New crosslinked cast films based on poly(vinyl alcohol): Preparation and physico-chemical properties

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Abstract. In this paper, we propose a green route to prepare insoluble poly(vinyl alcohol) (PVOH) cast films with potential application as antimicrobial packaging. First PVOH films were cast from different aqueous solutions and analyzed by Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA) to determine their physical properties under two storage conditions. In order to obtain insoluble films, PVOH was then crosslinked by citric acid (CTR) as confirmed by Nuclear Magnetic Resonance (NMR) analyses. The crosslinking reaction parameters (curing time, crosslinker content) were studied by comparing the characteristics of PVOH/CTR films, such as free COOH content and glass transition temperature (T_g) value, as well as the impact of the crosslinking reaction on mechanical properties. It was found that for 40 and 10 wt% CTR contents, 120 and 40 min of crosslinking times were necessary to bind all CTR respectively. Brittle films were obtained for 40 wt% CTR whereas 10 wt% CTR content led to ductile films. Finally, films containing hydroxypropyl- β -cyclodextrin (HP β CD), chosen as a potential vector of antimicrobial agent, were prepared. The obtained results show that the incorporation of HP β CD in the PVOH matrix does not mainly influence the physical and mechanical properties of the films.

Keywords: mechanical properties, poly(vinyl alcohol), cyclodextrin, crosslinking, cast films

1. Introduction

Poly(vinyl alcohol) (PVOH) is a non-toxic, biodegradable polymer used in food packaging applications owing to its high barrier properties to oxygen and carbon dioxide [1, 2]. However, due to its solubility in water, it is often combined with other polymers in multilayer structures, PVOH being located in the core layer. An alternative route to avoid the use of several polymers would be the crosslinking of PVOH. For this polymer, the most commonly used crosslinkers are dialdehydes, such as glyoxal [3] or glutaraldehyde [4, 5] and polycarboxylic acids. Among the latter, citric acid (CTR) [6, 7], succinic acid [8] and tartaric acid [9] have the advantage of being used as food additives. In partic-

ular, citric acid (food additive European code E330) is interesting for its low price. It is also well-known as crosslinking agent for compounds bearing hydroxyl groups (like polysaccharides and cyclodextrins) as already reported by our group [10, 11].

The aim of this study is to prepare antimicrobial films for food industry, which is emerging in the area of active packaging [12]. In order to confer a prolonged antimicrobial activity to PVOH crosslinked films, we develop an original approach which consists in adding cyclodextrin in the PVOH matrix. Cyclodextrins present several advantages for our application. These biodegradable cyclic oligosaccharides can be used to form inclusion complexes with antimicrobial agents, in order to release it onto

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the surface of the food [13–15]. The hydroxypropyl- β -cyclodextrin (HP β CD), selected for this study, is a derivative of the β -cyclodextrin (food additive E 459) and is non-toxic [16].

The objective of this work is to prepare new films based on PVOH and HP β CD, crosslinked by CTR via a green route. In order to optimize the preparation, different processing parameters such as the PVOH dilution ratio, the formulation of the initial batches with or without cyclodextrin and the crosslinking reaction time are studied. Relationships between processing and physico-chemical properties are investigated using several characterization techniques. The release kinetics of an active principle and the antibacterial activity of the optimized films will be discussed in a following paper.

2. Experimental procedures

2.1. Materials

Poly (vinyl alcohol) (PVOH, $M_w = 31\,000$ – $50\,000\text{ g}\cdot\text{mol}^{-1}$, 87–89% hydrolysis, powder) was purchased from Aldrich Chemicals (St. Quentin Fallavier, France). Hydroxypropyl- β -cyclodextrin (HP β CD) was provided by Roquette (Lestrem, France). This derivative of β -cyclodextrin (β CD) is very soluble in water ($>1000\text{ g/L}$). The mean Molar Substitution (MS), which is the average number of hydroxypropyl groups per anhydroglucose unit, is 0.65. Citric acid (CTR), sodium hydroxide and calcium acetate were commercial chemical grade products, supplied by Aldrich Chemicals.

2.2. Films preparation

For non-crosslinked PVOH films, PVOH was dissolved in distilled water at three concentrations (1, 5, 17 wt%) by mechanical agitation with helical blade (150 rpm), in the temperature range 75–90°C during 3 to 5 hours. The homogeneous solution was then slowly cooled at room temperature, cast onto a silicone plate and dried under a hood for 16 hours. To study the effect of PVOH dilution, a non-crosslinked PVOH film was prepared by compression molding at 220°C, 50 bars, and cooled down to room temperature at 1°C/min.

For crosslinked PVOH/CTR films, CTR was added in the homogeneous PVOH solution. The final reagents concentration was equal to 5 wt%. The solution was stirred by mechanical agitation and cast, using similar conditions as previously described. Once the film was formed, the crosslinking reaction

was achieved through a heat treatment at $130\pm 1^\circ\text{C}$ during increasing times (from 0 to 960 min). Two relative weight compositions of PVOH/CTR films were prepared: 90/10 and 60/40.

Crosslinked PVOH/CTR/HP β CD films, in weight proportions 80/10/10, were prepared following the same protocol as for films without HP β CD. The proportion of HP β CD in the film was fixed considering first an equimolar complex between HP β CD and the later added antimicrobial agent and secondly according to the European directive giving a limit for constituent's migration in food packaging at 10 mg/dm^2 [17].

The thickness of each film was $120\pm 20\text{ }\mu\text{m}$.

Two storage conditions have been used for the films. Dried films were obtained by keeping them at 60°C during 16 hours under vacuum. Hydrated films were obtained by conditioning at 58% Relative Humidity (R.H.) during three days (room temperature in an environmental chamber in the presence of NaBr saturated solutions).

2.3. Thermogravimetric analysis (TGA)

TGA was used to determine the water content and the thermal degradation of films. Experiments were performed on a TA Q50 (TA Instruments, United States) apparatus from ambient to 600°C with a heating rate of 5°C/min. The sample was placed in an open platinum pan under nitrogen.

2.4. Differential scanning calorimetry (DSC)

DSC measurements were performed on a TA Q100 (TA Instruments, United States) apparatus under ultra-pure nitrogen at a heating rate of 10°C/min. PVOH and PVOH/CTR films (with or without HP β CD) were analyzed, during the first heating, from –70 to 220°C and to 150°C, respectively. The glass transition temperature (T_g) was taken at the onset of the heat capacity jump and the melting point (T_m) at the maximum of the endothermic peak. The crystallinity degree (X_c) was calculated using the value of 162 J/g which is the most cited reference melting enthalpy for PVOH crystals [18–20]. Three replicates were analyzed for each film.

2.5. X-ray diffraction (XRD)

Wide-angle-X-ray scattering (WAXS) analysis was performed using a Rigaku rotating anode equipment (Rigaku, Japan) operating at 50 kV and 100 mA. The Cu K α radiation ($\lambda = 1.54\text{ }\text{\AA}$) was selected with a

point focusing monochromator. The WAXS patterns were recorded on MAR2300 imaging plates. Radial Intensity Profiles, $I(2\theta)$, were obtained by azimuthal integration of the 2D patterns.

2.6. Dynamic mechanical analysis (DMA)

DMA measurements were performed on a Rheometrics RSA III (TA Instruments, United States) apparatus operating in tensile mode at a frequency of 1 Hz using a dynamic strain amplitude $\epsilon_0 = 0.05\%$ in the temperature range $-50^\circ\text{C} < T < 150^\circ\text{C}$. Specimens with gauge width and length 6 mm×10 mm were cut out from the films of PVOH crosslinked or not.

2.7. Uniaxial tensile measurements

Uniaxial Tensile testing was conducted on a 4466 Instron (Instron, United Kingdom) machine at room temperature (22°C) using specimens with 24 and 5 mm of gauge length and width, respectively. The tensile tests were carried out at a constant crosshead speed of $14.4\text{ mm}\cdot\text{min}^{-1}$ which corresponds to an initial strain rate of 0.01 s^{-1} . The nominal stress σ_N and the nominal strain ϵ_N were defined as conventionally by the ratio of the force per the initial cross-section and the elongation per the initial length of the sample, respectively. Three replicates have been analyzed for each film.

2.8. Nuclear magnetic resonance (NMR)

^1H NMR was used to check the presence of unreacted reagents in films. Each film was immersed in water during 3 days under agitation. Once the film was removed, the solution containing released reagents was freeze-dried. The obtained solid was dissolved in D_2O and freeze-dried again. The final obtained solid was dissolved in D_2O and analyzed by ^1H NMR using a spectrometer Bruker Avance™ (Bruker Corporation, Germany) 300 MHz at room temperature.

2.9. Free COOH groups quantification

This quantification was undertaken by Ion Exchange Capacity (IEC) method through pH-metric titration using calcium acetate [21]. Each sample was dried 16 hours at 60°C before titration. Typically, 0.1 g of film sample was stirred in 100 mL of a calcium acetate solution during 2 hours. The formed acetic acid was titrated by a standard NaOH solution. The

amount of carboxylic functions was calculated following the Equation (1):

$$\text{IEC} [\text{mmol/g}] = \frac{C_b[\text{mmol/mL}] \cdot V_e[\text{mL}]}{\text{sample weight}[\text{g}]} \quad (1)$$

where C_b and V_e correspond to the concentration and the equivalent volume of the NaOH solution respectively. Three replicates were undertaken for each film.

3. Results and discussion

A TGA study concerning the thermal behavior of the initial reagents was first carried out (Figure 1). We noticed the lower degradation temperature of CTR (170°C) compared to the other reagents. Thus, the compression molding method at 220°C is not suitable for the preparation of PVOH/CTR films. Therefore, the solvent casting method was chosen as an alternative route for the preparation of our films.

Figure 1. TGA profiles of initial reagents

3.1. Effect of dilution on the physical properties of non-crosslinked PVOH films

Polymer dilution is expected to involve a disentanglement of the polymer coils. This phenomenon may induce an increase of crystallinity. This disentanglement may also affect drawability. At high dilution ratio, there is not enough entanglement to ensure a physical crosslinked network behavior, inducing a decrease of the drawability. So a preliminary study was carried out to investigate the effect of dilution on thermal and mechanical properties of PVOH films, in order to fix the optimal dilution ratio for the further study.

The impact of the dilution ratio during the cast preparation on these thermal transitions is detailed in Table 1. Results for the thermocompression molded film are included for the sake of comparison.

Table 1. Thermal characteristics of cast and molded films dried or conditioned at 58% R.H.

Concentration [%w/w]	Cast films						Molded film	
	1		5		17			
Conditioning	dried	58% R.H.	dried	58% R.H.	dried	58% R.H.	dried	58% R.H.
wt% water*	2±2	8±1	1±1	8±1	2±1	7±2	1±1	7±1
T _g [°C]	57±4	7±1	57±1	7±1	41±5	6±1	53±1	6±1
T _m [°C]	192±1	193±1	192±1	193±1	192±1	193±1	192±1	193±1
X _c [%]**	26±1	18±2	25±1	16±1	19±2	11±2	14±1	8±2

*water content determined by TGA

** X_c = crystallinity degree

As regards T_g and T_m , no major difference is observed whatever the film preparation method. In the dried conditions (corresponding to 2±1 wt% of water in the samples), films are characterized by a T_g around 55°C and a melting point T_m at 193°C. For comparison, the reported values for partially hydrolyzed PVOH are 80±5°C for T_g and 185±5°C for T_m [1]. In the present study, these relatively ‘low’ transition temperatures could be explained by the presence of acetate in this hydrolyzed PVOH (87–89%). Under 58% R.H. conditions (corresponding to about 10 wt% of water), compared to dried one, a T_g drop is observed for all samples, relevant to the plasticizer effect of water molecules which disrupt molecular hydrogen bonds between PVOH chains in the amorphous phase.

Crystallinity is higher for cast films than for the molded ones, and tends to increase with the dilution ratio. This phenomenon may be attributed to the effect of disentanglements with dilution which promotes crystallization, as expected [22]. With humidity, a significant decrease of X_c is observed for all samples, suggesting that water molecules destroy crystals. This is consistent with results already reported in literature which have shown that water dissolves gradually crystallites by attacking them at the crystalline/amorphous interface [23].

The evolution of the storage modulus, E' , and loss factor $\tan\delta$, as a function of temperature for molded and PVOH 5 wt% cast films is presented in Figure 2. In the studied temperature range, all samples exhibit only one relaxation characterized by a pronounced decrease of E' and a damping peak of $\tan\delta$. This phenomenon is assigned to the main α_a relaxation associated with the glass transition [24, 25]. As shown in Figure 2, this relaxation is rather independent of film preparation but is very sensitive to water content, in good agreement with DSC results. The peak temperature of $\tan\delta$ decreases from 65°C to about 20°C for dried and 58% R.H. films, respectively. Note

Figure 2. Dynamic mechanical response as a function of temperature of molded and 5 wt% cast PVOH films in dried and 58% R.H. conditions

that the broadness of the peak for humid samples comes from the water evaporation during the experiment.

The yield stress σ_y and the strain at break ϵ_{break} values of PVOH films conditioned at 58% R.H. are reported in Table 2. No result is reported for dried films because, in this case, all samples exhibit a very brittle behavior, related to the drawing temperature well below T_g .

All samples display a ductile behavior. No major influence of film preparation on the strain at break is noticed while an increase of σ_y is observed as initial PVOH concentration increases. One may have expected the reverse evolution considering the variation of the crystal content with the polymer concentration (Table 1). This shows that other structural parameters, than only the crystal content, play an important role in the initiation of plasticity, such as the number of tie molecules.

To sum up, these results do not show any significant difference between all cast films regarding struc-

Table 2. Mechanical data measured for the different films

PVOH concentration [%w/w]	Cast films			Molded film
	1	5	17	
σ_y [MPa]	10.3±0.6	9.1±0.3	13.8±1.8	14.7±1.5
ϵ_{break} [%]	126±18	140±16	127±32	120±36

tural and thermomechanical characterizations. These cast films exhibit similar behavior as the molded film. For the following studies, films will be prepared from a total concentration of reactants of 5 wt%, which is the easiest to process in terms of viscosity.

3.2. Influence of crosslinker amount and crosslinking time on structure of PVOH/CTR films

The crosslinking reaction involved in this study consists in the esterification between hydroxyl functions of PVOH and carboxylic functions of CTR as presented in Figure 3a.

The esterification is activated by the preformation of CTR anhydride under the heat treatment. The CTR being a triacid, residual COOH are present in the three-dimensional network at the end of the reaction. Previous works showed that the esterification occurs from 130°C [11].

A constant temperature of $130 \pm 1^\circ\text{C}$ was applied for all this study. Two weight proportions of CTR (10 and 40 wt%) representative of low and high crosslinker contents were chosen. For both cases, there is an excess of OH due to PVOH compared with COOH

functions. Indeed, there are 10 functions OH for 1 function COOH for 10 wt% CTR films, and 2 functions OH for 1 function COOH in 40 wt% CTR films. The reaction time varied from 0 to 960 min.

As shown on Figure 3b, films are transparent. Visual observations showed that the yellowing and the brittleness increase with CTR content and crosslinking time. With 10 wt% CTR, there is a slight yellowing from 120 min and films are never brittle. With 40 wt% CTR, yellowing is observed from 40 min. Films are brittle from 60 min. The yellowing is due to CTR dehydration and formation of a double bond sensitive to oxidation [26].

To check the efficiency of covalent bonding of the different reagents, eventual unreacted CTR and PVOH were obtained by D_2O extraction of PVOH/CTR films. The ^1H NMR spectra of residual reagents in relation to crosslinking time is presented on Figure 4 (range 4–0 ppm).

The magnitude of the signal for soluble part of the films has been amplified in order to reveal eventual residual compounds and compared to initial reagents. The chemical shifts for PVOH and CTR were attributed to protons also represented on Figure 4.

Figure 3. (a) Expected reaction between PVOH and CTR and (b) picture of PVOH/CTR 90/10 film

Figure 4. Comparison of ^1H NMR spectra for residual reagents in PVOH/CTR films related to CTR ratio and reaction time and protons of CTR and PVOH 88%

We notice that the quantity of residual compounds progressively decreases with crosslinking time. For 40 wt% CTR films, PVOH is not detected after 20 min as well as CTR after 120 min. This means that for this CTR content, a crosslinking time of 120 min is necessary to bind all CTR to PVOH matrix. For 10 wt % CTR films, after 40 minutes, CTR is not detected whereas PVOH is still present after 960 min. This indicates that for 10 wt% CTR, even after 960 min, a weak amount of non cross-linked PVOH chains remains in the films. Nevertheless, the amount of those residual compounds for all the films up to 120 min is very low (less than 0.1%, determined by weight measurements). It is well known that the glass transition of the crosslinked polymers depends not only on the main chain rigidity, but also on crosslinking density. In

this study, the effect of crosslinking conditions on the PVOH/CTR network is thus investigated considering the evolution of the glass transition. In Figure 5a, typical thermograms for several crosslinking times are shown for both kinds of films. All samples exhibit a heat capacity jump, which is clearly curing time-dependent. The evolution of T_g as a function of crosslinking time is represented on Figure 5b for both storage conditions.

In the case of non crosslinked films (time = 0 min), a plasticizer effect of CTR is observed whatever the storage conditions. As expected, this effect is more pronounced for higher CTR concentration. In dried conditions, PVOH exhibits a T_g at 57°C, while this latter decreased to 42°C and 28°C for PVOH/CTR-90/10 and PVOH/CTR-60/40 respectively. Similar drop is observed for hydrated non crosslinked films.

Figure 5. Effect of crosslinking parameters and storage conditions on T_g for different PVOH/CTR films: (a) DSC profiles and (b) T_g as a function of crosslinking time

Then, the T_g progressively increases with crosslinking time for both proportions of CTR. This increase is slower for 10 wt % CTR than for 40 wt% CTR films. In the latter case, an abrupt rise of T_g is observed followed by a leveling off beyond 60 min of heating whatever the storage conditions. Considering that T_g increases with crosslink density, this may suggest that no major evolution of the PVOH/CTR-60/40 network structure occurs above a curing time of 60 min. However, one can observe a decrease of the heat capacity jump ΔC_p from a crosslinking time of 40 to 360 min. Note that this effect does not occur for PVOH-CTR 90-10. This observation may indicate that the amorphous phase content which relaxes at T_g decreases with crosslinking time for the PVOH/CTR-60/40. Several assumptions could be proposed to explain this result. An increase of crystallinity has been rejected because no ordered phase is evidenced for 40 wt% CTR whatever the crosslinking time, as it will be shown later. A subsequent crosslinking reaction inducing a restriction of the molecular motions between chemical entanglements is suggested and will be discussed further below.

For dried films, the value of T_g with high crosslinking time (from 240 min) is surprisingly quite similar for both CTR concentrations. However, T_g rise for 90/10 films is not so smooth. In fact in the dried state, T_g results from several main combining parameters: the crosslinking density and the hydrogen bonds between hydroxyl groups of PVOH chains but also the intrinsic flexibility of PVOH and CTR chains. As shown in literature, these two parameters acted by a compensation effect between the weakening of the chemical network and the plasticizing effect of the introduced more or less flexible linkers [27]. When films are hydrated and swollen under equilibrium, the decreasing gap of T_g for 10 wt% CTR is much more pronounced than the one for 40 wt% CTR. Indeed, the greater proportion of

PVOH hydroxyl groups is, the more they could interact with water molecules resulting in a more pronounced plasticizer effect of water.

The quantification of residual (or free) COOH groups could also provide some additional information about the formation of the PVOH-CTR network. The esterification reaction, catalyzed by intramolecular CTR anhydride formation (Figure 6) highlighted the origin of these free COOH groups. If CTR is consumed according to this intramolecular mechanism, namely 2/3 COOH functions have reacted. Then, the final theoretical COOH amount values should be around 0.5 and 1.9 mmol/g for PVOH/CTR-90/10 and PVOH/CTR-60/40 films respectively.

The comparison of free COOH quantification and T_g evolution for the two films is given on Figure 7. As expected, free COOH functions amount decreases with crosslinking time for both proportions of CTR. A higher decrease is obviously observed for films with 40 wt% CTR. After 120 minutes, the amount of residual COOH functions remains constant regardless initial amount of CTR. At this crosslinking time, all CTR is covalently bound as previously proved by NMR (Figure 4). For PVOH/CTR-90/10 (Figure 7a), the experimental value (0.60 ± 0.12 mmol/g) is close to the theoretical one (0.5 mmol/g). Note that the plateau for T_g and residual COOH are reached for the same crosslinking time (90 min). In the case of PVOH/CTR-60/40 (Figure 7b), the behavior is different. First the COOH experimental value at the plateau (0.76 ± 0.13 mmol/g) is lower than the theoretical one (1.9 mmol/g). Then, the maximum in T_g is achieved from around 40–60 min while at this time COOH value is still decreasing. In addition, we notice that at 40–60 min, the COOH value is about 2–3 mmol/g and close to the calculated one according to the crosslinking mechanism. This can be explained by the fact that for high proportions of CTR, the esterification occurred in two steps. The

Figure 6. Scheme of intramolecular CTR anhydride formation and esterification between CTR and A-OH = PVOH

Figure 7. Free COOH groups and T_g of hydrated PVOH/CTR films as a function of crosslinking time for (a) PVOH/CTR 90/10 and (b) PVOH/CTR 60/40

first one may correspond to the grafting of CTR on PVOH chains. Then the spatial proximity between COOH functions already grafted allows the formation of anhydrides via an intermolecular mechanism and therefore additional post-esterification reaction involving chemical groups close to previous crosslinking points. This phenomenon has no major effect on T_g value neither on the global crosslinking degree but may result in a decrease of the heat capacity jump at T_g as previously mentioned.

3.3. Physical and mechanical characterization of PVOH/CTR films

It is interesting to check if some crystallinity is present in initial PVOH/CTR films and remains after crosslinking reaction. PVOH/CTR films exhibit a degradation phenomenon well below the melting point of PVOH ($T_m = 185 \pm 5^\circ\text{C}$). Therefore, DSC cannot be used to highlight any melting peak in this case. So, X-ray diffractograms of PVOH/CTR films were recorded as a function of crosslinking time (Figure 8). Whatever the CTR content and crosslink-

ing time, only one broad diffraction located at around $2\theta = 20^\circ$ is observed without any evidence of crystalline peak which suggests that all samples are mainly in disordered state.

In Figure 9, typical DMA curves of three hydrated PVOH/CTR-90/10 films are shown: non cross-linked one and two crosslinked ones. An increase of the main relaxation temperatures with crosslinking time is observed, in good agreement with previous DSC results. As expected, the storage modulus E' increases with the heating time, below as well as above T_g , relevant to an increase of the crosslink density which rigidifies the polymer network. Additionally, one can notice the presence of two peaks in the $\tan\delta$ curves indicating various relaxations in the amorphous phase, even in the non crosslinked sample. This could suggest that the concentration of CTR is not homogeneous at local scale inside the sample.

The effect of crosslinking conditions on tensile behavior is illustrated on Figure 10. For the non-crosslinked films ($t = 0$ min), one can observe the

Figure 8. WAXS patterns of hydrated PVOH/CTR films for different crosslinking times

Figure 9. Dynamic mechanical response as a function of temperature of hydrated PVOH/CTR 90/10 films for different crosslinking times

Figure 10. Nominal stress–strain curves of the PVOH/CTR films for different proportions of CTR and crosslinking times under uniaxial drawing at $T = 22^\circ\text{C}$ at 58% R.H.

plasticizer effect of CTR indicated by an improvement of ductility as CTR concentration is increased. PVOH/CTR-60/40 samples exhibit a brittle behavior from 40 min curing, related to the highly crosslinking density preventing any plastic deformation. Owing to their brittleness, we decided to focus our attention only on the films containing 10% CTR. All samples exhibit a homogeneous deformation. The stress level increases and the strain at break significantly decreases as the crosslinking time is

increased. This behavior is related to the reduction of the chemical entanglement mass involving an enhancement of the rigidity and reduction of the limit of extensibility of chain segments between entanglements.

3.4. Influence of HP β CD on films properties with 10% of CTR

One of the main objectives of this study is to incorporate HP β CD in the polymer matrix. This cyclodextrin derivative would be used as a vector for prolonged release of a food preservative. As PVOH, HP β CD possesses OH functions which may react with COOH functions of CTR, allowing it to take part of the three-dimensional network. Because films with 40 wt% CTR are too brittle from 40 min of crosslinking, only films containing 10 wt% CTR are studied. Thus, the influence of the HP β CD addition on film properties was investigated on films containing 80 wt% PVOH, 10 wt% HP β CD and 10 wt% CTR using similar approach as previously. In that case, PVOH/HP β CD/CTR-80/10/10 and PVOH/CTR-90/10 cast solutions contain similar quantities of OH groups per gram.

Figure 11. ^1H NMR spectra in D_2O of residual reagents of PVOH/CTR/HP β CD films with 10 wt% CTR and 10 wt% HP β CD for three crosslinking times

The ^1H NMR spectra of unreacted reagents obtained by solvent extraction for PVOH/HP β CD/CTR cross-linked films is presented on Figure 11. As previously, the intensity of the spectra has been magnified to reveal the low amounts of residual compounds. As observed for PVOH/CTR films (Figure 4), CTR is completely bound at 120 min, whereas PVOH and HP β CD are not completely bound even after 960 min. However the amounts of residual reagents are very low ($<0.1\%$, determined by weight measurements).

The kinetics of the crosslinking reaction is evaluated following the free COOH content as a function of crosslinking time (Figure 12). Results show the same behavior as for PVOH/CTR films with 10 wt% CTR (Figure 7). COOH functions amount decreases with crosslinking time and reaches a quasi-plateau. The final amount of the free COOH groups is the same with or without HP β CD. The concentration of 10 wt% HP β CD does not modify the crosslinking kinetics.

Figure 12. Free COOH quantification of PVOH/CTR and PVOH/HP β CD/CTR films with 10 wt% CTR as a function of crosslinking time

Figure 14. Strain at break at 22°C of PVOH/CTR and PVOH/HP β CD/CTR films, conditioned at 58% R.H., as a function of crosslinking time

It is also important to study the effect of HP β CD on film flexibility through T_g analysis (Figure 13). We notice no plasticizer effect of HP β CD on non-crosslinked films ($t = 0$ min). The incorporation of HP β CD in the polymer network seems to rigidify it. HP β CD is a bulky and rigid molecule. Its presence should decrease the global mobility of polymer chains.

Finally, drawing experiments were carried out and values of strain at break are reported on Figure 14. For all crosslinking times, the presence of HP β CD does not affect significantly the drawability of films. All samples present a ductile behavior.

4. Conclusions

Films based on PVOH and crosslinked with CTR, have been prepared in two steps by solvent casting method followed by heat treatment. Different characteristics of the films (chemical structure, T_g , crystallinity and tensile properties) were studied in relation to their formulation and the crosslinking time. Films with high content of CTR (40 wt%) are too brittle for the considered food application while films

Figure 13. (a) DSC profiles of PVOH/HP β CD/CTR films and (b) values of T_g as a function of crosslinking time with or without HP β CD

with low content of CTR (10 wt%) are transparent and show a ductile behavior. However, we highlighted that even after 960 min of crosslinking, a weak quantity of PVOH is not bound. We could expect that an intermediate formulation of PVOH and CTR could be more suitable for the targeted application. Moreover, during the crosslinking reaction, a part of COOH functions remains free. We could take advantage of these acid functions for further food storage. Finally, the incorporation of 10 wt% of cyclodextrin derivative as food additive carrier does not influence the characteristics of the films containing 10 wt% CTR. This formulation will be used for further studies.

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