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PROPERTIES OF CHEMICALLY MODIFIED GELATIN FILMS

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Abstract - Edible and/or biodegradable films usually have limited water vapor barriers, making it difficult to use them. Thus, the objective of this work was to evaluate the effect of a chemical reticulation treatment with formaldehyde and glyoxal on the mechanical properties, water vapor permeability, solubility and color parameters of gelatin-based films. Formaldehyde and glyoxal were added to the filmogenic solution in concentrations ranging from 3.8 to 8.8 mmoles/100 mL of filmogenic solution and 6.3 to 26.3 mmoles/100 mL of filmogenic solution, respectively. The treatments caused a reduction in permeability to water vapor and in solubility. Only the treatment with formaldehyde caused a significant increase in rupture tension for concentrations above 6.3 mmoles/100 mL of filmogenic solution. Scanning electron microscopy indicated a loss of matrix orientation due to the chemical reticulation treatment.
Keywords: Films gelatin formaldehyde glyoxal.

INTRODUCTION

Edible and/or biodegradable films are produced from macromolecules, including proteins, that are able to form continuous and cohesive matrices where the protein-protein and protein-other component interactions directly influence film characteristics. The mechanical barrier characteristics are affected by environmental conditions and most protein-based films have limited water vapor barriers making it difficult to use them.

Gelatin is a protein that is widely used in the pharmaceutical and food industries, and it is produced on a large scale at relatively low prices. Due to its functional properties it has been utilized in the production of edible and/or biodegrable films (Sobral et al., 2001); however like the majority of protein-based films, it has a limited barrier to water vapor.

The increase in degree of cross-linking may cause a reduction in water vapor permeability through the reduction in diffusivity and an improvement of mechanical characteristics (Cuq, 1996). Chemical modifications, aiming at an increase in the degree of protein cross-linking depend on the reactivity of the protein constituents, the specificity of the modifing agent (Wong and Wong, 1992), the amino acid composition, the reactivity of amino acid and the tridimensional structure of the protein molecule (Means and Feeney, 1971). Generally, chemical reactivity of proteins depends on the side chain, the amino acid composition and the free amino and carboxyl groups (Means and Feeney, 1971). The most reactive protein groups are serine (primary -OH), hydroxiproline (secondary -OH), threonine (secondary -OH), tyrosine (phenolic -OH), aspartic acid (-COOH), glutamic acid (-COOH), lysine ($-NH_2$) and arginine ($-C(:NH).NH_2$) (Finch, 1983).

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Alterations in charge on the protein surface affect the solubility and extent of protein-protein interactions and could be related to the film formation properties (Phillips et al., 1994). The hydrocolloids currently used in edible and/or biodegradable film formation, gelatin stands out for its good chemical reactivity given the number and variety of reactive groups on its chain (Clark and Courts, 1977). Anhydrides, aziridines, epoxydes, aldehydes and hexones have been used for gelatin modification (Clark and Courtis, 1977), with formaldehyde being one of the most frequently used reagents in gelatin reticulation for nonfood uses. Dialdehydes, especially glutaraldehyde and glyoxal, are also frequently used for this purpose (Clark and Courts, 1977; Finch, 1983). Formaldehyde, glyoxal and glutaraldehyde react with the amino acid side chain, particularly with the lysine ε-NH_2 group, forming bonds similar to those in the formation of the Schiff base (Fraenkel-Conrat et al., 1947).

Reactions between formaldehyde and gelatin (Moll et al., 1974) with pH ranging from 6 to 7, were followed by an increase in molecular weight and viscosity and a decrease in water absorption capacity, where cross-linking seemed to interfere with the natural alignment of molecules, perhaps leading to disturbances in the helicoidal formation (Moll et al., 1974; Coopes, 1974). Decreases in solubility and resistance in the intestinal tract were observed by Pina et al. (1996) for gelatin capsules modified with formaldehyde. Chemical modifications using formaldehyde, glutaraldehyde and gossypol in the production of biofilms based on proteins extracted from cottonseed indicated a significant decrease in solubility and an increase in puncture force (Marquié et al., 1995), suggesting a better filmogenic matrix structuring. The use of formaldehyde reactions suggests that the cross-linking drastically reduces chain mobility and makes the ε-lysine groups inaccessible. Reactions with formaldehyde led to the formation of more resistant films, indicating that these films may react with other groups besides ε-lysine, producing a more cohesive protein chain (Marquié et al., 1997). Adding an excessive amount of glyoxal to the filmogenic solution it was observed that part of the reagent reacts with the lysine group and the other remains in the free form, causing a decrease in the cohesion of the polymeric matrix by reducing the intermolecular forces in the protein chain and consequently in film resistance (Marquié et al., 1997). Bonds formed between glutaraldehyde and protein result in a larger decrease in rupture strength in protein-based films extracted from cottonseed flour due to the decrease in the intermolecular forces (Marquié et al., 1997). For soybean protein films cross-linked with formaldehyde (through vaporization), Rhim et al. (2000) observed that the treatment did not alter tensile strength; however, they verified a significant reduction in the elongation and the solubility of the films in several solvents. On the other hand, for gluten films modified with formaldehyde, Micard et al. (2000) verified a increase in the tensile and Young's moduli and a reduction in solubility in water in relation to the films untreated. Studying the influence of different cross-linking treatments (glutaraldehyde, dimethyl suberimidate and dimethyl 3,3'-dithiobispropionimidadteglutaraldehyde) of collagen membranes, Charulatha and Rajaram (2003) observed that the chemical treatment caused an increase in thermal stability and tensile strength. The objective of this study was to evaluate the effect of changes in the polymeric matrix through the addition of reticulant agents on solubility in water, water vapor permeability, color parameters, morphology and mechanical properties of gelatin-based modified films in relation to films that had not been chemically modified.

MATERIALS AND METHODS

Materials

The protein source used to produce the films was bovine hide type B gelatin (bloom = 270.0 g; particle size < 0.60 mm; protein content = 88.92 ± 0.02%; ash = 0.78 ± 0.01%; moisture content = 10.3 ± 0.1%) donated by Leiner Davis Gelatin Brazil (São Paulo, Brazil); formaldehyde solution (HCHO, 35%), glyoxal solution (HCOCHO, 40%) and glycerol were obtained from Merck (São Paulo, Brazil). Magnesium chloride ($Mg(NO_3).6H_2O$) was purchased from Sinth (São Paulo, Brazil).

Production of Films

The following films were produced: NF – native film (without modification); FMF – formaldehyde-modified film and GMF – glyoxal-modified film. Concentrations of 3.3, 6.3, 8.8 mmole/100 mL of filmogenic solution of formaldehyde and concentrations of 6.3, 8.8, 11.3, 17.5 and 26.3 mmole/100 mL of filmogenic solution of glyoxal were used. All the films contained 10 g of gelatin/100 g of filmogenic solution and 4.5 g of glycerol/100g of filmogenic solution.

The films were prepared by gelatin hydration (25 °C, 60 min), gelatin solubilization in distilled water using a mechanical shaking bath (50 °C, 15 min) and addition of glycerol and reticulant agents (formaldehyde and glyoxal). After solubilization and addition of plasticizer and reticulant agents, the solution was maintained under mechanical shaking for a period of 15 min at 50°C and then spread on

acrylic plates (9.0 cm diameter) and dried at room temperature (24-48 h). Film thickness (average of 15 random measures) was kept constant through the mass/area relation and was determined using a digital micrometer (Mitutoyo Corp., Tokyo, Japan). Thickness was kept constant at 0.080 ± 0.004 mm. Before analysis, the samples were conditioned for 72 h in a desiccator containing $MgNO_3$-saturated saline solution (50 ± 3% RH; 25 ± 2°C). All film characterizations were performed at temperatures from 24 to 26 °C and relative humidities of 50 to 60 % RH.

Soluble Matter

The percentage of water-soluble matter (SM) was determined according to the method proposed by Cuq et al. (1997). Samples (2.0 cm in diameter) were immersed in 50 mL distilled water and the system was kept under slow mechanical shaking (25 °C, 24 h). Initial mass was determined from the sample moisture content. After this period, the samples were removed from the solution and dried in a forced air oven (105 °C, 24 h). Determinations were done in triplicate.

Water Vapor Permeability

The water vapor permeability (WVP) of the films was determined gravimetrically in triplicate according to method ASTM E96-95 (ASTM, 1995). The cells were filled with silica gel and the film was fixed with paraffin. The cells were packed in desiccators containing $MgNO_3$-saturated saline solution (50 ± 3 % RH). The desiccators were incubated under electronic temperature control (BOD; Tecnal, TE-390) at a temperature of 25 ± 2 °C. The RH gradient was 50:0 % (outside RH: inside RH). The cells were weighed daily (± 0.0001g) until a constant weight was achieved. Water vapor permeability was calculated using Equation 1:

$$WVP = \frac{w}{t}\frac{x}{AP_o(RH_1 - RH_2)} \quad (1)$$

Where w/t is the change in mass (flux, g/h), x is the film thickness (mm), A is the area of the film surface exposed to permeant (m^2), P_0 is the vapor pressure of pure water (KPa) and ($RH_1 - RH_2$) is the relative humidity gradient used in the experiment. At 25°C, P_o is 3.159 KPa.

Mechanical Properties

Five determinations of the tensile strength (TS) and elongation (E) of the films obtained with a texturometer model TA.XT2 (TA Instruments, New Castle, U.S.A.) according to method ASTM D882-95 (ASTM, 1995), were averaged. Initial distance of separation and velocity were fixed at 50 mm and 1 mm/s, respectively. Tensile strength was calculated by dividing the maximum force for film rupture by the area of the transverse section, and elongation (E) was calculated from the ratio of increase in length to original length (Δl/lo), expressed as a percentage.

Color Parameters

The total difference in color (ΔE^*), croma a*, croma b*, L* and opacity were determined in triplicate using a colorimeter COLORQUEST II (Hunterlab, Virginia). The films were superposed on a white standard (L* = 84.67, a* = -0.55 and b* = 0.68) and the total difference in color was determined according to Equation 2, where values of ΔL*, Δa* and Δb* represent the difference between the color parameter of the sample and the color parameter of the white standard (Jangchud and Chinnan, 1999).

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

Using the equipment software, opacity was calculated as the relationship between the opacity of the film superposed on the black standard (P_{black}) and the film superposed on the white standard (P_{white}), according to Equation 3.

$$\text{Opacity} = \frac{P_{black}}{P_{white}}100 \quad (3)$$

Determination of Amino Acid Content of the Gelatin

The amino acid content of the gelatin was determined according to Spackman et al. (1958) by acid hydrolysis (HCl, 6 N) in an ion-exchange column in a post-column reaction with ninhydrin, using a liquid chromatograph DX300 (Dionex, Sunnyvale, U.S.A.).

Scanning Electron Microscopy

The films were equilibrated in desiccators containing silica gel (25°C) for a period of seven days and then fractured and fixed in stubs using copper conducting adhesive tape. The samples were then conditioned at 50 ± 3 % RH, 25± 2°C for 48 h and subsequently coated with gold in a sputter coater model SCD 050 (Bal-Tec, Liechtensten, Austria) at 25 °C and a pressure of $2x10^{-5}$ Torr for 180 s. The coated samples were observed under a scanning electron microscope model JSM- 5800LV (Japan Electron Optics Limited, Tokyo, Japan) at 10 kV.

Statistical Analysis

Statistical analyses were carried out using the SAS program (Version 6.8, SAS Inc.) and the differences between the means were determined with the Tukey multiple test.

RESULTS AND DISCUSSION

Barrier Properties and Soluble Matter

Formaldehyde-modified films (FMF) showed a significant reduction in water vapor permeability in relation to native films (NF) at all concentrations tested (Table 1). For glyoxal-modified films, the reduction in permeability was only observed for concentrations above 11.3 mmoles/100 mL of filmogenic solution. Formaldehyde reticulation was possible at concentrations below 8.8 mmoles/100 mL of filmogenic solution, above which, instant gelation of the filmogenic solution was observed.

Although reticulant reagents have been overused in relation to the available lysine concentration (Table 2), formaldehyde may have had greater access to lysine or to other reactive groups such as Cys and Hys, according to Galietta et al. (1998), resulting in an increase in the degree of reticulation, greater polymeric matrix structuring and a consequent reduction in permeability to water vapor. For soybean protein-based films modified with formaldehyde, Ghorpade et al. (1995) observed a reduction in water vapor permeability from 0.84 to 0.79×10^{-9} g/m.s.Pa in relation to the unmodified film. Micard et al. (2000) also observed a reduction in water vapor permeability from 7.6 to 6.7×10^{-12} g mol/m.s.Pa for gluten protein-based films treated with formaldehyde in relation to unmodified films.

Table 1: Water vapor permeability (WVP) as a function of concentration (C) of reticulant agent for native films (NF), formaldehyde-modified films (FMF) and glyoxal-modified films (GMF) at 25°C.

Film	C (mmoles/100 mL of filmogenic solution)	WVP (g.mm/h.m^2.kPa)
NF	0.0	0.198 ± 0.003^{a}
FMF	3.8	$0.170 \pm 0.002^{c,d}$
	6.3	$0.169 \pm 0.009^{e,d}$
	8.8	0.155 ± 0.008^{e}
GMF	6.3	0.193 ± 0.007^{a}
	8.8	0.186 ± 0.005^{a}
	11.3	0.181 ± 0.006^{b}
	17.5	0.179 ± 0.003^{b}
	26.3	$0.174 \pm 0.007^{b,c}$

Note: different letters represent significant differences ($p < 0.05$) between averages obtained with the Tukey test.

Table 2: Amino acid content of type B gelatin used.

Amino Acid	g AA/100g gelatin
Aspartic acid	7.46 ± 0.12
Threonine	2.11 ± 0.06
Serine	3.62 ± 0.06
Glutamic acid	11.28 ± 0.33
Proline	12.52 ± 0.23
Glycine	32.63 ± 0.97
Alanine	10.88 ± 0.29
Valine	2.18 ± 0.06
Methionine	0.42 ± 0.10
Isoleucine	1.44 ± 0.06
Leucine	3.00 ± 0.06
Tyrosine	0.40 ± 0.001
Phenylanine	1.99 ± 0.05
Lysine	3.46 ± 0.11
Ammonium	0.59 ± 0.04
Histidine	0.77 ± 0.01
Arginine	9.90 ± 0.28

The solubility (Figure 1) of chemically modified films (FMF, GMF) was significantly lower than the solubility of native films (NF, solubility = 31.1 %) within the concentration range evaluated. Formaldehyde reticulation was possible at concentrations below 8. 8 mmoles/100 mL of filmogenic solution, above which, instant gelation of the filmogenic solution was observed. For gelatin-based formaldehyde-modified films (without plasticizer), Moll et al. (1974) observed that the cross-linking between the gelatin molecules is short term in the first stage; however, far-off molecules do not react instantly, and that reaction is long term. Thus, higher initial concentrations of the reticulant agent may have improved access to reactive groups, causing a reduction in solubility with the increased concentration of reticulant agent. Similar previously obtained results show the effect of formaldehyde concentration on the percentage of soluble matter in modified cottonseed protein-based films (Marquié et al., 1997), where an increased formaldehyde concentration caused a higher reduction in solubility. A reduction in solubility from 22 to 17 % was verified for gluten-based films as a result of formaldehyde treatment (Micard et al., 2000). Galietta et al. (1998) also observed a reduction from 43.0 to 36.0 % for formaldehyde-treated whey protein-based films.

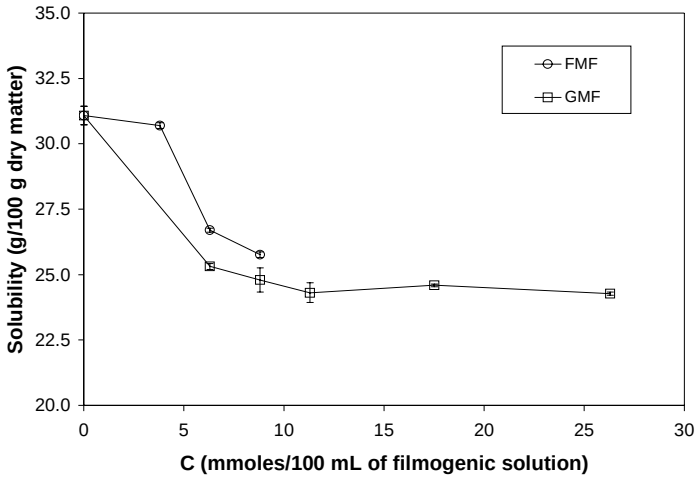

Figure 1: The effect of concentration of reticulant agent (formaldehyde or glyoxal) on the water solubility (g/100 g dry matter) of gelatin-based films.

Mechanical Properties

The results indicated a significant increase in tensile strength with the increase in formaldehyde concentration above 6.3 mmoles/100 mL of filmogenic solution in relation to unmodified films and glyoxal-modified films, as observed in Table 3.

With regard to the glyoxal treatment (Table 3), it was also verified that the increase in glyoxal concentration up to 8.8 mmoles/100 mL of filmogenic solution initially caused an increase in tensile strength in relation to the native film, followed by a slight decrease for concentrations above 11.3 mmoles/100 mL of filmogenic solution. With an excessive amount of glyoxal, one may ascertain that only part of the glyoxal is involved with cross-linking and the other part should be free in the polymeric matrix, probably causing a decrease in cohesion (Marquié et al., 1997). The type of bond formed (length, spatial arrangement, etc) is probably responsible for the lower the degree of molecular orientation and less cohesion than what was found with formaldehyde, which is a smaller molecule. An increase in tensile strength with an increase in glyoxal concentration followed by a decrease was also reported for cottonseed-flour protein based films (Marquié et al., 1997).

With the exception of concentrations of 3.8 and 6.3 mmoles/100 mL of filmogenic solution the elongation of films treated with formaldehyde and glyoxal, respectively, did not vary significantly. The results observed may be related to morphological alterations, since the increase in the degree of cross-linking of the polymeric matrix as a function of the increase in the concentration of reticulant agent, may make gelatin renaturation into characteristic collagen structures difficult (Babin and Dickinson, 2001). For gelatin-based films modified by glutaraldehyde, Bigi et al. (2000) observed a significant increase in tensile strength from 1 to 3.5 MPa with a decrease in elongation from 40 to 10 % as the glutaraldehyde concentration increased from 0.05 to 2.5 %. On the other hand, using soybean-isolate protein-based films modified with glutaraldehyde, Rhim et al.

(2000) verified no significant variations in the tension strength of the modified film (8.3 MPa) in relation to the unmodified film (8.2 MPa); however, the elongation increased significantly from 30 to 100 %.

The reaction with formaldehyde resulted in films with tensile strengths higher than the tensile strength observed for the glyoxal-treated film. This may be related to the reticulation capacity of formaldehyde. Studying the effect of the concentration of different reticulant agents (formaldehyde, glyoxal and glutaraldehyde) on the rate of cross-linking, Robinson (1964) verified that regardless of the concentration used, the time involved in gelation of the aqueous solution of gelatin treated with glutaraldehyde is considerably shorter than the time observed for formaldehyde and glyoxal under the same conditions as a function of the possibility of cross-linking by both reactive groups in this reagent. However, for modified cottonseed protein-based films, Marquié et al. (1997) observed that the formaldehyde-modified films had higher tensile strengths than glutaraldehyde- and glyoxal-treated films. The increase in tensile strength in modified films due to the increase in formaldehyde concentration was also observed by Marquié et al. (1995, 1997) for cottonseed protein-based films and by Usha and Ramasami (2000), for colagen fibers. Generally, the mechanical properties of reticulated films seem to be a function of the spatial arrangement after reticulation, and thus, an increase in concentration of the reticulant agent may have a positive or a negative effect on the cohesion of the polymeric matrix formed.

Table 3: Tensile strength (TS) and elongation (E) as a function of concentration (C) of reticulant agent for native films (NF), formaldehyde-modified films (FMF) and glyoxal-modified films (GMF).

Film	C	TS (MPa)	E (%)
NF	0.0	15.12 ± 0.05^{b}	39.24 ± 0.80^{b}
FMF	3.8	14.42 ± 0.14^{b}	42.92 ± 0.28^{a}
	6.3	19.27 ± 0.55^{c}	38.19 ± 0.44^{b}
	8.8	23.10 ± 1.31^{a}	37.30 ± 1.94^{b}
GMF	6.3	15.32 ± 0.12^{b}	41.24 ± 0.34^{a}
	8.8	18.17 ± 0.40^{c}	37.30 ± 5.23^{b}
	11.3	17.67 ± 2.04^{c}	36.16 ± 2.95^{b}
	17.5	17.42 ± 1.57^{c}	38.59 ± 2.81^{b}
	26.3	14.97 ± 0.97^{c}	38.13 ± 0.44^{b}

Note: different letters in the same column represent significant differences ($p < 0.05$) between averages obtained with the Tukey test, C = mmoles of formaldehyde or glyoxal/100 mL of filmogenic solution.

Color Parameters

The results indicated (Table 4) that the treatments with formaldehyde and glyoxal caused significant alterations of the film color parameters.

The formaldehyde-modified films had a significant increase in the parameter luminosity (L^*), explaining visual observation of the shine. The values of the chromatic coordinates a^* and b^* were higher than those for the unmodified film, corresponding to an increase in the yellow color. Visually, however, this effect was not significant. For the parameter opacity, no significant difference was observed between the formaldehyde-modified film and the native film. Micard et al. (2000), observed no alterations of the color parameters when formaldehyde-treated gluten films were produced, although, in this study, the formaldehyde had been boiled off during conditioning in hermetic vessels containing formaldehyde/ethanolic solution instead of being added directly to the filmogenic solution. The variations in the color parameters were confirmed by the ΔE^* values, although significant variations in the color parameters with the increase in formaldehyde concentration were not observed (Table 4). For the glyoxal, however, an increase in its concentration caused significant decreases ($p < 0.05$) in the L^* value and significant increases in a^* and b^* in relation to both the native film (NF) and the formaldehyde-modified films (FMF), indicating an increase in intensity of the yellow color. The glyoxal-modified films also had a higher opacity than the native film and the formaldehyde-modified film (Table 4). The differences observed were visually perceptible due to the intense yellow color observed when glyoxal was used to modify films. The increase in the intensity of the yellow color was reported for glutaraldehyde-modified gelatin microcapsules (Akin and Hasirci, 1995), and these results are related to the formation of CH = N bonds between the protein-free amino groups and the glutaraldehyde. The products of the gelatin modification with glyoxal also involve the formation of this type of bonds, wich may have been responsible for the more intense yellow color in the glyoxal-modified films.

Table 4: Color parameters (L*, a*, b*, ΔE* and opacity) of native and chemically modified films.

Film	C	L*	a*	b*	ΔE*	Opacity
NF	**0.0**	84.05 ± 0.3^{b}	-0.49 ± 0.04^{a}	1.54 ± 0.01^{g}	-	16.85 ± 0.08^{c}
	3.3	87.42 ± 0.14^{a}	-0.83 ± 0.03^{c}	1.76 ± 0.10^{e}	3.59 ± 0.10^{e}	16.81 ± 0.11^{c}
FMF	**6.3**	87.50 ± 0.05^{a}	-0.88 ± 0.07^{c}	1.89 ± 0.08^{e}	3.61 ± 0.03^{e}	16.79 ± 0.16^{c}
	8.8	87.27 ± 0.19^{a}	-0.88 ± 0.07^{c}	2.01 ± 0.04^{f}	3.44 ± 0.10^{e}	16.87 ± 0.27^{c}
	6.3	84.32 ± 0.15^{b}	-1.16 ± 0.04^{a}	14.15 ± 0.69^{d}	12.14 ± 0.38^{d}	17.47 ± 0.07^{b}
GMF	**8.8**	83.39 ± 0.12^{b}	-1.14 ± 0.04^{a}	17.83 ± 0.51^{c}	14.94 ± 0.38^{c}	17.67 ± 0.05^{b}
	11.3	$83.00 \pm 0.07^{b.c}$	$-1.06 \pm 0.09^{a.b}$	19.07 ± 0.09^{c}	15.86 ± 0.06^{c}	17.66 ± 0.11^{b}
	17.5	82.51 ± 0.01^{c}	$-0.92 \pm 0.04^{b.c}$	21.64 ± 0.19^{b}	17.71 ± 0.13^{b}	$17.90 \pm 0.11^{a.b}$
	26.3	81.60 ± 0.15^{d}	-0.76 ± 0.04^{c}	25.22 ± 0.07^{a}	20.19 ± 0.06^{a}	18.14 ± 0.16^{a}

Note: different letters in the same column represent significant differences ($p < 0.05$) between averages obtained with the Tukey test, C = mmoles of formaldehyde or glyoxal/100 mL of filmogenic solution, ΔE^{*} = total color difference in relation to the native film.

Scanning Electronic Microscopy

The morphology of the film was evaluated in relation to the surface. Films treated with formaldehyde and glyoxal having the lowest water vapor permeability in relation to the native film were analyzed.

The morphology of the native film surface (Figure 2a) showed a fiber-shaped arrangement with some discontinuity between regions. The appearance of these regions may be related to the process of drying in regions rich in glycerol. In these regions, the water migration was facilitated, causing the appearance of regions of discontinuity, that generated preference patterns for water migration that may be related to the higher water vapor permeability obtained for the native film when compared to the modified films. With regard to the surface structure of films treated with formaldehyde (Figure 2b), a cohesive arrangement with partial loss of orientation was verified where the polymeric matrix had some degree of entanglement with longitudinal orientation. The morphology of the glyoxal-modified film (Figure 2c) had a cohesive matrix with agglomerated regions within the polymeric matrix.

When the effects of both chemical treatments on the modified-film surfaces were compared, it was verified that the formaldehyde-modified film had a more compact polymeric matrix and that the agglomerates observed on the surface may have been responsible for the higher water vapor permeability of the glyoxal-modified film.

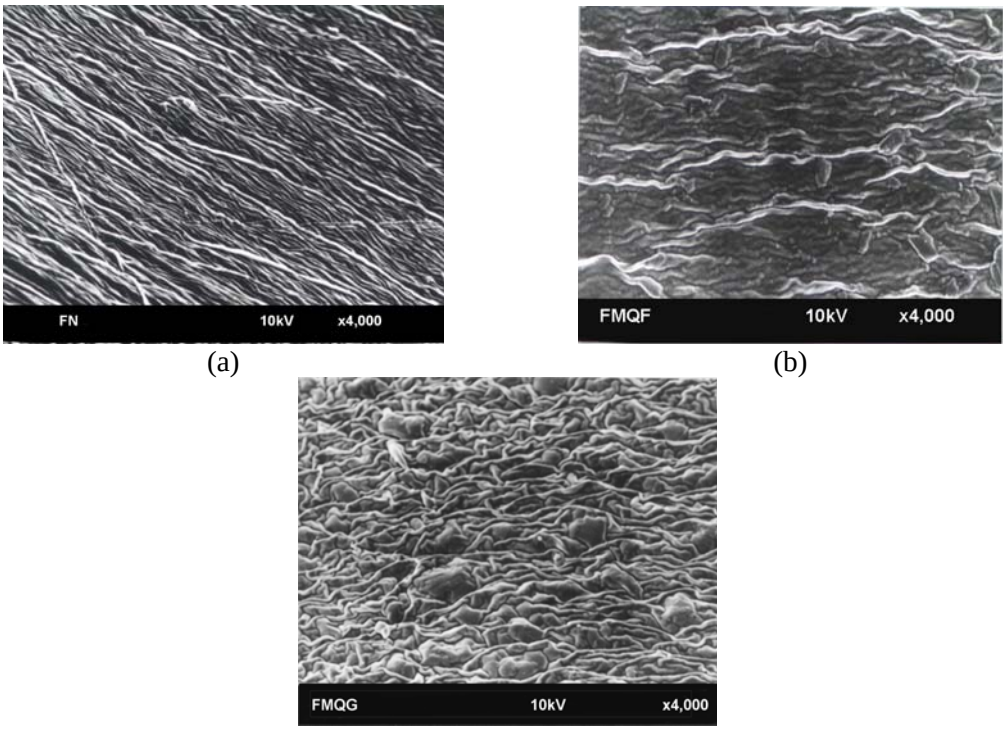

Figure 2: Photographic image obtained through scanning electron microscopy of the following films: native (a), formaldehyde-modified (b) and glyoxal-modified (c).

CONCLUSIONS

Films reticulated with formaldehyde and glyoxal had higher strengths, lower water vapor permeabilities and higher opacities and greater color differences, than the untreated films. Formaldehyde-based films showed a significant increase in strength as a function of the increase in concentration of the reticulant agent in comparasion with glyoxal-modified films. Generally, it was verified that the properties of the reticulated films seem to be a function of spatial arrangement after reticulation. The increase in concentration of the reticulant agent may have a positive or a negative effect; therefore the excess of free reagent in the polymeric matrix could have resulted in a reduction in the cohesiveness of the matrix and in a drecrease in the mechanical and barrier properties.

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