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# Structure–properties relationship in cross-linked high amylose starch cast films

Bernard Rioux[a], Pompilia Ispas-Szabo[b], Abdellatif Aït-Kadi[c], Mircea-Alexandru Mateescu[b], Julianna Juhász[a,*]

[a]*Faculté de Pharmacie, Université Laval, Pavillon Vandry, Sainte-Foy, Que., Canada G1K 7P4*
[b]*Department of Chemistry–Biochemistry, Université du Québec à Montréal, C.P. 8888 Succ. A, Montreal, Que., Canada H3C 3P8*
[c]*Chemical Engineering Department CERSIM, Université Laval, Sainte-Foy, Que., Canada G1K 7P4*

The paper is dedicated to Abdellatif Aït-Kadi, recently passed away

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## Abstract

Cross-linked high amylose starch cast films were prepared to study the effect of cross-linking degree on various properties in normal environmental conditions. Mechanical tensile properties (Young's modulus, elongation at break, tensile strength), water vapour transmission rate (WVTR) and oxygen permeability coefficients of cast films were determined as a function of cross-linking degree and percentage of free humidity. Cross-linking degree and degree of crystallinity are closely related and seem to have non-negligible opposite effect on the properties of interest. By using increased amounts of cross-linking agents, the effect of cross-linking degree tends to reduce the degree of crystallinity modulating thus mechanical properties, water vapour permeability and oxygen permeability coefficients. Yield strength, tensile strength at break, WVTR versus cross-linking degree showed a non-monotonous behaviour. Maximal values for these properties were reached for moderate cross-linking degree. Optimal crystalline/amorphous ratio in the films may induce interactions and balanced effects, which would be responsible for the non-linear behaviour of some of the investigated properties. By cross-linking with epichlorohydrin in the range 1–10 g crosslinker/100 g polymer, the mechanical properties of films are still related to water content and water vapour permeability remains high compared to some synthetic polymeric materials.

*Keywords*: Cross-linked high amylose starch; Contramid™; Casting film; Crystallinity; Mechanical properties; Oxygen permeability; Water vapour permeability

## 1. Introduction

Native properties of polysaccharides can be changed by chemical modification of their structures. High amylose starch can be modified via reactions of hydroxyl groups (esterification, etherification, oxidation) and properties as solubility, swelling rates, solution and gel rheology, ability to form gels and films, rate of biodegradability, etc. can be changed. Bifunctional agents (e.g. epichlorohydrin) may be used to cross-link high amylose starch chains and create hydrogels. This approach has been used several years ago to introduce a new controlled released system based on the Cross-linked high amylose starch (CLHAS) as matrix for controlled drug release (Lenaerts, Dumoulin, & Mateescu, 1991; Mateescu, Cartilier, Dumoulin, & Lenaerts, 1992) under the brand name of Contramid™. For CLHAS tablets, prepared by direct compression, it was found that a linear increase in cross-linking degree (CLD) generates a non-monotonous variation of drug release time (Lenaerts et al., 1991; Mateescu et al., 1992). Maximal release time was obtained at moderately low CLD. A slight increase of CLD results in a drastic decrease of the release time. A relationship between the drug release kinetics and the morphological aspects of CLHAS powders or tablets was found (Dumoulin, Alex, Szabo, Cartilier, & Mateescu, 1998; Ispas-Szabo, Ravenelle, Hassan, Preda, & Mateescu, 2000).

The correlation of X-ray diffraction data for powders and tablets with in vitro dissolution assays characterized by

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* Corresponding author. Tel.: +1-418-656-2131p3690; fax: +1-418-656-2305.

*E-mail address:* julianna.juhasz@pha.ulaval.ca (J. Juhász).

*Abbreviations*: CLHAS, cross-linked high amylose starch; CLD, cross-linking degree, conventionally expressed as the amount of cross-linking agent (g)/100 g polymer; %FH, free humidity of films, the amount of water retained by the films in the described conditions of storage; %RH, relative humidity of the ambient environment; WVTR, water vapour transmission rate

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release time of 90% of drug ($t_{90\%}$) and by mechanical behaviour of swollen tablets suggested that an optimal ratio of crystalline/amorphous could be responsible for the tablet integrity during dissolution and consequently for the desired release properties (Ispas-Szabo et al., 2000). It was observed that only a relatively narrow range of CLD allows a special stabilization of polysaccharide chains, responsible for the optimal release properties of the matrix. This particular behaviour was ascribed to the three dimensional structure of CLHAS organized in this case as a stable network. The possibility of chains to be stabilized by physical hydrogen association can substantially contribute to network formation and a moderate crystallinity will control the water front penetration into the tablet (Dumoulin et al., 1994a; Ispas-Szabo et al., 2000; Mateescu, Dumoulin, Delmas, Lenaerts, & Cartilier, 1993). In these conditions, the tablet shape is maintained over the dissolution period by the formation of an elastic gel, controlling the release of the dissolved drug in aqueous media. The network formation seems to be essential for a better stabilization of CLHAS structure and thus responsible for good mechanical and release properties.

A purpose of this study was to get a preliminary evaluation of the potential use of CLHAS to transdermal drug delivery. In selection of polymers suitable for use as matrices for transdermal drug delivery, the criteria to be considered are numerous, notably: cost, purity and acceptability for medical devices, ease of modifications, ease of fabrication and good stability. High amylose starch generally met all this criteria. Therefore, it was of interest to evaluate the mechanical properties, water vapour and oxygen permeation of CLHAS cast films in correlation with their CLD. In addition, in recent years, biodegradable films have found growing commercial importance because of environmental problems of non-biodegradable and non-renewable polymeric materials. Numerous studies have been done so far on starch-based films (Arvanitoyannis, Kalichevsky, & Blanshard, 1994; Parris, Dickey, Kurantz, Moten, & Craig, 1997; Ramkumar & Bhattacharya, 1997; Rindlav, Hulleman, & Gatenholm, 1997). Since starch is a hygroscopic material and films' properties of interest depend highly on their water content, experiments have been carried out with films having low values of free humidity percentage (%FH) to study their behaviour when submitted to normal environmental conditions.

## 2. Materials and methods

### *2.1. Materials*

High amylose starch powder (corn starch Hylon VII) containing at least 70% amylose (less than 30% amylopectin) was obtained from National Starch Co. (Bridgewater, USA). Epichlorohydrin, acetic acid and the other current reagents were obtained from Sigma Chemical Comp. (St Louis, USA) and used without further purification.

#### *2.1.1. Synthesis of cross-linked high amylose starch*

High amylose starch was cross-linked with epichlorohydrin following an experimental procedure described elsewhere (Mateescu, Lenaerts, & Dumoulin, 1995). Briefly, for each synthesis, 300 g of native amylose powder and 1.75 l of 1.48 M sodium hydroxide were mixed in a planetary mixer under a constant temperature of 50 °C for gelatinization. After 1 h, volumes (measured at 23 °C) of 2.53, 5.06, 12.65, 15.20 or 25.33 ml of epichlorohydrin, corresponding to the different CLD used, were, respectively, added in each synthesis batch. The CLD was conventionally defined (Mateescu, Schell, Dimonie, Todireanu, & Maior, 1984) as the amount of epichlorohydrin (g) used to cross-link 100 g of high amylose starch in the specific conditions (e.g. CLHAS-6.0 is obtained with an initial ratio 6/100 cross-linking agent/polymer). The reaction was continued for 1 h under moderate heating (50 °C). The mixture was neutralized with acetic acid and then stored in an Erlenmeyer flask at 4 °C for one week to permit retrogradation. Gel was thoroughly washed on a Büchner funnel with a solution of water/acetone 15:85 (v/v) in a first step and then three times with water/acetone 60:40 (v/v). The CLHAS was finally dried with acetone 100% three times and exposed to air during 48 h. The dry polymer was sieved and particles smaller than 500 μm were kept and stored at room temperature into hermetic plastic bags.

#### *2.1.2. Films preparation*

Starch gels were first prepared from a dispersion of CLHAS in distilled water (3% w/w). The dispersions were heated under continuous mixing in a closed chamber for 12 h at temperatures depending on the CLD of the CLHAS in order to obtain clear homogenous gels: 91 °C for CLHAS-1.0, 88 °C for CLHAS-2.0, 80 °C for CLHAS-5.0, 78 °C for CLHAS-6.0 and 72 °C for CLHAS-10.0.

Cast films were prepared using different amounts of gels (50, 60 and 70 g) in order to obtain films with different thicknesses. Gels were poured into homemade polypropylene dishes (182.4 $cm^2$). To avoid bubble formation, gels were spread uniformly over the entire surface and dried at 23 °C and 65% of relative humidity (RH) for 3 days. After drying, cast films were removed from the dishes and stored for 4 days in a closed jar at 23 °C and 100% RH, in order to increase their flexibility.

#### *2.1.3. Specimens preparation and conditioning*

The mechanical properties of at least 15 specimens were measured from their load-time profiles. The film specimens were cut for measurements. Three uncut samples of each film were also kept apart in order to determine the percentage of free humidity (%FH) of the specimens after storage as a function of CLD. Samples' dimensions were in accordance with ASTM-D638 guidelines ($w \times L = 3$ mm $\times$ 30 mm, where $w$ is the width and $L$ the length of the specimen). The thickness of each specimen was measured at three different positions using a micrometer and the mean thickness was used for

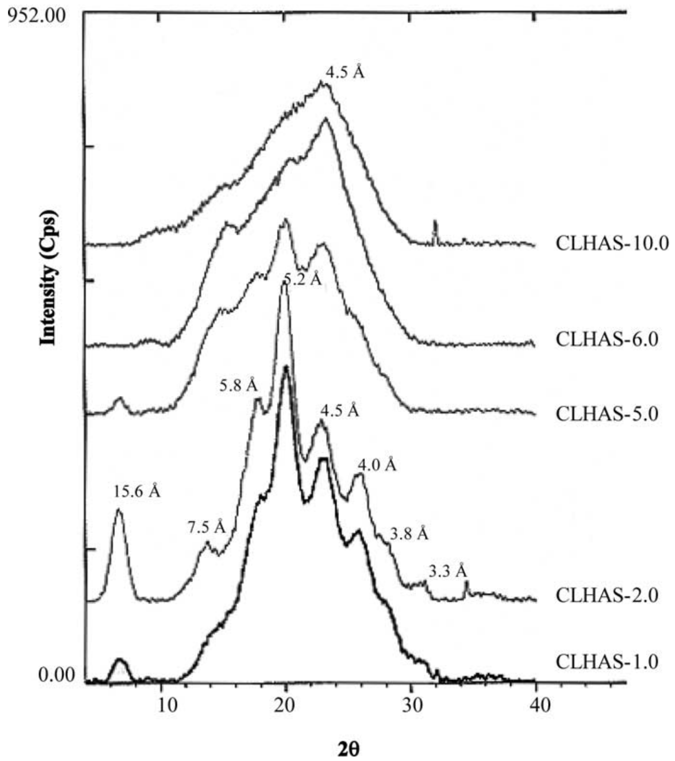

Fig. 1. X-ray diffraction pattern for CLHAS films conditioned at 20 °C/65% RH for 48 h.

the evaluation of mechanical properties. Specimens were stored for 48 h, at room temperature, under three different conditions (0, 65 and 100% RH). For each group of specimens, an uncut sample of the film was stored under the same conditions.

### 2.2. Methods

The %FH of the CLHAS films was determined by drying the uncut samples of the films after storage in a vacuum oven (Precision Scientific, NAPCO #5861, Winchester, USA) and by weighing these samples, before and after drying, with a precision balance (Denver Instruments Co. A-250, Denver, USA). This %FH parameter represents the estimated amount of water retained by the films in the conditions described earlier. The %FH was calculated as follow:

$$\%\mathrm{FH} = \frac{W_\mathrm{b} - W_\mathrm{a}}{W_\mathrm{b}} 100 \tag{1}$$

where $W_\mathrm{b}$ and $W_\mathrm{a}$ are, respectively, the weight of the sample before and after drying. Mean value of %FH was calculated for all films stored under particular conditions since the %FH of the films did not vary markedly with CLD. Percentage values of FH were 0.3% (0% RH), 8.5% (65% RH) and 13.3% (100% RH).

#### 2.2.1. X-ray diffraction

X-ray diffraction spectra were carried out on a Siemens D 5000 diffractometer, operating in reflectance mode at Co $\mathrm{K}_\alpha$ wavelength $\lambda = 1.79018$ Å over an angular range 5–50°. The relative crystallinity (%X) values were estimated for all CLHAS films following the method of Nara and Komiya (1983). The area of the crystalline peak diffraction relative to the total area of the diffractogram was taken as a measure of the relative crystallinity. Thus, diffractograms were baseline-corrected by drawing a straight line between $2\theta = 4°$ and $2\theta = 38°$. The upper diffraction peak area and the total diffraction area over the $2\theta$ diffraction angle 4–38° were integrated using the image processing software Visilog (Noesis Vision, St Laurent, Canada).

#### 2.2.2. Mechanical testing

Measurement of mechanical properties was performed using an Instron Universal testing machine (model 3111) with a 5 kg load cell and a constant crosshead speed of 5 mm/min. Young's modulus, elongation at break, stress at break and yield strength were computed from load-time curve. Mean values (of at least 15 samples) of properties of interest as a function of CLD and %FH were considered.

#### 2.2.3. Determination of water vapour transmission rate

Water vapour transmission rate (WVTR) of the CLHAS films was determined by using a home-made closed device (Chemical Engineering Department, Laval University) with two chambers separated with a specimen of the CLHAS film

Table 1
Values of the relative degree of crystallinity (%) as a function of CLD with respect to Fig. 1. Calculations have been made by the method described by Nara and Komiya (1983)

| CLD | Relative degree of crystallinity (%) |
|---|---|
| 1.0 | 26 |
| 2.0 | 22 |
| 5.0 | 14 |
| 6.0 | 12 |
| 10.0 | 9 |

of 3.14 $cm^2$. The upper chamber contained a small recipient with an amount of distilled water, which generated an environment saturated with water vapour (100% RH). After passing through the film, the moisture was removed from the carrier gas by absorption into a tube containing 200 g of desiccant (Driedrite, BDH Co., Toronto, Canada). The whole system was maintained at a constant temperature (23 or 37 °C) with an oil bath connected to the apparatus. Nitrogen, the carrier gas, was circulated at a constant and very low flow rate in the lower chamber in order to carry water vapour; the gas was first diffused toward an absorption tube, containing the same desiccant, in order to eliminate any humidity or oil traces and then passed trough the diffusion cell. The WVTR was calculated from linear regression of the slope of the desiccant weight gain versus time and then dividing the slope by the area of the film. The WVTR has been determined twice for each CLD and each temperature. Mean values of WVTR are expressed as a function of CLD.

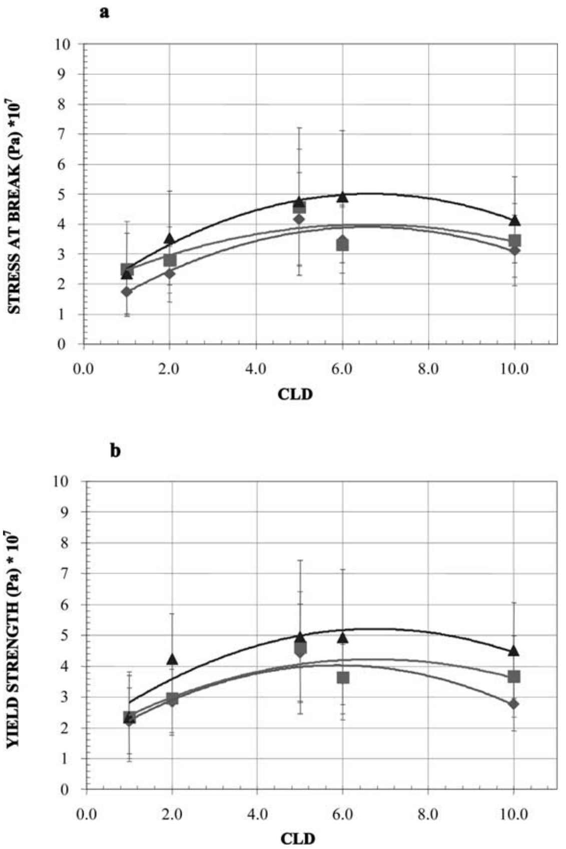

Fig. 2. (a) Tensile at break as a function of CLD for CLHAS films. (b) Yield strength as a function of CLD for CLHAS films (▲ 0% RH; ■ 65% RH; ◆ 100% RH).

### 2.2.4. Determination of oxygen permeability coefficient

Oxygen permeability of CLHAS cast films were first determined using Mocon OX-TRAN 2/60 apparatus (Mocon, Minneapolis, USA) using film specimen of 2 cm of diameter. The equipment permitted testing of six samples at the same time with specially designed aluminium foil masks. The thickness of each sample was taken at three different positions with a micrometer. Mean value of thickness was used for the computation of oxygen permeability coefficients. A gas mixture composed of 97% nitrogen and 3% hydrogen was used as carrier. Temperature was set at 23 °C and RH of pure oxygen and carrier gas was set at 65%. Duration of 3 h was allowed to reach equilibrium with the carrier before testing with oxygen. Oxygen permeability was given directly by the software used with the OX-TRAN 2/60 and the oxygen permeability coefficient ($D$) was calculated Eq. (2):

$$D = \frac{P_{\text{oxygen}} \times p}{T_{\text{f}}} \tag{2}$$

where $P_{\text{oxygen}}$ is the oxygen permeability, $p$ is the pressure of oxygen used and $T_{\text{f}}$ is the mean thickness of the cast film. Tests were repeated twice for each CLD.

## 3. Results and discussion

Fig. 1 shows X-ray diffraction spectra of films stored at room conditions (20 °C/65%(RH) with a %FH of 8.3%. Results of the calculation of relative degree of crystallinity are presented in Table 1 indicating that the degree of crystallinity decreases as the CLD increases.

Native amylose is semi-crystalline and can adopt different crystalline structures (A, B, C and V). The A, B, and C-structures consist of packed double helix. The V-type conformation is a single helix structure resulting of amylose complexed with some components such as water, iodine, butanol and fatty acid. Peaks at $2\theta = 19.5°$ clearly showed the presence of double helix B-type structure, as previously observed in CLHAS powders (Dumoulin et al., 1998). Such results were expected since retrograded starches are reported to exhibit B-type crystallinity (Roos, 1995). For increasing CLD, B-type structure began to be more disorganized while V-type structure became more important relative to B-type structure. Films with moderate CLDs (CLHAS 5.0 and CLHAS-6.0) indeed showed a moderate-low relative crystallinity degree where both B and V-type structures are still present. Further increase of CLD caused the diffractogram patterns to become broader.

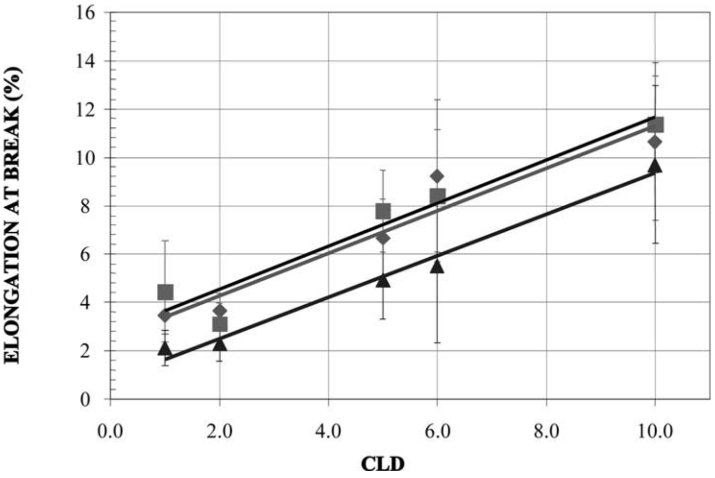

Fig. 3. Elongation at break as a function of CLD for CLHAS films (▲ 0% RH; ■ 65% RH; ◆ 100% RH).

For CLHAS-10.0 (the highest CLD considered in this study), the peaks at $2\theta = 21°$ and $2\theta = 19.5°$ are not well-separated (Fig. 1) showing crystalline structures not well defined. Films become more amorphous, the peak of B-type structure at 19.5° almost disappears and a broader region at $2\theta = 16–24°$ is observed. The higher density of covalent cross-links (8.54 Å) does not allow required flexibility of chains to be close enough for physical stabilization by hydrogen bounds (4.5–5.4 Å) generating thus a low degree of crystallinity (Mateescu et al., 1993).

Figs. 2–4 show the results obtained for tensile mechanical tests. As can be seen, relatively high standard deviations have been found in the computation of the mechanical properties. In this case, firm conclusions cannot be made but some tendencies can be observed.

Young's modulus values were plotted as a function of CLD showing for each %FH a slight decrease with the increase of CLD. Values were comparable with those previously found in different starch-based films (Bader & Göritz, 1994). Very little variation was observed (less than 13%) between CLHAS-1.0 and CLHAS-10.0 even if the amount of epichlorohydrin added for CLHAS-10.0 was 10 times the one for CLHAS-1.0. For instance, at 100% FH the Young's modulus values were of $1.45 \times 10^9$ Pa for CLHAS-1 and $1.38 \times 10^9$ Pa for CLHAS-10 while at 65% FH, the values were $1.82 \times 10^9$ Pa for CLHAS-1 and $1.62 \times 10^9$ Pa for CLHAS-10. The crystallinity may indeed act, as a reinforcing agent in the amorphous structure observed for anhydrous as well as for hydrated samples. A slight decrease of Young's modulus CLD is consistent with results of X-ray diffraction, which show a decrease of crystallinity as the CLD increases.

It can also be noticed that as %FH increases, Young's modulus decreases for each CLD value. As an example, the Young's modulus values for CLHAS-6 decreased from $1.97 \times 10^9$ Pa at 0% FH to $1.51 \times 10^9$ Pa at 65% FH and $1.35 \times 10^9$ Pa at 100% FH. This behaviour was expected since water is known to act as a plasticizer in the CLHAS matrix (Hoseney, 1994). At moderately low CLD (i.e.

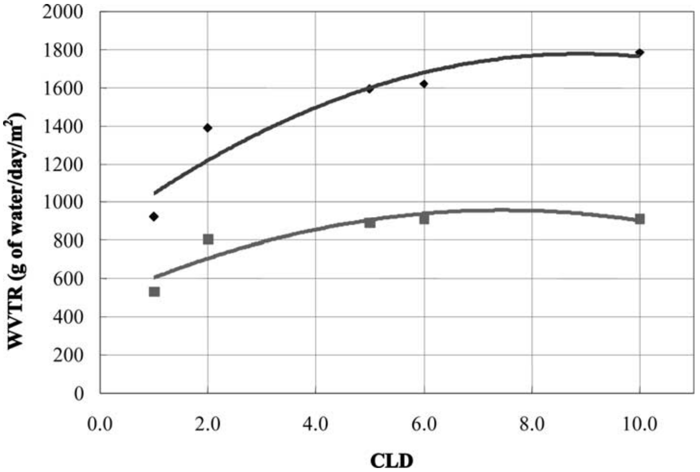

Fig. 4. WVTR as a function of CLD for CLHAS films (◆ $T° = 37°C$, ■ $T° = 23°C$).

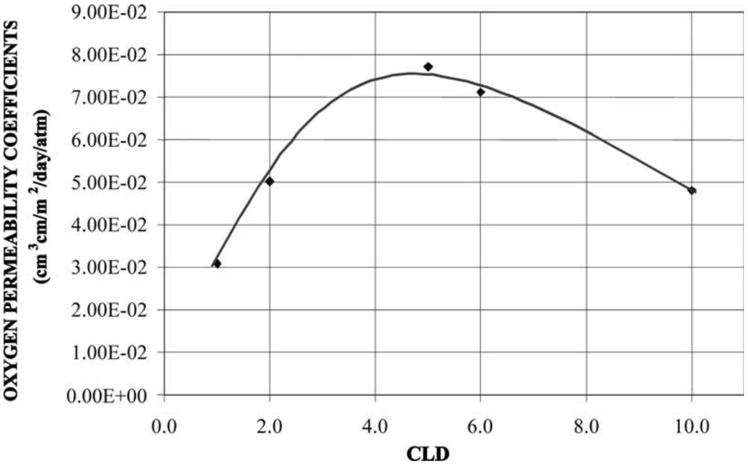

Fig. 5. Oxygen permeability coefficients as a function of CLD for CLHAS films ($T^\circ = 23$°C).

CLHAS-6.0), the polymer is less crystalline and the low cross-linking allows enough flexibility of chains to be stabilized by hydrogen bonding in a polymer network.

Fig. 2 presents tensile strength and stress at break dependency upon CLD. The first part of the curves shows that, for every %FH, tensile strength increases with increasing CLD reaching a maximum around CLHAS-6.0 (Fig. 2a). Generally for elastomers, yield strength increases as CLD increases (Nielson, 1974). The second part of the curves shows that tensile strength of the films decreases as CLD reaches 10.0. Tensile strength decreases when plasticizer is added (i.e. as %FH increases), which is consistent with previous observations (Bader & Göritz, 1994). Thus, the dependency of tensile at break upon the CLD showed also a maximum at CLHAS-6.0. At low CLD, higher crystallinity can explain a certain mobility of the film chains and the low tensile yield strength, while a slight increase of CLD up to CLHAS-6.0 will induce a decrease of crystallinity associated with polymeric network stabilized by H-bonding and higher tensile yield strength. At higher CLD (CLHAS-10.0), the mobility of chains is reduced and lower stabilization by H-association and lower yield strength were found. It should be noted that at low %FH (0.3%), absolute values for the yield strength and stress at break are almost the same for the same CLD (Fig. 2b).

Temperature at which mechanical tests have been performed are well below common starches' $T_g$. Therefore, mobility of the chains in the amorphous part is greatly reduced (Bader & Göritz, 1994) and this could explain why CLHAS films with low %FH show higher brittle stress strain behaviour. When water, as plasticizer, is retained by the CLHAS matrix, the network chains become more flexible and can be deformed more easily. This shows that CLHAS films become more ductile and flexible, which is in agreement with previous observations of Bader and Göritz (1994). Fig. 3 shows the slow transition between brittle behaviour and ductile behaviour with increasing %FH. As expected, percentage of elongation at break generally increases with the increase %FH. Cross-linking seems to have a greater positive effect on elongation at break. This is consistent with behaviour observed in elastomers since a decrease in crystallinity brings an increase in elongation at break (Nielson, 1974).

Fig. 4 shows the WVTR of the CLHAS films plotted as a function of CLD and temperature. A non-linear dependence is observed between WVTR and CLD, especially at 23 °C. The WVTR increases until it reaches a maximum at CLHAS-6.0. The curve at 37 °C is located higher than the one at 23 °C as expected, partly because of the higher value of water vapour pressure in the upper chamber. In both curves, WVTR increases until CLD reaches 6.0. Then, WVTR tends to remain constant or even decreases, especially at 37 °C.

Fig. 5 shows oxygen permeability coefficients values plotted versus CLD which has a well-defined bell-like shape, with a maximum in the region CLHAS-5.0–CLHAS-6.0.

A non-monotonous dependence of some of the mechanical parameters (yield stress and stress at break), WVTR and oxygen permeability coefficient as a function of CLD, was found for CLHAS films. This particular behaviour was also observed on CLHAS tablets. It was shown that the CLHAS-6.0 tablets exhibit longer release times and higher crushing resistance (Ispas-Szabo et al., 2000), lower hydration kinetics of tablets (Dumoulin, Clement, Mateescu, & Cartilier, 1994b), lower swelling in aqueous media (Moussa & Cartilier, 1996), and reduced water evaporation kinetics (Dumoulin et al., 1998), showing that optimal properties are obtained for moderate CLD.

As shown by X-ray diffraction data (Fig. 1), CLHAS polymeric material contains a certain percentage of ordered structure and an important amorphous part. When CLHAS powder is suspended in water, this non-ordered part would be more soluble, more flexible and able to form a gel more rapidly. In homogenous suspension form heated for a prolonged period at $T > T_g$, CLHAS powder's oriented structures were destroyed (gelatinized) and then, when cooled, gelified. By casting, the system loses gradually water and some polysaccharide chains reorganize to form films.

Conditions at which films were produced have a great influence on crystallinity. Previous studies showed that the degree of crystallinity in starch-based films depends on the starch type, crystallization rate and %FH (Cheetham & Tao, 1998; Joupilla, Kansikas, & Roos, 1998; Lawton, 1996; Nara & Komiya, 1983; Rindlav et al., 1997). By changing one of the parameters mentioned earlier, it is possible to obtain starch films with variable crystallinity. In this study, because retrogradation conditions were kept constant for all CLHAS, the formation of more complex crystalline structures in films is facilitated at low CLD (Table 1 and Fig. 1) when more CLHAS chains are part of the crystalline phase. In this particular case, it is possible to establish an inverse correlation between CLD and relative degree of crystallinity (Table 1). It is possible to consider CLHAS as a monolithic system but it could also be viewed as a largely amorphous matrix, possibly containing a microcrystalline phase.

This hypothesis could explain the very slow decrease of Young's modulus as a function of CLD. Observations in other polymeric materials tend to show that CLD should slightly increase Young's modulus (Nielson, 1974). In the particular case of CLHAS films, degree of crystallinity seems to balance the effect of CLD and this maybe why Young's modulus is almost constant at increasing CLD.

The influence of CLD seems to be responsible for the increases shown by the first part of the curves in Fig. 2a and b. In dry films, the chains are able to move in certain limits and to resist to an external strength causing the brittleness, strain stress behaviour of the films. Usually, the cross-linking enhances polymers stability. In the particular case of high amylose starch, this aspect is superposed with specific conformations of polysaccharide chains, which can be modulated by CLD variation. For a limited range of moderate-low CLD, particular conformation can be achieved, conferring a slight increase in mechanical stability of films. In the second part of the curves, decreases in yield strength and stress at break at increasing CLD could also be due to the effect of higher cross-linking which induced high heterogeneity in the spacing between cross-links (Nielson, 1974). This heterogeneity will distribute most of the applied stress on the chains, which are not stabilized by H-bonding. These chains break first, transfer the stress to other chains forcing them to either break or slip in order to relieve that stress. Another explanation could be that if rigid CLHAS crystallites are acting as reinforcement in an amorphous CLHAS matrix, a lower degree of crystallinity will induce a decrease in yield strength (Nielson, 1974).

Balanced effect of CLD and degree of crystallinity at CLHAS-5.0 and CLHAS-6.0 can be seen on Figs 4 and 5. In the first part of the curves with an increase in WVTR and in coefficient of oxygen permeability, crystallites seem to control the diffusion rate. Crystallites are denser than amorphous structures so water and oxygen can hardly diffuses through them. The decreases, constituting the second part of the curves, are probably due to the effect of CLD that begins to take over the effect of degree of crystallinity. Diffusion was slowed probably because of the increased number of cross-links in the network. Arvanitoyannis et al. (1994) suggested than molecular diffusion through the perpendicular axis of an amylose-based films is governed by the activation energy necessary to produce sufficient chains separation to permit the passage of the molecules. At high degree of cross-linking the activation energy will be higher and molecular diffusion will be slowed.

## 4. Conclusions

It is possible to obtain CLHAS films with improved mechanical properties by cross-linking with epichlorohydrin or other bifunctional agents. Microscopic crystalline structures, as well as CLD, have influences on some of the stress strain mechanical properties and permeation properties to water vapour and oxygen. In an attempt to explain the particular behaviour of CLHAS films' properties, a hypothesis of the existence of a balanced effect generated by CLD and degree of crystallinity has been proposed.

By cross-linking high-amylose starch with epichlorohydrin, CLHAS films remain hydrophilic and show brittle stress strain behaviour. Values of WVTR are quite high, mostly because of this hydrophilic behaviour and cross-linking with epichlorohydrin does not have significant effects up to CLD 10.

Flexibility in normal environmental conditions has to be improved in order to produce good quality CLHAS films for various applications.

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