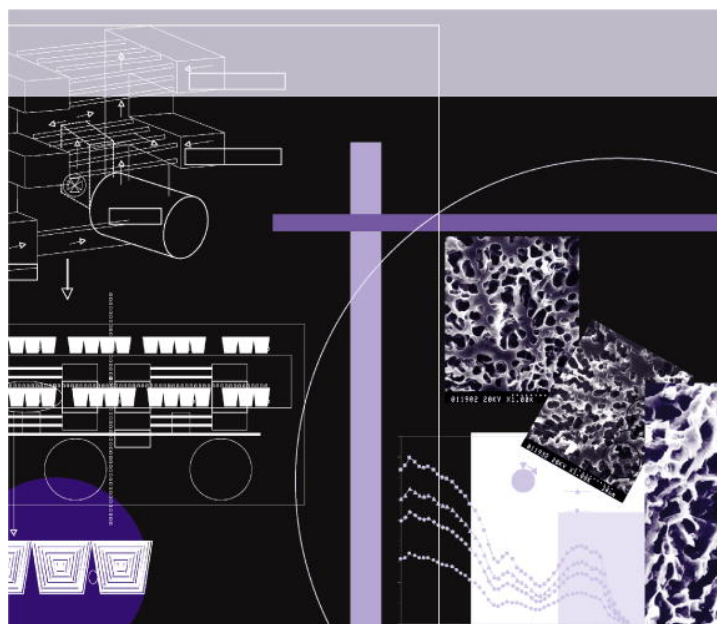




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The effect of the degree of hydrolysis of the PVA and the plasticizer concentration on the color, opacity, and thermal and mechanical properties of films based on PVA and gelatin blends

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Abstract

The objective of this work was to study the color, opacity, crystallinity, and the thermal and mechanical properties of films based on blends of gelatin and five different types of PVA [poly(vinyl alcohol)], with and without a plasticizer. The effect of the degree of hydrolysis of the PVA and the glycerol concentration on these properties was studied using colorimetry, differential scanning calorimetry (DSC), X-ray diffraction (XRD) and tensile mechanical tests. All films were essentially colorless ($\Delta E^* < 5$) and with low opacity ($Y \leq 2.1$). The DSC results were typical of partially crystalline materials, showing some phase separation characterized by a glass transition ($T_g = 40$ – 55 °C), related to the amorphous part of the material, followed by two endothermic peaks related to the melting ($T_m = 100$ – 160 and 170 – 210 °C) of the crystallites. The XRD results confirmed the crystallinity of the films. The film produced with PVA Celvol® 418 (DH = 91.8%) showed the highest tensile resistance (tensile strength = 38 MPa), for films without plasticizer. However, with glycerol, the above-mentioned PVA and the PVA Celvol® 504 produced the least resistant films of all the PVA types. But, although the mechanical properties of the blended films depended on the type of PVA used, there was no direct relationship between these properties and the degree of hydrolysis of the PVA. The properties studied were more closely dependent on the glycerol concentration. Finally, the mechanical resistance of the films presented a linear relationship with the glass transition temperature of the films.

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Keywords: Biopolymer; Poly(vinyl alcohol); Biodegradable films; Glycerol; Physical properties; Casting

1. Introduction

The amount of research involving the production and characterization of biodegradable films has increased substantially, due mainly to interest in minimizing the ecological impact caused by using synthetic packaging. A significant proportion of this research on films has been made using biopolymers from renewable sources, i.e. products or byproducts derived from agriculture or from agro-industries (Tharanathan, 2003).

Usually films based on biopolymers are highly sensitive to environmental conditions, especially to the relative air humidity, and generally present low mechanical resistance, although protein films may show good elasticity (Gennadios et al., 1994; Torres, 1994). As a result, several researchers have tried to develop films based on mixtures of biopolymers and synthetic polymers, even with polymers that are not necessarily biodegradable, such as low density polyethylene (Ghorpade et al., 1995).

However, there are some synthetic polymers from non-renewable sources that are biodegradable, such as poly(vinyl alcohol) (PVA) (Matsumura et al., 1999). PVA has been used in several studies on biopolymer based materials

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produced by casting or extrusion (Lui and Peng, 2005). With respect to films produced by casting, the studies have involved blends of PVA with polysaccharides, such as starch (Chiellini et al., 2001a; Jayasekara et al., 2004; Iman et al., 2005; Guohua et al., 2006), gellan (Sudhamani et al., 2003) and konjac glucomannan (Xiao et al., 2000), and with proteins, such as wheat gluten (Dicharry et al., 2006), collagen (Alexy et al., 2003; Sarti and Scandola, 1995) and gelatin (Chiellini et al., 2001b,c; Bergo et al., 2006). Chiellini et al. (2001c) showed that films made with blends of gelatin and PVA were effectively biodegradable.

Gelatin is widely used in the photographic, pharmaceutical and food industries, since it is a protein that can be produced in abundance at relatively low cost and showing interesting functional properties (Arvanitoyannis, 2002). In addition to its more conventional functional properties, gelatin presents outstanding film forming properties, and as a result has been widely used in studies involving edible films, which are also biodegradable materials. Several papers can be found on films based on pure gelatin (Sobral et al., 2001; Carvalho and Grosso, 2004; Thomazine et al., 2005; Vanin et al., 2005; Yakimets et al., 2007) or on mixtures with other biopolymers (Arvanitoyannis et al., 1997, 1998).

Gelatin is a protein of animal origin obtained from collagen by acidic or alkaline hydrolysis (Gennadios et al., 1994; Arvanitoyannis, 2002). The most remarkable characteristics of gelatin are its solubility in water and its ability to form thermo reversible gels. From a structural point of view, gelatin differs from other proteins due to its considerable absence of internal order and the random configuration of its polypeptide chains in aqueous solution (Arvanitoyannis, 2002). From a polymer science point of view, gelatin is a heterogeneous system constituted of 20 different amino acids. Sobral et al. (2001) showed that 50% of the amino acids of a pigskin gelatin were polar, being ionic (e.g. lysine, histidine, aspartic acid and glutamic acid) and non-ionic (e.g. serine, threonine, tyrosine, glutamine). Thus, half of the gelatin monomers show the potential to interact with other polar polymers, such as PVA.

Similar to gelatin, poly(vinyl alcohol) (PVA) is soluble in water, its solubility in water being influenced by its degree of hydrolysis, molecular weight, particle size distribution and crystallinity (Peppas and Merrill, 1977). With respect to the dry polymer, as in the case of films, the properties of the PVA are especially affected by the molecular weight and the degree of hydrolysis (Pal et al., 2006). Since PVA is obtained by the hydrolysis of poly(vinyl acetate), different types of PVA can be produced, depending on the degree of hydrolysis involved, this corresponding to different amounts of hydroxyl groups in the polymer. Consequently, the potential to interact with other polar polymers would be expected to vary as a function of the degree of hydrolysis.

Although gelatin is probably the protein most used in studies on films based on mixtures with PVA, no reports were found in the specialized literature dealing with the

details of the effects of the different types of PVA on the film properties. Thus, the objective of this work was to study the color, opacity, thermal properties, crystallinity and mechanical properties of films based on blends of gelatin with five different types of PVA, stressing the effects of the degree of hydrolysis and of three plasticizer concentrations, on the above mentioned physical properties.

2. Materials and methods

2.1. Materials

The macromolecules used for film production were: pigskin gelatin (bloom = 242–248; molecular weight $\approx 5.2 \times 10^4$ Da; moisture content = 9.3%) donated by Gelita South America (São Paulo, Brazil) and five types of poly(vinyl alcohol) with different degrees of hydrolysis (DH) and molecular weight (M_n , furnished by supplier) (Celvol[®] 504, DH = 88%, M_n = 31–50 kDa; Celvol[®] 418, DH = 91.8%, M_n = 85–124 kDa; Celvol[®] 425, DH = 95.7%, 85–124 kDa; Celvol[®] 350, DH = 98.6%, M_n = 146–186 kDa; Celvol[®] 125, DH = 99.7%, M_n = 85–124 kDa), which were donated by Celanese (Dallas, USA). Glycerol (Sinth) was used as the plasticizer.

2.2. Film production

The films were produced in the wet mode from a mixture of gelatin (solution A) and PVA (solution B) solutions. Solution A was prepared as follows: the gelatin (1 g/100 g of solution) was hydrated for 30 min, and then dissolved at 55 °C (Sobral et al., 2001) using a thermostatic bath (Marconi, Model TE 184). The glycerol was then added and the solution held at 55 °C for a further 30 min. To prepare solution B, the PVA (1 g/100 g of solution) was first homogenized in distilled water and then dissolved at 90 °C (Chiellini et al., 2001a) with magnetic stirring (Tecnal-TE085).

Solutions A and B were mixed together and homogenized for 15 min at room temperature with magnetic stirring, so as to produce film forming solutions with 2 g macromolecules/100 g film forming solution with the same proportions of gelatin and PVA, and plasticizer concentrations of 0, 25 and 45 g glycerol/100 g macromolecules. These solutions were dispersed in 12×12 cm² acrylic plates and subjected to drying (30 °C for 24 h) in an oven with air circulation (Marconi-MA 037). The thickness of the films was maintained constant at 0.080 ± 0.008 mm, controlling the ratio of dry mass of film forming solution/support area.

2.3. Film characterization

Before any characterization was carried out, all the films were conditioned in desiccators with saturated solutions of NaBr (58% relative humidity) at 25 °C for 7 days. All the tests were undertaken in air-conditioned rooms

($T = 22\text{ }^{\circ}\text{C}$ and relative humidity between 55% and 65%) to obtain the correct measurements of the mechanical properties (tensile test): color, opacity, thermal properties and crystallinity.

2.4. Color and opacity

The color and opacity were determined in triplicate using a HunterLab colorimeter (model Miniscan XE), working with D_{65} (day light) and a measuring cell with an opening of 30 mm. The color of the films was expressed as the total difference in color (ΔE^*) according to Eq. (1), where the values of ΔL^* , Δa^* and Δb^* were the differences between the color parameter of the sample and the color parameter of the white standard (Gennadios et al., 1996):

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \quad (1)$$

Film opacity was determined according to the HunterLab method in the reflectance mode (Paschoalick et al., 2003). Opacity (Y) was calculated from the relationship between the opacity of the film superposed on the black standard (Y_{black}) and that of the film superposed on the white standard (Y_{white}) according to the following equation:

$$Y = \frac{Y_{\text{black}}}{Y_{\text{white}}} 100 \quad (2)$$

2.5. Mechanical properties

The mechanical properties of the films, taking the average of five determinations, were determined by way of a tensile test using the TA.XT2 texturometer (TA Instruments, Surrey, UK). The samples were first cut into rectangles ($10 \times 1.5\text{ cm}^2$). The initial separation distance and the velocity were fixed at 80 mm and 0.9 mm/s, respectively (Thomazine et al., 2005). The tensile strength (force/initial cross-sectional area) and elongation at break ($\Delta l/l_0$) were determined directly using the software Texture Expert V.1.15 (SMS) from the stress \times strain curves, and the elastic modulus was calculated as the slope of the linear initial portion of this curve.

2.6. Thermal properties

The thermal properties of the films were determined using a DSC TA 2010 differential scanning calorimeter controlled by a TA 5000 module (TA Instruments, New Castle, DE, USA) according to Sobral et al. (2001). Before the analysis, the films ($\sim 10\text{ mg}$) were conditioned for 7 days in aluminum pans on silica gel. The temperature range used was -50 to $150\text{ }^{\circ}\text{C}$ with a heating rate of $5\text{ }^{\circ}\text{C}/\text{min}$ in an inert atmosphere ($45\text{ mL}/\text{min}$ of N_2). The glass transition (mid-point) temperature (T_g) and the melting (peak) temperature (T_m) were calculated using the software Universal Analysis V1.7F (TA Instruments).

2.7. X-ray diffraction

Film crystallinity was evaluated qualitatively (Bergo and Sobral, 2007) by measuring the X-ray diffraction (XRD) using an X-ray diffractometer (Rigaku) with a Cu source, working at room temperature with a current of 40 kV and 30 mA, and with the beam falling on a sample area of about $7 \times 12\text{ mm}^2$ with the angle (2θ) shifting from 10° to 30° .

2.8. Statistical analyses

Statistical analyses were carried out using the SAS program (Version 9.1, SAS Institute Inc., Cary, NC, USA) and the differences between the means were determined by the Duncan multiple test ($P < 0.05$).

3. Results and discussion

3.1. Color and opacity of the blended films

Table 1 shows that the color of the blended films, expressed as the total difference in color, depended on the type of PVA, without any particular relationship between this difference and the degree of hydrolysis of the PVA, for all the glycerol concentrations studied.

With respect to the films without plasticizer, it was observed that the PVA Celvol[®] 504 produced the most highly colored films ($P < 0.05$). However, with 25% of glycerol, in general the PVA Celvol[®] 504 produced films with the same color as the other types of PVA, except for PVA Celvol[®] 125, which produced films with the lowest value for ΔE^* ($P < 0.05$). With 45% of glycerol, the overall difference in color of the blended films was close to 2.5, although some significant difference could be observed. The increase in glycerol concentration caused a decrease ($P < 0.05$) from 3.4–4.3 for the films with no plasticizer to 2.2–2.7 for the films with 45% of glycerol. This effect of the plasticizer was probably related to a dilution effect, due to its increasing concentration in the film forming solution, since glycerol is a colorless component (Sobral et al., 2005).

Overall, the films produced in this work presented similar colors to those produced with pure gelatin and plasticized with various polyols ($\Delta E^* = \sim 3$) (Vanin et al., 2005), suggesting that PVA, irrespective of the type, did not significantly alter the color of the gelatin-based films. However, the blended films produced during this work were less colored than the films made with muscle proteins from Nile Tilapia ($\Delta E^* = 10\text{--}14$) (Paschoalick et al., 2003), but more colored than ovalbumin based films ($\Delta E^* = 1.7\text{--}2.3$) (Gennadios et al., 1996).

In addition, analyzing the results for opacity (Table 1), the films produced with the PVA with the highest degree of hydrolysis (e.g. Celvol[®] 125) were less ($P < 0.05$) opaque than those produced with a PVA with a lower degree of hydrolysis (e.g., Celvol[®] 504). However, although all the

Table 1
Effect of the PVA type and glycerol concentration (C_p) on the color difference (ΔE^*) and opacity of films based on blends of gelatin and PVA

C_p	PVA type	Degree of hydrolysis (%)	ΔE^*	Opacity
0	Celvol® 504	88	4.3 ± 0.2^a	2.0 ± 0.3^{bc}
	Celvol® 418	91.8	3.4 ± 0.3^b	1.4 ± 0.0^d
	Celvol® 425	95.7	3.3 ± 0.2^{bc}	1.7 ± 0.2^{cd}
	Celvol® 350	98.6	3.5 ± 0.5^b	1.3 ± 0.1^{de}
	Celvol® 125	99.7	3.5 ± 0.4^b	0.9 ± 0.1^{ef}
25	Celvol® 504	88	3.5 ± 0.5^b	3.1 ± 0.4^a
	Celvol® 418	91.8	3.3 ± 0.2^{bc}	2.1 ± 0.3^b
	Celvol® 425	95.7	3.2 ± 0.2^{bc}	1.5 ± 0.4^d
	Celvol® 350	98.6	3.0 ± 0.1^{bcd}	0.7 ± 0.0^{fg}
	Celvol® 125	99.7	3.0 ± 0.0^{cde}	0.7 ± 0.1^{fg}
45	Celvol® 504	88	2.7 ± 0.1^{def}	1.6 ± 0.1^{cd}
	Celvol® 418	91.8	2.4 ± 0.2^{fg}	2.0 ± 0.5^{bc}
	Celvol® 425	95.7	2.2 ± 0.3^g	0.6 ± 0.10^{fg}
	Celvol® 350	98.6	2.7 ± 0.1^{def}	0.6 ± 0.2^{fg}
	Celvol® 125	99.7	2.5 ± 0.3^{efg}	0.4 ± 0.1^g

C_p = g glycerol/100 g of macromolecules. Different letters on the same column indicates significant differences ($P < 0.05$) between the means, determined with the Duncan test, using the statistical package SAS.

films produced in this work showed very low values for opacity, and as such could be considered as practically transparent (Opacity $\rightarrow 0$), they were still more opaque than the films produced solely with pure gelatin ($Y = 0.2$ – 0.8) (Vanin et al., 2005).

3.2. Thermal properties

Overall, it can be seen that the blended films showed partially crystalline structures, and thus the DSC plots obtained during the first scan (Fig. 1) presented a glass transition (T_g) related to the amorphous part of the material, followed by two endothermic peaks related to the melting (T_m) of the crystallites. Such behavior was similar to that found by Sarti and Scandola (1995) and Chiellini et al. (2001b,c), who studied films made with PVA and collagen or gelatin, respectively, but was different from the results of films based on pure gelatin (Sobral et al., 2001; Vanin et al., 2005), which presented only one endothermic peak. According to Yakimets et al. (2007), the melting peak observed in the DSC curves of gelatin films indicated the presence of the triple-helical structure.

The DSC curves of the second scan were also typical of partially crystalline materials. Sobral and Habitate (2001) and Sobral et al. (2001), analyzing pure gelatin and films based on gelatin plasticized with sorbitol, respectively, reported that with cryogenic cooling after the first scan, the microcrystalline interactions of the macromolecules did not have enough time to occur resulting in a completely amorphous material. That is why the above authors observed no endotherm peaks on the DSC curves of the second scan, different from the results of the present work. Moreover, they observed that the T_g was displaced to lower values as compared to those of the first scan. In

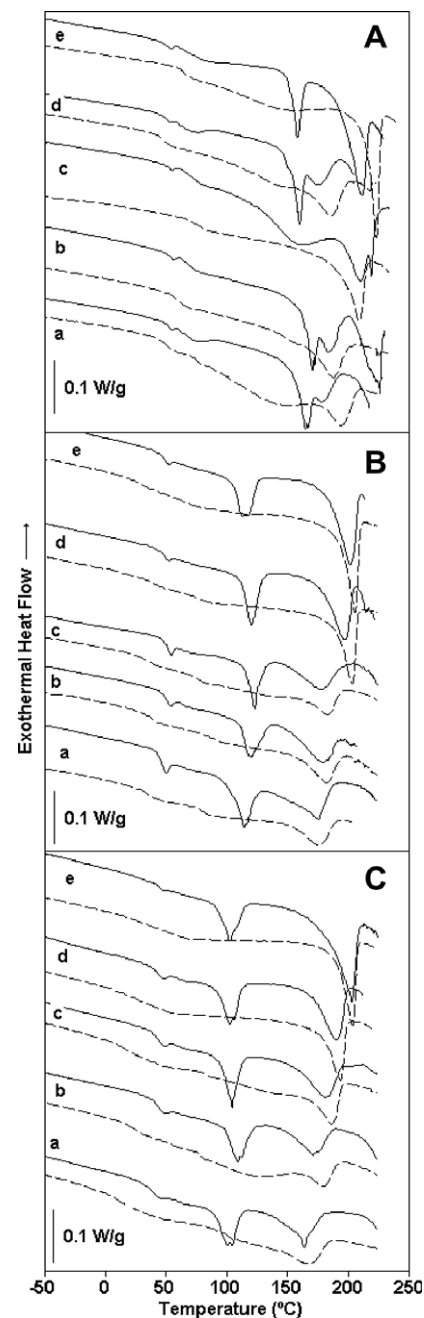


Fig. 1. Examples of DSC curves of films based on blends of gelatin and PVA with (A) 0, (B) 25 and (C) 45 g glycerol/100 g macromolecules: (—) 1st and (---) second scan. The lowercase letters in all graphics indicate the PVA type: (a) Celvol® 504, (b) Celvol® 418, (c) Celvol® 425, (d) Celvol® 350 and (e) Celvol® 125.

the present work, this trend was only observed in the case of the blended films with plasticizer (Table 2). The T_g of the blended films without plasticizer, detected in the second scan, was higher than that detected in the first one (Table 2). In addition, the increase in glycerol concentration resulted in better-defined endothermic peaks, increasing the difference between the T_m of these two peaks. All T_g values presented in Table 2 were lower than that obtained for the pure PVA films by Ramaraj (2007).

Table 2

Effect of PVA type and glycerol concentration (C_p) on the glass transitions (T_{g1} , T_{g2}) and melting temperatures (T_{m1} , T_{m2}) determined on first or second scans, of films based on blends of gelatin and PVA

C_p	PVA type	Degree of hydrolysis (%)	First scan				Second scan			
			T_{g1}	T_{g2}	T_{m1}	T_{m2}	T_{g1}	T_{g2}	T_{m2}	
0	Celvol® 504	88	53.4 ± 0.8 ^a	63.6 ± 2.4 ^a	162.3 ± 3.2 ^a	183.9 ± 8.9 ^a	60.4 ± 14.5 ^a	–	191.5 ± 4.2 ^a	
	Celvol® 418	91.8	53.2 ± 1.1 ^a	67.2 ± 3.5 ^a	167.9 ± 3.6 ^a	182.8 ± 0.8 ^a	61.5 ± 3.6 ^a	151.6 ± 0.5 ^a	187.9 ± 0.5 ^a	
	Celvol® 425	95.7	51.4 ± 2.1 ^a	69.2 ± 2.8 ^a	160.2 ± 3.2 ^a	210.0 ± 0.1 ^a	75.2 ± 0.2 ^a	–	207.6 ± 1.8 ^{ab}	
	Celvol® 350	98.6	52.8 ± 3.4 ^a	67.5 ± 10.2 ^a	164.7 ± 6.8 ^a	196.9 ± 32.0 ^a	62.4 ± 20.4 ^a	157.4 ± 36.2 ^a	202.4 ± 23.1 ^{ab}	
	Celvol® 125	99.7	51.7 ± 0.4 ^a	67.2 ± 3.9 ^a	157.2 ± 1.5 ^a	219.5 ± 11.9 ^a	73.9 ± 13.4 ^a	154.7 ± 46.7 ^a	225.4 ± 3.0 ^b	
25	Celvol® 504	88	48.2 ± 1.5 ^a	–	117.8 ± 4.7 ^a	174.7 ± 0.8 ^a	37.1 ± 3.6 ^a	82.1 ± 2.0 ^a	178.6 ± 3.9 ^a	
	Celvol® 418	91.8	49.6 ± 1.7 ^a	–	118.8 ± 1.8 ^a	176.2 ± 3.2 ^a	35.0 ± 7.9 ^a	82.7 ± 10.1 ^a	182.4 ± 0.3 ^a	
	Celvol® 425	95.7	48.9 ± 3.7 ^a	–	116.9 ± 8.9 ^a	179.8 ± 3.2 ^a	29.6 ± 7.4 ^a	82.2 ± 7.8 ^a	187.0 ± 5.6 ^a	
	Celvol® 350	98.6	48.4 ± 0.1 ^a	–	118.8 ± 1.4 ^a	197.2 ± 0.9 ^b	35.3 ± 5.9 ^a	69.4 ± 5.1 ^a	201.4 ± 2.3 ^b	
	Celvol® 125	99.7	49.0 ± 0.3 ^a	–	114.1 ± 1.1 ^a	201.2 ± 0.8 ^b	26.7 ± 2.0 ^a	65.5 ± 10.7 ^a	207.9 ± 3.7 ^b	
45	Celvol® 504	88	41.4 ± 2.5 ^a	–	104.6 ± 5.7 ^a	164.7 ± 1.2 ^a	22.8 ± 13.5 ^a	87.8 ± 20.0 ^a	170.5 ± 4.9 ^a	
	Celvol® 418	91.8	43.4 ± 1.9 ^a	–	104.8 ± 6.0 ^a	171.0 ± 0.7 ^b	23.7 ± 2.1 ^a	®	176.7 ± 4.1 ^a	
	Celvol-425	95.7	43.8 ± 0.9 ^a	–	105.3 ± 1.1 ^a	182.7 ± 3.7 ^c	23.7 ± 9.6 ^a	84.4 ± 4.1 ^a	188.7 ± 2.8 ^b	
	Celvol® 350	98.6	45.2 ± 1.7 ^a	–	104.3 ± 1.7 ^a	191.2 ± 1.1 ^d	24.5 ± 2.0 ^a	–	196.5 ± 4.0 ^{bc}	
	Celvol® 125	99.7	43.3 ± 0.3 ^a	–	104.2 ± 1.9 ^a	204.5 ± 2.8 ^c	34.1 ± 7.2 ^a	60.4 ± 12.5 ^a	205.6 ± 3.0 ^c	

Note: (–) Value not observed; C_p = g of glycerol/100 g of macromolecules (gelatin + PVA); different letters for the same C_p , represent significant differences ($P < 0.05$) between averages, determined with the Duncan test, using the statistical package SAS.

In the case of films with no plasticizer, two T_g signals were also observed (Fig. 1), the second T_g occurring at least 10 °C above the first T_g (Table 2). Sarti and Scandola (1995) also observed two T_g s in films based on PVA and gelatin, with no addition of plasticizer. However, in the present work, the addition of glycerol favored miscibility between the gelatin and the PVA, such that under these circumstances, a second T_g could not be observed. All these behaviors: that is the occurrence of two endothermic peaks in the DSC curves of the first scan of all blended films; the occurrence of two T_g s in DSC curves of the first scan of films blended without plasticizer; and the detection of an endothermic peak in DSC curves of the second scan of practically all the blended films, could be an indication that the gelatin and PVA did not constitute a fully miscible system (Sarti and Scandola, 1995). Similarly, Wang et al., (2007) also observed phase separation between the PVA and a complex polysaccharide (carboxymethyl-chitosan) when this last component was in high content.

Considering that the values of the first T_m of the blended films (Table 2) were consistent with those reported by Vanin et al. (2005) for gelatin films with 10% of glycerol (~125 °C), and that the value of the second T_m was similar to those found by Zhai et al. (2002) for PVA gels (~222 °C) and by Chiellini et al. (2001b,c) for pure PVA (191 °C), it could be suggested that the first melting was associated with a fraction rich in gelatin, whereas the second endotherm was due to a fraction richer in PVA, or at least to a situation where the PVA was in excess with respect to the gelatin.

Despite all the complexity of the behaviors discussed above, for the same plasticizer concentration, there was practically no effect of the PVA type on the thermal properties of the blended films ($P > 0.05$) (Table 2). On the other hand, as expected in the case of glycerol, an increase

in its concentration shifted all the thermal properties to lower values (Table 2). This behavior, called the plasticizer effect, is well known in the field of films based on biopolymers (Coupland et al., 2000; Sothornvit and Krochta, 2001).

3.3. Crystallinity

The films based on blends of gelatin and PVA produced in the present work were subjected to X-ray diffraction (XRD) analyses. Some typical examples of the results obtained from these analyses are presented in Fig. 2. Overall, irrespective of the PVA type and plasticizer concentration, the XRD patterns obtained were typical of partially crystalline materials, with a characteristic peak at $2\theta = 20^\circ$, which is consistent with the results observed in the DSC studies (Fig. 1), and agreeing with the results obtained by Kaczmarek and Podgórski (2007) working with pure PVA films. Similar XRD patterns can be observed in the studies of Berge and Sobral (2007) with pure gelatin films, and in that of Xiao et al. (2000) for pure PVA films. Pal et al. (2006), studying the crystallinity of films obtained from blends of gelatin and PVA, observed similar diffractograms for films based on pure gelatin ($2\theta = 20^\circ$) or pure PVA ($2\theta = 22.5^\circ$), but observed three prominent peaks at $2\theta = 11^\circ$, 17° and 25° for the blended films. Yakimets et al. (2005, 2007), studying the crystallinity of pure gelatin films, also observed a characteristic peak at $2\theta = 7-8^\circ$. According to Yakimets et al. (2007), this peak corresponded to the presence of a small amount of triple-helical structure, characteristic of the rod-like triple helices of collagen, 300 nm long and 1.5 nm wide.

In a way, it was to be expected that the blended films from gelatin and PVA would be partially crystalline materials, because the films made with both pure gelatin and

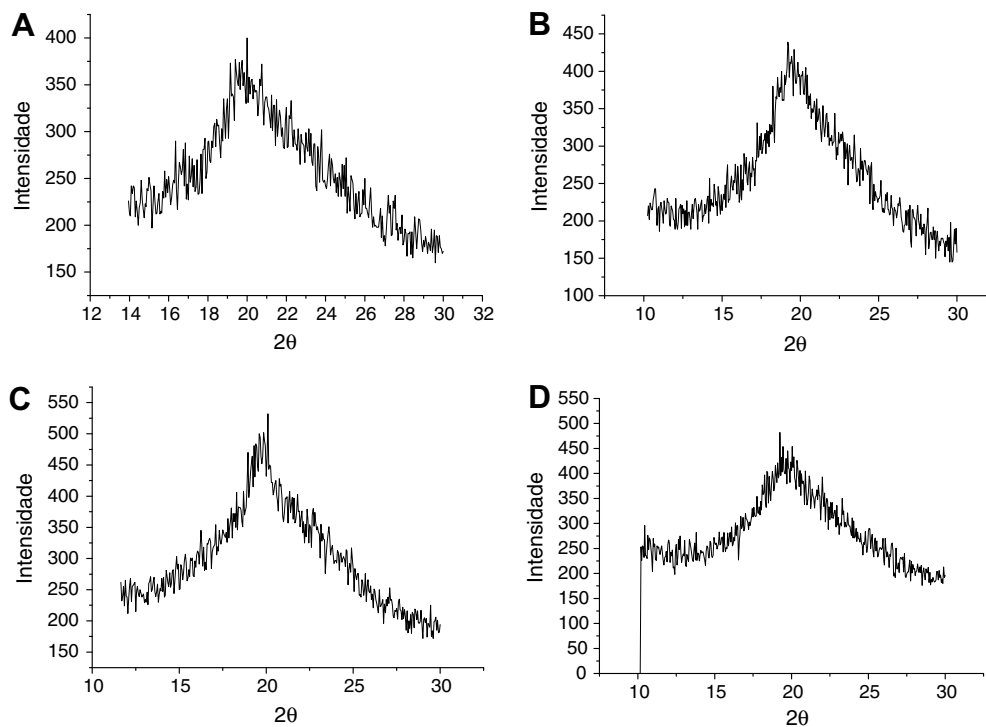


Fig. 2. Examples of patterns obtained by X-ray diffraction of the films based on blends of gelatin and (A,B) PVA Celvol® 418 and (C,D) PVA Celvol® 425 and with (A,C) 25 g and (B,D) 45 g glycerol/100 g macromolecules.

pure PVA, showed partially crystalline structures. PVA has a flexible structure, which favors close molecular packing and crystallization (Xiao et al., 2000), and the crystallization of gelatin is due to its tendency to re-naturation (Yakimets et al., 2005). Xiao et al. (2000) observed that films made with blends of PVA and konjac glucomannan presented partially crystalline structures, even though this biopolymer is a completely amorphous material. In general, a decrease in the intensity of the crystallinity peaks

(at $2\theta = 20^\circ$) of the films produced with PVA with the highest degree of hydrolysis, was observed in this work.

3.4. Mechanical properties

The mechanical properties of the films based on blends of gelatin and PVA depended on the type of PVA used, with no particular relationship between these properties and the degree of hydrolysis of the PVA, but depending

Table 3

Effect of the PVA type and the glycerol concentration (C_p) on the tensile strength (TS), elongation at break (EB) and elastic modulus (EM) of films based on blends of gelatin and PVA

C_p	PVA type	Degree of hydrolysis (%)	TS (MPa)	EB (%)	EM (MPa)
0	Celvol® 504	88	21.8 ± 2.6^{cd}	8.0 ± 1.3^g	10.3 ± 0.7^b
	Celvol® 418	91.8	38.0 ± 13.4^a	14.3 ± 3.1^g	15.2 ± 4.8^a
	Celvol® 425	95.7	25.4 ± 5.5^{bc}	37.0 ± 6.3^f	8.2 ± 1.8^b
	Celvol® 350	98.6	24.7 ± 6.6^{bc}	44.0 ± 6.5^f	15.3 ± 7.8^a
	Celvol® 125	99.7	27.8 ± 4.9^b	56.5 ± 9.9^e	10.3 ± 2.1^b
25	Celvol® 504	88	15.9 ± 4.4^h	36.6 ± 15.0^b	4.2 ± 2.7^d
	Celvol® 418	91.8	19.0 ± 1.5^{gh}	99.7 ± 1.9^a	1.6 ± 0.1^d
	Celvol® 425	95.7	23.2 ± 1.9^{fg}	91.4 ± 12.5^a	2.0 ± 0.2^d
	Celvol® 350	98.6	20.4 ± 0.9^{fg}	104.8 ± 9.8^a	1.9 ± 0.3^d
	Celvol® 125	99.7	22.1 ± 2.4^{fg}	92.5 ± 3.9^a	2.0 ± 0.4^d
45	Celvol® 504	88	5.7 ± 0.4^{eg}	106.1 ± 6.7^f	0.4 ± 0.1^c
	Celvol® 418	91.8	10.3 ± 1.6^{de}	168.0 ± 6.1^{bcd}	0.3 ± 0.1^{cd}
	Celvol® 425	95.7	11.9 ± 1.7^{bcd}	164.3 ± 13.9^d	0.4 ± 0.1^{cd}
	Celvol® 350	98.6	13.2 ± 2.0^{cde}	176.6 ± 10.6^b	0.5 ± 0.1^{cd}
	Celvol® 125	99.7	12.8 ± 1.0^{cd}	172.6 ± 27.9^{cd}	0.6 ± 0.1^{cd}

Note: C_p = g of glycerol/100 g of macromolecules (gelatin + PVA). Different letters on the same column indicates significant differences ($P < 0.05$) between the means, determined with the Duncan test, using the statistical package SAS.

on the glycerol concentration. In the case of the films without plasticizer, the film which showed the highest tensile resistance ($P < 0.05$) was the one produced with PVA Celvol® 418 (DH = 91.8%), with a tensile strength of 38 MPa (Table 3). However, with glycerol, the above-mentioned PVA and the PVA Celvol® 504 (lowest DH = 88%) produced the least resistant films of all the PVA types, amongst which no significant differences were observed.

With respect to the rigidity of the films blended without plasticizer, the highest values for the elastic moduli were those for the films produced with PVA Celvol® 418 and 350. The presence of glycerol seems to have interfered with any possible effect of the DH of the PVA studied, there being no significant difference between the values obtained for all the films. Similarly, Chiellini et al. (2001a) observed that an increase in the plasticizer concentration allowed one to equalize the resistance (TS values) and rigidity (EM values) of PVA films containing sugar cane bagasse or orange and apple pomace.

With respect to the elongation at break (EB) of the films blended without plasticizer, the PVA Celvol® 125 produced the films with the highest ($P < 0.05$) EB values (56%) (Table 3). The lowest ($P < 0.05$) EB values were presented by the films based on PVA Celvol® 418 (8%) and 504 (14%). With 25% and 45% of glycerol, only the PVA® Celvol 504 provided films with low elasticity. It should be noted that this behavior is not a simple effect of plasticization, i.e. due to an increase or decrease in macromolecular mobility caused by the presence of PVA in the gelatin matrix. If this was the case, the films that presented the highest TS would have shown the lowest EB values, and vice versa (Thomazine et al., 2005; Vanin et al., 2005), but this was not the case, as seen in the data presented in Table 3.

Analyzing the effect of the glycerol used as plasticizer, it can be observed that the increase in its concentration caused a reduction in the resistance (decrease in TS) and stiffness (decrease in EM) and an increase in the flexibility (increase in EB) of the films. This behavior, typical of the plasticization phenomenon, is a consequence of the increase in molecular mobility with the increase in plasticizer concentration, as discussed previously (see thermal properties section). Similar behavior can be observed in the work of Chiellini et al. (2001a).

Besides the interactions between the gelatin and PVA, the mechanical properties of the blended films should be related to the degree of crystallinity of the films, which, in turn, is more associated with the molecular weight than with the degree of hydrolysis of the PVA (Mallapraga and Peppas, 1996). However, the crystallinity study carried out in this work was qualitative, and it was therefore practically impossible to mathematically model these characteristics. However, it is well known that the glass transition of partially crystalline polymers is directly influenced by the degree of crystallinity of the material. Thus, by comparing the results for TS (Table 3) with the respective T_g values obtained in the first scan (Table 2), which actually corre-

spond to the state of the films subjected to the tensile tests, it can be observed that there was a linear relationship between TS and T_g (Fig. 3). This relationship can be expressed as Eq. (3), whose parameters were obtained by linear regression ($R^2 = 0.880$; $P < 0.0001$) using the software Microcal™ Origin™ V.5.0.

$$TS = 1.6T_g - 58.3 \quad (3)$$

where TS is the tensile strength (MPa) and T_g is the glass transition temperature (°C) of the blended films.

This linear relationship between the mechanical properties as a function of the glass transition of films based on biopolymers was previously observed by Honary and Orafi (2002), studying the effect of different molecular weight polyethylene glycols on the mechanical properties of hydroxypropylmethylcellulose films, and by Vanin et al. (2005) for films based on pure gelatin plasticized with glycerol, propylene glycol or diethylene glycol. However, Moore et al. (2006) showed that the TS of films based on feather keratin and plasticized with glycerol, increased with the T_g , following a parabolic trend.

The values for tensile strength and elongation at break of the films based on blends of gelatin and PVA produced in the present work, were higher than those determined in various other works on films based on blends of PVA and polysaccharides, such as films made from methylated-corn starch and PVA, irrespective of the PVA type used (Guohua et al., 2006); those made from gellan and PVA (Sudhamani et al., 2003) and also films produced with corn starch and PVA and containing natural fiber as fillers (Chiellini et al., 2001a). In addition, Chiellini et al. (2001a) produced films from blends of waste gelatin and PVA and found values of $TS \cong 8$ MPa and $EB \cong 140\%$, which are similar to those of the blended films produced with 45% glycerol in the present research (Table 3). It is also worth noting that the films produced without plasticizer in the present work, were more resistant and less stretchable than those produced by the above-mentioned authors.

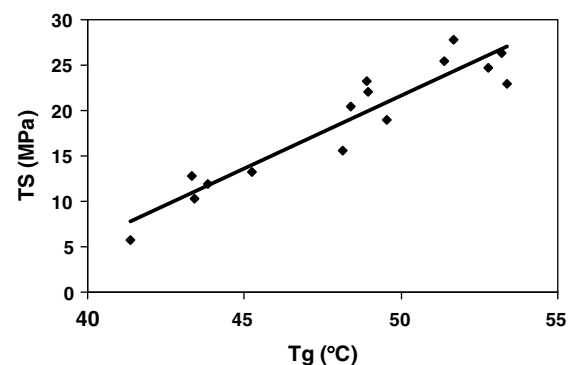


Fig. 3. Tensile strength (TS) as a function of the glass transition temperature (T_g) of films based on blends of gelatin and five types of PVA and with 0, 25 and 45 g of glycerol/100 g of macromolecules.

4. Conclusions

All the PVA types tested produced good films in blends with the gelatin. All the blended films were macroscopically homogeneous. However, in Physical–chemical terms, these films did not necessarily constitute homogeneous systems, since phase separation was observed throughout the DSC curves.

The films produced with the five types of PVA involved were practically colorless and without opacity. Overall, the physical properties studied in this work were affected by the type of PVA, but with no direct relationship with the respective degree of hydrolysis.

Also, the mechanical properties of the blended films could not be correlated with the respective degree of hydrolysis of the PVA type involved. Nevertheless, these properties were linearly related with the glass transition temperature of the blended films, which, in turn, was strongly affected by the crystallinity of the material and by the plasticizer concentration.

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