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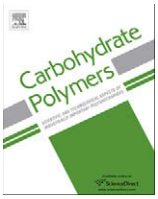

Effect of cellulose fibers on the crystallinity and mechanical properties of starch-based films at different relative humidity values

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ABSTRACT

The objective of this study was to investigate the effect of the addition of cellulose fibers on the mechanical and physicochemical properties of starch-based films plasticized with glycerol. Film samples were prepared from solutions with 3% of cassava starch, with the addition of 0, 0.10, 0.30 and 0.50 g of fibers/g of starch. The mechanical properties of samples conditioned at different relative humidity (RH) values were determined through tensile and stress relaxation tests. SEM micrographs of the films showed a homogeneous and random distribution of the cellulose fibers, without pores or cracks. Films with fibers were more crystalline and had higher tensile strength and rigidity, but lower elongation capacity. On the other hand, addition of cellulose fibers increased the stability of starch-based films subjected to RH variations, solving a classical problem encountered with this kind of film. Thus, the addition of cellulose fibers to starch-based films is an effective way to prepare stronger and more stable films.

1. Introduction

Starch-based films have low permeability to gases and poor water vapor barrier properties. However, for some applications, the main drawback associated with the use of this kind of film as packaging material is its mechanical properties. Starch-based films must to resist to the stresses they are submitted to when used to produce packaging. Therefore, the improvement of their resistance to traction forces is an important factor in making their use viable (Dole, Joly, Espuche, Alric, & Gontard, 2004; Funke, Bergthaller, & Lindhauer, 1998; Garcia, Martinho, & Zaritzky, 2000; Gáspar, Benkó, Dogossy, Réczey, & Czigány, 2005; Lourdin, Coignard, Bizot, & Colonna, 1997; Müller, Yamashita, & Laurindo, 2008; Wollerdorfer & Bader, 1998). Also, starch-based films are very sensitive to high relative humidity (RH). It is well known that they can roll or bend spontaneously at high RH and become difficult to handle.

The mechanical properties of films are traditionally linked to their tensile strength, determined from unidirectional tensile strength tests. Experimental stress–strain curves are used to calculate the film tensile strength, deformability modulus and elongation at break. These properties are dependent on the polymeric chain packing, chains interactions and film thickness, as well as being strongly affected by the RH of the environment (Cuq, Gontard, Cuq, & Guilbert, 1996; Lourdin et al., 1997; Rindlav, Hulleman, & Gatenholm, 1997). From the stress–strain curves it is not possible to determine with precision the influence of the elastic and viscous components on the viscoelastic behavior of these films. Film viscoelasticity can be evaluated from static relaxation tests, determining the decrease in the residual force (or stress) after a given deformation (or strain) (Chandra & Sobral, 2000; Cuq et al., 1996; Mark et al, 1984) or from dynamic mechanical analysis – DMA (Miura et al., 1999; Vicentini & UNESP, 2003). In DMA tests the elastic and viscous components can be quantified from the elastic and viscous modulus. In static relaxation tests, the level of deformation applied before determining the stress relaxation must be in the linear region of the stress–strain curve, i.e., in the elastic region, which can be estimated from previous tests on unidirectional traction (Indrani & Rao, 2007; Rao, 2003).

Cuq et al. (1996) reported data on stress relaxation tests of films prepared with fish myofibrillar proteins. Mechanical relaxation was recorded after deformation in puncture tests and a rheological model based on the Maxwell elements was used to model the viscoelasticity. Stress relaxation tests were performed with discs (40 mm of diameter), which were submitted to puncture tests before relaxation. The authors reported that film thickness did not influence the model parameters. In a similar study, Chandra and Sobral (2000) estimated the viscoelastic parameters of films prepared from fish (tilapia) myofibrilar proteins. Film samples were conditioned at RH = 58% for four days and submitted to elongations of 1% before the stress relaxation test. The experimental results were represented with three different models: Maxwell (one spring and one hydraulic dashpot in series), generalized Maxwell (two Maxwell elements in parallel) and Burgers model (one

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Maxwell element in series with one spring and one hydraulic dashpot in parallel). A slight influence of the film thickness on the model parameters was observed.

Vicentini (2003) investigated the viscoelastic properties of starch-based films from dynamic essays (DMA) and using the Kelvin model to represent the experimental data on stress relaxation. Film samples were submitted to elongations of 1% and the stress relaxation was determined for 70 s. This author observed that the elastic component was more important than the viscous component and that film thickness influenced the rheological behavior.

It is well known that material crystallinity influences the mechanical properties of starch-based films. Determining the changes in the crystallinity of films after their preparation (starch retrogradation) can provide important information on their useful-life (Corradini et al, 2005; Hulleman, Kalisvaart, Janssen, Feil, & Vliegenthart, 1999; Van Soest & Vliegenthart, 1997).

The goal of this study was to evaluate the influence of the addition of cellulose fibers on the rheological behavior of starch-based films, conditioned at different relative air humidity values, from stress relaxation tests.

2. Materials and methods

2.1. Film preparation

Films were prepared by casting, from cassava starch suspension with 3% in weight of starch (Yoki Alimentos S.A., Paranavai – Brazil), using glycerol as the plasticizer (0.30 g/g of starch), cellulose fibers at concentrations of 0 (without fibers, WF), 0.10 (P10), 0.30 (P30) and 0.50 (P50) g of fibers/g of starch (e.g., for P10, there are 0.1 g of cellulose fibers for each gram of starch) and guar gum (0.01 g/g of starch) to avoid fibers sedimentation. Eucalyptus cellulose fibers were softwood short fibers of 1.2 mm, obtained from Klabin S.A., Lages – Brazil. Film-forming mixtures were poured onto plexiglass plates and dried at 40 °C for 16 h in an oven with circulating air. The films moisture after drying ranged from 0.098 g of water/g dry solids (P50) to 0.120 g of water/g dry solids (without fibers, WF). Samples of dried films were conditioned at 25 °C in desiccators with relative humidity (RH) values of 58% (saturated solution of NaBr) and 75% (saturated solution of NaCl).

2.2. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) micrographs of the film samples were obtained using a Philips XL-30 scanning electron microscope. The samples were coated with a fine gold layer using a BAL—TEC, model SCD 005 sputter coater. All samples were examined using an accelerating voltage of 10 kV. P50 samples were frozen with liquid nitrogen and fractured before analysis, while WF samples were cut with a scissor.

2.3. X-ray diffraction

The crystallinity of the starch films and starch films reinforced with cellulose fibers, conditioned under different RH conditions, were investigated by X-ray diffraction. The analysis was performed with a Philips X'Pert diffractometer -Netherlands, using copper radiation K_α ($\lambda = 1.5418$ Å), voltage of 40 kV and operation current of 30 mA. All essays were performed with $2\theta = 2°$ and $2\theta = 80°$, pitch of 0.05°/s. WF and P50 samples were conditioned at RH values of 58% and 75% for 72 h before the essays. The relative crystalinity index was calculated using Eq. (1) (Köksel, Sahbaz, & Özboy, 1993; Snyder & Bish, 1989).

$$Xc = \frac{Ac}{At} = \frac{Ac}{Ac + Aa} \quad (1)$$

where Ac is the crystalline area, Aa is the non-crystalline area and At is the total area.

2.4. Mechanical tests

Tensile tests were based on the ASTM D-882-91 (1996), using a texture analyzer (Stable MicroSystem – TAXT2i, Surrey-UK) with a 25 kg load cell. Rectangular film samples with dimensions 25.4 × 100 mm were used to perform the tensile tests at 0.8 mm/s. Ten samples of each film formulation were tested in order to determine the elongation at break (ε), tensile strength (T) and Young modulus (Y). The elongation at break determined for each film sample was used to determine the elongations to be applied to stress relaxation tests. These tests were performed after applying tension (stretching) to film samples to reach 10% and 20% of their elongation capacities. The stress developed by the film under tension was recorded at 0.04 s intervals, for 1 min. The relaxation ratio at 60 s was determined using Eq. (2) (Peleg, 1979).

$$R_{\text{RELAX}} = \frac{F(60s)}{F_0} \times 100 \quad (\%) \quad (2)$$

where F_0 is the force at $t = 0$ and $F(60\text{s})$ is the force at $t = 60$ s.

The experimental results for the stress relaxation were normalized and analyzed with the empirical model proposed by Peleg, given in Eq. (3) (Laurindo & Peleg, 2007; Peleg, 1979).

$$\frac{F(t)}{F_0} = 1 - \frac{c_1 \cdot t}{c_2 + t} \quad (3)$$

The parameters c_1 and c_2 were estimated by non-linear regression using the software Matlab 7.0 (Mathworks, Natick, MA, USA). In this model, $1 - c_1$ and c_1/c_2 provide information on the material viscoelastic characteristics. The value of $1 - c_1$ can be seen as a "degree of solidity", while the ratio c_1/c_2 represents the initial rate of the stress decay.

3. Results and discussion

3.1. Scanning electron microscopy (SEM)

Micrographs of the WF films (Fig. 1, top) show a homogeneous and continuous material and those of the surfaces and fractures of the P50 films (Fig. 1, bottom) show homogeneous and random distributions of cellulose fibers, without pores or cracks. It can be seen, in the fracture micrographs, that the cellulose fibers are well cemented in the continuous phase. Avérous, Fringant, and Moro (2001) reported results on composites prepared from starch and cellulose fibers, using glycerol as plasticizer. They also observed, from SEM micrographies, that cellulose fibers were embedded into the thermoplastic starch matrix. According to these authors, this phenomenon is due to strong interaction between cellulose fibers and the plasticized starch matrix. Lignin is considered a highly reactive thermoplastic polymer. Besides, it is assumed that lignin is essentially located at the fibers surface, doing covalent bond with cellulose molecules (Kunanopparat, Menut, Morel, & Guilbert, 2008). The hydroxyl groups of lignin can interact with glycerol and starch, acting as an interfacial compatibilizer between fibers and starch, and leading to films with higher tensile strength. This behavior was also observed for gluten films added of natural fibers, as reported by the authors above.

3.2. Crystallinity

Diffractograms of WF and P50 samples, both conditioned at RH values of 58% and 75% for 72 h, are shown in Fig. 2. The WF samples are less crystalline than the P50 samples, at both RH values

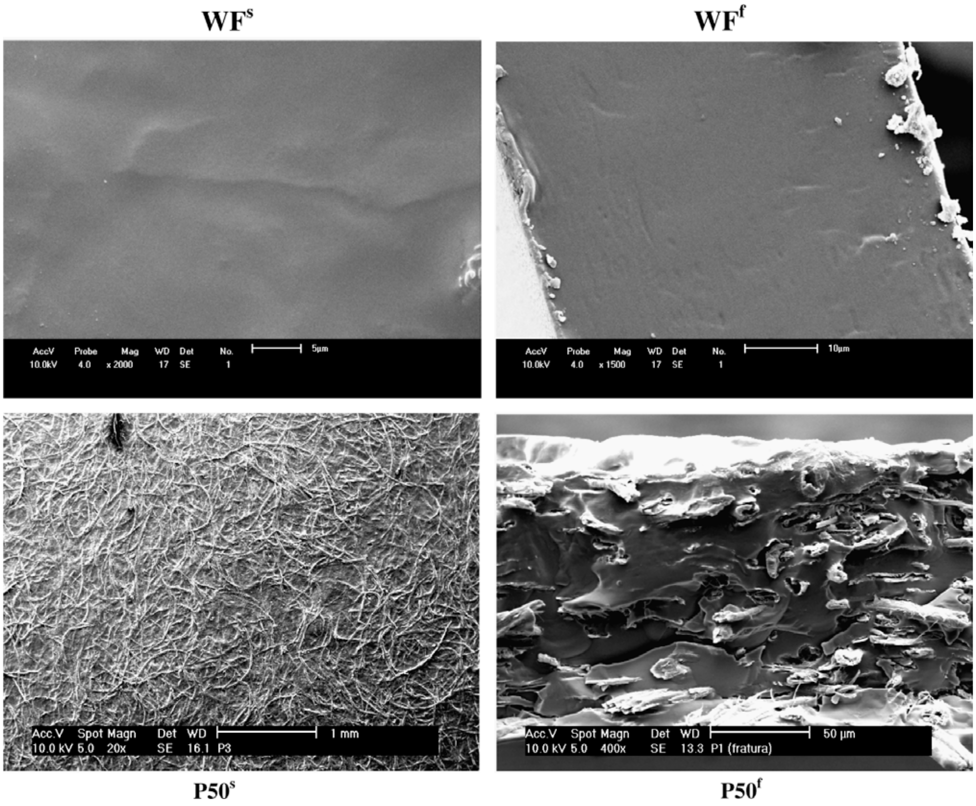

Fig. 1. Scanning electron microscopy of cassava starch films. Films without fibers (WF) on the top and films with 0.50 g fibers/g starch cellulose fibers (P50) on the bottom. The upper indexes *s* and *f* denote surface and fracture, respectively.

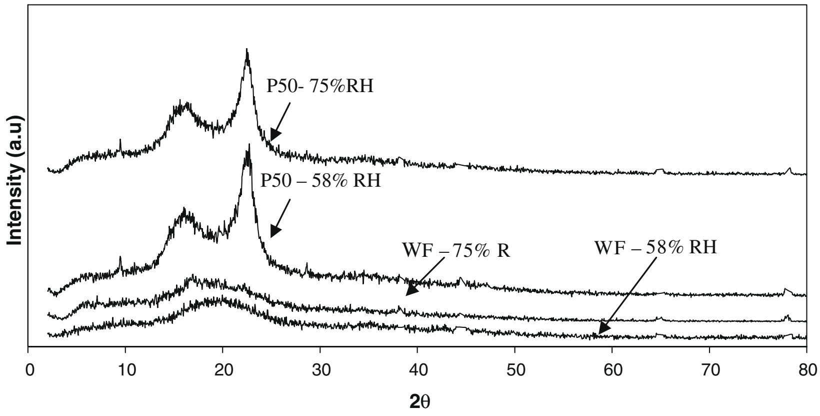

Fig. 2. Diffractograms of P50 and WF films conditioned at RH of 58% and 75% for 72 h.

investigated. These results suggest that cellulose fibers increased the crystallinity of the composite films, as has been reported by other authors, who attributed this phenomenon to the more crystalline nature of cellulose fibers (Amash & Zugenmaier, 2000; Ma, Yu, & Kennedy, 2005). P50 samples had two crystallinity peaks; a first peak close to $2\theta = 23°$, with intensity higher than 600 u.a., and a second peak close to $2\theta = 16°$, with intensity higher than approximately 300 u.a. Ma et al. (2005) reported the results for the diffraction analysis of composites of corn starch and cellulose fibers, plasticized with glycerol. Samples with 20% of cellulose fibers had an intense crystallinity peak close to 22.5° and another peak close to 15°.

The relative indexes given in Table 1 show that the RH value of the conditioning air influenced the material crystallinity. The crystallinity index of the WF films was higher for films conditioned at RH = 75%. Similar results were reported by van Soest and Vliegenthart (1997), investigating the aging of starch films plasticized with glycerol. They explained this behavior considering that higher amount of plasticizer increased the mobility of the starch

Table 1
Crystallinity index (Xc) of starch films prepared without fibers (WF) and with addition of 0.50 g of fibers/g of starch (P50), conditioned at relative humidity values of 58% and 75%.

Sample	RH (%)	Xc (%)
WF	58	0
	75	5
P50	58	50
	75	53

Table 2
Tensile strength (T), elongation at break (ε), Young modulus (Y), Maximum Stress, at $t = 0$ (F_0) and Film relaxation ratios (R_{RELAX}).

Sample*	T (MPa)	ε (%)	Y (MPa)	F_0 (N)	R_{RELAX}
WF.58.10	1.59 ± 0.16^a	83 ± 17^d	21 ± 9^a	3.6 ± 0.5	19 ± 1
WF.58.20				6.3 ± 0.7	23 ± 1
WF.75.10	1.39 ± 0.21^a	101 ± 15^e	11 ± 1^a	1.9 ± 0.4	60 ± 5
WF.75.20				4.0 ± 0.6	58 ± 3
P10.58.10	8.39 ± 1.5^c	22 ± 5^b	217 ± 12^d	17.8 ± 1.3	21 ± 1
P10.58.20				30.7 ± 0.9	27 ± 3
P10.75.10	4.92 ± 0.43^b	25 ± 3^b	37 ± 2^b	2.1 ± 0.3	54 ± 3
P10.75.20				3.7 ± 0.4	54 ± 2
P30.58.10	16.78 ± 2.72^d	15 ± 3^a	449 ± 85^e	22.7 ± 4.0	27 ± 1
P30.58.20				28.6 ± 4.8	30 ± 2
P30.75.10	10.43 ± 1.31^c	17 ± 4^{a,b}	83 ± 31^c	7.2 ± 0.6	41 ± 3
P30.75.20				13.0 ± 2.4	40 ± 2
P50.58.10	26.69 ± 1.92^e	14 ± 2^a	1047 ± 72^f	26.2 ± 3.2	36 ± 1
P50.58.20				35.2 ± 2.8	35 ± 2
P50.75.10	19.34 ± 1.09^d	13 ± 4^a	211 ± 57^d	21.3 ± 2.4	38 ± 2
P50.75.20				35.2 ± 4.9	38 ± 1

* __.__.__. The three-parameter code relates to Film formulation. Conditioning RH. Percentage of the film elongation capacity. The same letter in the same column do not differ significantly at $p < 0.05$.

chains. Besides, the rate of crystallization increases with increasing water content. Rindlav et al. (1997) investigated the influence of drying processes on the crystallinity of potato starch films, and reported that higher moisture levels lead to more crystalline films. The crystallinity index of the P50 films changed only slightly as a function of the RH of the conditioning air (variation of 3% in 50%, Table 1). This behavior may be due to a stabilizing effect of the cellulose fibers on the starchy polymeric matrix, mainly on the amylose molecules that undergo a reduction in mobility (Ma et al., 2005).

4. Mechanical tests

4.1. Tensile tests

The results for the tensile strength (T), elongation at break (ε) and Young modulus (Y) obtained from the traction tests, and the maximum force (force at $t = 0$, F_0) from the mechanical relaxation tests, are given in Table 2. The addition of cellulose fibers increased considerably the tensile strength and Young modulus of the films, and reduced their elongation capacity. This reinforcing effect of cellulose fibers is in agreement with previous results published in the literature (Curvelo, Carvalho, & Agnelli, 2001; Funke et al., 1998; Gáspar et al., 2005; Ma et al., 2005). These results reflect the chemical and structural compatibility between starch and cellulose chains (Avérous & Boquillon, 2004; Ma et al., 2005). The partition of glycerol between the starch matrix and fibers is also reported as a phenomenon that influences the Young modulus of composite films, due to the desplasticization of starch matrix (Kunanopparat et al., 2008).

Representative stress–strain curves of P30 samples conditioned at RH = 58% and 75% are presented in the Fig. 3. The quasi-linear behavior of these curves for small elongations (detail inserted in the figure) allows performing force relaxation tests until elongation of 20% of film elongation capacity, ε ($0.20 \times \varepsilon$). The linear behavior showed in the Fig. 3 was observed for all samples (WF, P10, P30 and P50), for both RH.

4.2. Stress relaxation tests

The experimental stress relaxation curves of films conditioned at RH values of 58% and 75% and elongated to 10% ($0.10 \times \varepsilon$) and 20% ($0.10 \times \varepsilon$) of their elongation capacities are shown in Fig. 4. The stress relaxation behavior was similar, for both film elongations ($0.10 \times \varepsilon$ and $0.20 \times \varepsilon$). All curves presented the characteristic shape of viscoelastic materials, with a residual stress decreasing to an asymptotic value (Cuq et al., 1996; Peleg, 1979). The viscoelastic behavior has been also reported in previous studies on starch-based films (Vicentini, 2003) and on films based on fish myofibrillar proteins (Chandra & Sobral, 2000; Cuq et al., 1996).

The results also showed that addition of cellulose fibers greatly reduced the influence of the air RH on the mechanical properties of the films. For example, the values of F_0 for P50 samples conditioned at RH values of 58% and 75% were very similar, for both tested elongations ($0.10 \times \varepsilon$ and $0.20 \times \varepsilon$). Also, the ratio $F_0(0.20 \times \varepsilon)/F_0(0.10 \times \varepsilon)$ decreased when cellulose fibers were added to the formulations. For instance, WF films conditioned at RH = 58% had a ratio of 1.8, while P50 films had a ratio of 1.3.

The addition of fibers reduced the effect of air RH on the relaxation ratio $F_0(\mathrm{RH} = 58\%)/F_0(\mathrm{RH} = 75\%)$. For P50 films this ratio was close to 1 for an elongation of 20% of the film elongation capacity.

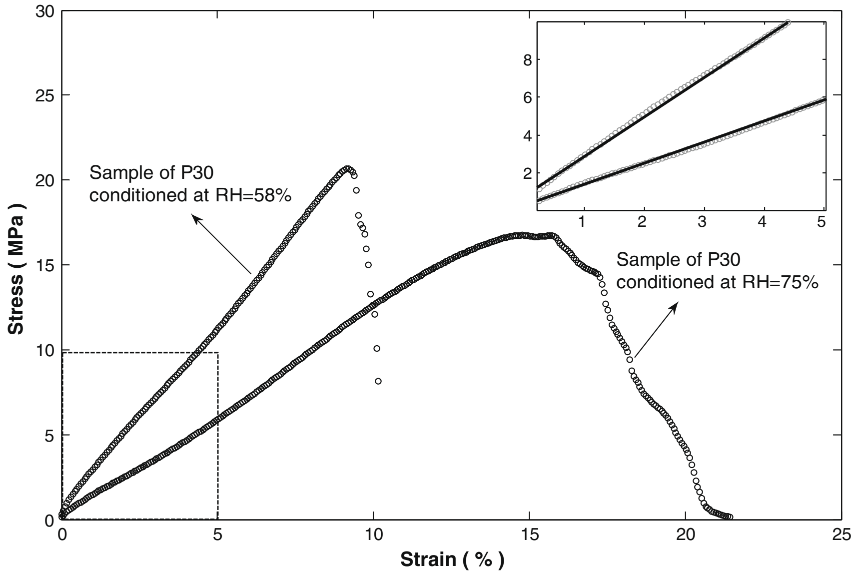

Fig. 3. Stress–strain curves of P30 samples conditioned at RH = 58% and 75%. The linear stress–strain behavior is evidenced by the detail inserted in the figure.

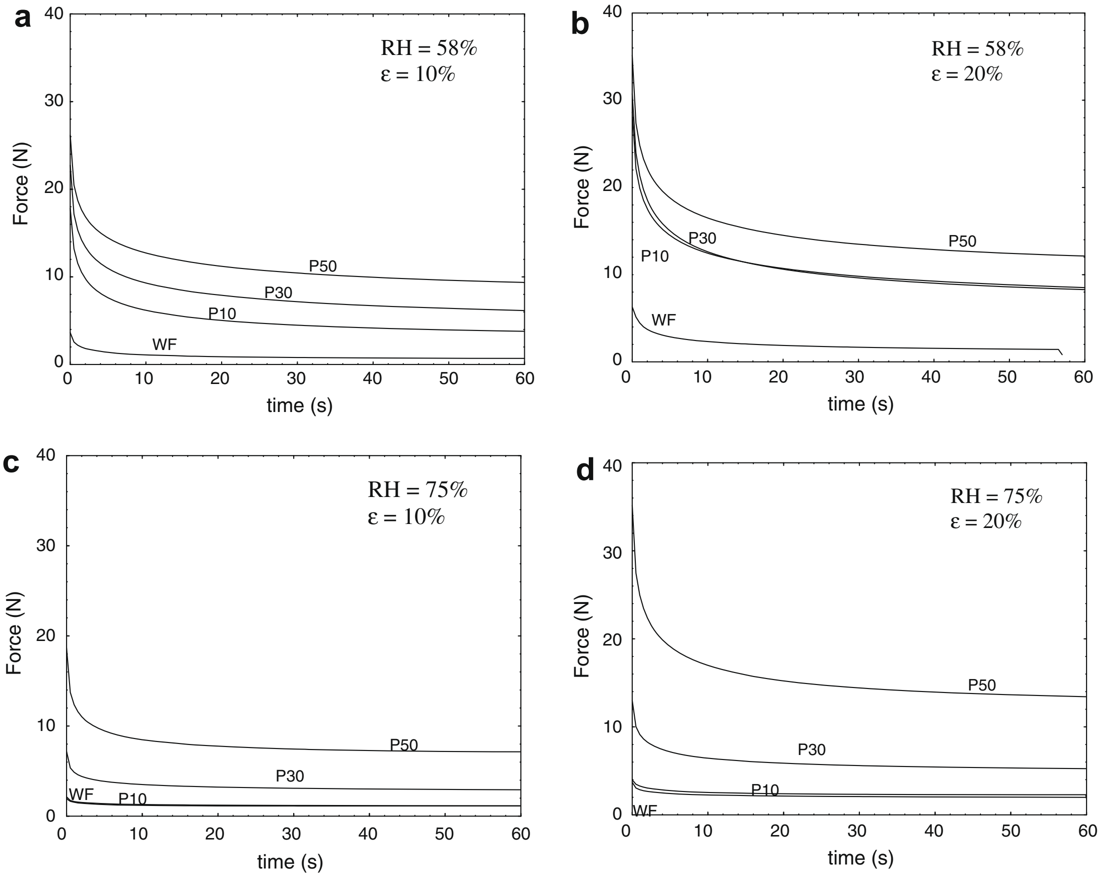

Fig. 4. Experimental stress relaxation curves: (a) Films conditioned at RH = 58%, elongated to 10% of elongation at break, (b) Films conditioned at RH = 58%, elongated to 20% of elongation at break, (c) Films conditioned at RH = 75%, elongated to 10% of elongation at break (d) Films conditioned at RH = 75%, elongated to 20% of elongation at break.

These results indicate that addition of cellulose fibers is an effective way to stabilize starch-based films, which are known to be very sensitive to relative air humidity. It was observed that samples of P50 can be exposed to very high RH (95%) without folding or bending spontaneously.

The values of the parameters c_1 and c_2 of the Peleg's model (Eq. (3)), determined from the relaxation data, are shown in Table 3. According to Peleg (1979), $(1 - c_1)$ can be seen as degree of solidity, while (c_1/c_2) is the initial stress decay rate. When $(1 - c_1)$ goes to 1 the material behaves as an elastic solid, and when $(1 - c_1)$ goes to zero the material behavior is controlled by the viscous component. Fig. 5a shows an example of fitting experimental data of force relaxation with Eq. (3). As an accurate estimation of c_2 is important to determine the ratio (c_1/c_2), the value of c_2 was determined from the first twenty experimental data of force relaxation (Fig. 5b).

Table 3
Mechanical properties of starch and fibers composites.

Sample*	c_1 (−)	c_2 (1/s)	Degree of solidity $(1 - c_1)$ (-)	Initial stress decay rate (c_1/c_2) (s)
WF.58.10	0.82	1.42	0.18	0.57
WF.58.20	0.79	2.20	0.21	0.36
WF.75.10	0.43	1.22	0.57	0.35
WF.75.20	0.44	1.95	0.56	0.22
P10.58.10	0.79	1.80	0.21	0.44
P10.58.20	0.74	2.12	0.26	0.35
P10.75.10	0.46	1.30	0.54	0.36
P10.75.20	0.46	1.49	0.54	0.31
P30.58.10	0.73	1.93	0.27	0.38
P30.58.20	0.71	2.04	0.29	0.35
P30.75.10	0.59	1.18	0.41	0.50
P30.75.20	0.60	1.45	0.40	0.41
P50.58.10	0.65	2.06	0.35	0.31
P50.58.20	0.66	1.93	0.34	0.34
P50.75.10	0.62	1.10	0.38	0.57
P50.75.20	0.62	1.66	0.38	0.38

[*] __.__.__. The three-parameter code relates to Film formulation. Conditioning RH. Percentage of the film elongation capacity.

The results given in Table 3 show that the addition of cellulose fibers increased films' elastic component. However, at RH = 75%, addition of cellulose fibers caused a reduction in the degree of solidity of the films. For P50 at RH = 75%, the degree of solidity decreased from 0.57 to 0.38 (reduction of 33%). Table 3 shows that WF films have a high sensitivity to air RH. The degree of solidity $(1 - c_1)$ varied from values characteristic of an elastic solid (0.56–0.57) to values characteristic of a viscous material ("liquid") (0.21–0.18). The addition of cellulose fibers reduced this difference, i.e., it reduced the influence of RH on the viscoelastic properties of the films. For the P50 films, the degree of solidity is about the same (0.34–0.38) for RH = 58% and RH = 75% RH. This interesting effect of RH and cellulose fiber concentration on the elastic and viscous behavior of the starch-based films prepared in this study is shown in Fig. 6. This Figure illustrates how cellulose fibers affect the degree of solidity of the films and shows a region where starchy films have low sensitivity to air RH. It can be observed too that there was no sensible effect of elongation ($0.10 \times \varepsilon$ and $0.20 \times \varepsilon$) on the force relaxation behavior of all investigated composite films, mainly at RH = 75%. Therefore, the addition of cellulose fibers has two effects on the starch films, increasing their mechanical resistance and their stability under high air RH.

The force decay rate at the beginning of the stress relaxation, calculated by the value of (c_1/c_2), was influenced by three factors,

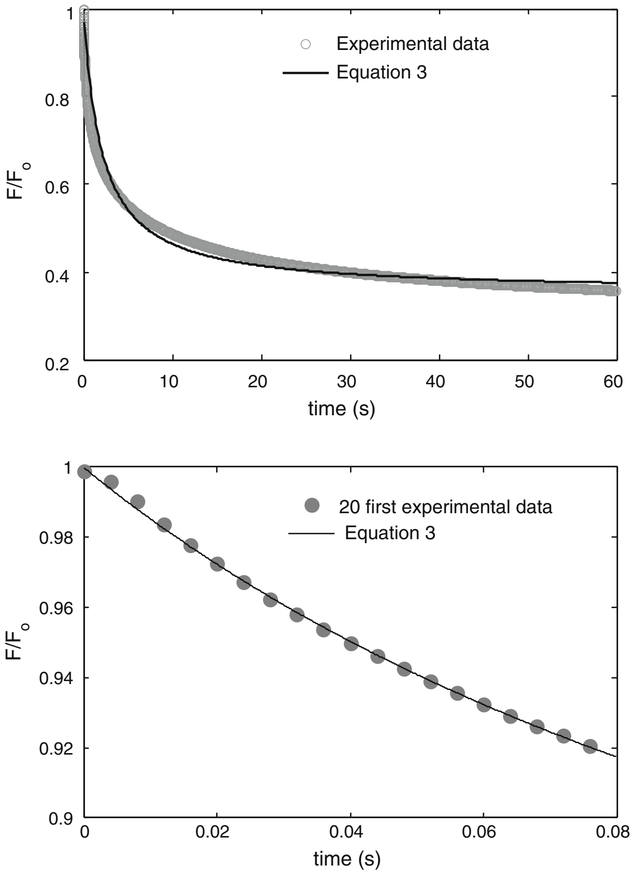

Fig. 5. (a) Example of fitting the whole experimental data of force relaxation with Eq. (3). (b) Fitting the first twenty experimental data of force relaxation for an accurate estimation of c_2.

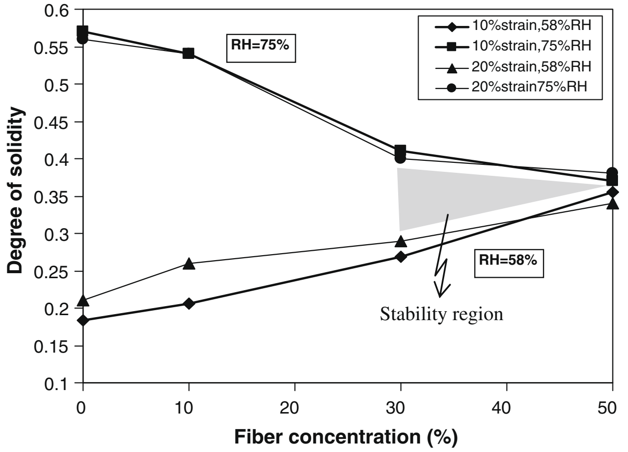

Fig. 6. Influence of RH and cellulose fiber concentration on the degree of solidity of starch-based films.

i.e., fibers concentration, RH used for conditioning the films and film elongation before force relaxation. It is a complex problem, even for a fixed elongation. However, for all cases, fibers addition had a stabilizing effect, but water sorption caused an opposite effect, plasticizing the samples.

Dynamic analysis of viscoelasticity in biofilms reinforced with fibers has been reported in the literature, indicating that fibers promote an increase in the film elastic modulus. A possible explanation for it is the chemical and structural similarity between starch and cellulose chains, reducing starch chain mobility and leading to an increase in the elastic component of these viscoelastic materials (Avérous & Boquillon, 2004; Avérous et al. 2001; Lu, Weng, & Cao 2006; Ma et al. 2005).

5. Conclusions

Films with fibers have higher tensile strength and are more rigid, but have lower elongation capacity. On the other hand, addition of cellulose fibers increases the stability of starch-based films in relation to variations in relative air humidity, solving a classical drawback associated with this kind of film. Thus, the addition of cellulose fibers to starch-based films is a promising way to prepare stronger and more stable films.

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