

PREPARATION AND CHARACTERIZATION OF CROSSLINKED POLY (VINYL) ALCOHOL FILMS WITH WATERPROOF PROPERTIES

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ABSTRACT

Objective: The purpose of this work is to cross link PVA with glutaraldehyde to develop new films with increased waterproof properties.

Methods: Cross linking of PVA with glutaraldehyde was conducted at 70°C at a 1:10 and 1:5 PVA: glutaraldehyde ratios. pH and reaction times of 5.5 and 6.5 and 1 and 6h were employed, respectively. The resulting films were analyzed for Cross linking degree, crystallinity, water sorption, swelling, contact angle, and tablet water uptake when stored for 45 days at 100% relative humidity.

Results: Reactions conducted at a pH of 5.5 rendered the largest Cross linking degrees. Cross linked films were less crystalline, flexible and hydrophilic. Further, they had a lower ability to swell and uptake water than the parent PVA. Moreover, compacts stored for 45 days and coated with cross linked films had a low water sorption ability than those coated with non-crosslinked PVA.

Conclusion: Cross linking of PVA with glutaraldehyde rendered films with a tight polymeric network, a reduced hydrogen bonding capacity, more hydrophobicity, and better waterproof properties in compacts containing hydro labile drugs.

Keywords: Poly (vinyl) alcohol, Glutaraldehyde, Cross linking, Waterproof, Film, Dip- coating.

INTRODUCTION

Over the past few years, there has been a growing interest to develop materials with a film forming capacity and waterproof properties which can be used to protect hygroscopic bioactive substances. These films can be placed on the surface of tablets to reduce water vapor and oxygen migration and to stabilize hygroscopic components [1]. They could also allow for a controlled release of moisture sensitive drugs. On the other hand, formulation of film-based drug products involves the optimization of several factors including the selection of the appropriate film forming polymer and testing the resulting physical properties [2]. In this scenario, PVA is an excellent candidate since it has an outstanding chemical stability and excellent film forming properties. It is also biodegradable, innocuous, non-toxic, non-carcinogenic and has good biocompatible properties. It has also been used as a water-soluble film for packaging [3].

Nevertheless, PVA itself does not have the ideal water vapor barrier and mechanical properties due to its elevated sensibility to environmental conditions which limits its application as a desirable film coating material [4]. In an attempt to improve the functionality of PVA-based films, several researchers have pursued physical and chemical treatments to modify the polymer network [5]. Physical treatments included UV and γ -irradiation; whereas, chemical treatments have been attempted by cross-linking with aldehydes, polycarboxylic acids, TEOS and others [6, 7]. Aldehydes bond easily to PVA, but exhibit some toxicity and high cost, which limits their further application [8]. Conversely, bi-functional aldehydes, especially, glutaraldehyde (GA) are the preferred Cross linking agent due to its low cost, commercial availability, good reactivity and very low toxicity. GA reacts with the hydroxyl functional groups of PVA chains, under acidic conditions forming acetal bonds [9]. However, there are no reports on the specific applications of this cross linked material as waterproof material for hydro labile drugs. In this study, the effect of PVA-glutaraldehyde ratio (1:5; 1:10), pH (5.5 and 6.5) and reaction time (1 and 6h) on the physicochemical and water sorption properties of the resulting cross linked PVA films were evaluated.

MATERIALS AND METHODS

Materials

Poly (vinyl) alcohol (lot P04102697) with 95.3% hydrolysis degree and 80 kDa molecular weight was purchased from Belchem International

(Long wood, FL). Glutaraldehyde (lot 02, 50% solution) was obtained from Flow Chem S. A. (Medellin, Columbia). Acetone (lot K449111814-337) was obtained from Calbiochem (Darmstadt, Germany).

Cross linking reactions

Approximately, 5 g of PVA was first dispersed in distilled water for 30 minutes and then dissolved at 90 °C with magnetic stirring (RH-KT/C, IKA, Campinas, Brazil) for 30 minutes to obtain a 5% w/v PVA concentration. Approximately, 50 mL of this solution was transferred to a round bottom flask containing 50 mL of a 50% v/v glutaraldehyde solution and pH was adjusted according to the conditions listed on table 1. This flask was put in a reactor composed of a heating mantle (Centricol, Medellin, Columbia) coupled with a condenser. The reaction runs were conducted at a 1:5 and 1:10 PVA: glutaraldehyde ratios at 70°C, a pH of 5.5 and 6.5, for 1 or 6h.

Table 1: Reaction conditions for Cross linking PVA with glutaraldehyde

pH	PVA: Glutaraldehyde ratio	Time (h)
5.5	1:10	1
5.5	1:10	6
5.5	1:5	1
5.5	1:5	6
6.5	1:10	1
6.5	1:10	6
6.5	1:5	1
6.5	1:5	6

The wet gels obtained were then washed with acetone, filtered and dried on an oven (U50, Memmert, Schwabach, Germany) at 45°C for 48h and then kept in a desiccator over silica gel.

Fourier transforms infrared characterization (FT-IR)

The analysis was conducted on a Perkin-Elmer spectrophotometer (Perkin Elmer, CA, USA) equipped with the Spectra software (Spectrum BX, vs. 5.3.1, CA, USA). Spectra were recorded between 4000 and 400 cm^{-1} and the resolution, interval length and number of scans employed were 16, 2.0 and 16 cm^{-1} , respectively.

Powder X-ray diffractograms

Powder X-Ray diffractograms were obtained on a PANalytical diffractometer (Model, Empyrean 2012, Westborough, MA) operated at 40 kV and 30 mA, and equipped with a monochromatic Cu K α ($\alpha_1=1.5460 \text{ \AA}$, $\alpha_2=1.54438 \text{ \AA}$) X-ray radiation. Diffractograms were obtained over a 5 to 50° 2 θ range at a scan step and step time of 0.039 and 38.2 s, respectively. The degree of crystallinity was calculated from the Peak fit software (Seasolve, Inc, Framingham, MA) by separating the crystalline and amorphous scattering radiation using the baseline selection tool.

Swelling ratio

Dry square films (5 mm thick, 10 mm in diameter) were weighed and immersed in a 20 mL distilled water bath at 37°C. At different time points, the films were taken out, the excess water was carefully removed with tissue paper from the film surface, and films were weighed immediately. This analysis was conducted for 72h. Swelling ratios were determined from the weight change before and after swelling and expressed as:

$$SR = (w_t - w_0) / w_0 \quad (1)$$

Where, W_t is the swollen film weight at time t and W_0 is the film initial weight.

Water sorption studies

It was performed on a moisture sorption analyzer (Aqualab, Decagon Devices, Pullman, WA). The sample pan assembly was cleaned with ethanol and dried before each run. Samples of ~ 3g were tested. Even though dried samples were employed, an initial drying phase at 45°C was executed. Once a stable reading (weight change of no more than 0.01%) was obtained for 10 min, the sample was considered dry. Runs were conducted at 25 °C at water activity steps from 0.1 to 0.9. Water uptake in the sample was considered at equilibrium when a stable reading (a weight change of no more than 0.01% or maximum drying time of 240 min) was reached.

The resulting sorption curves were fitted to the GAB (Guggenheim, Andersen and de-Boer) sorption model [10]. This model has a theoretical background derived from the BET theory with a simple mathematical form with only three parameters (C , k and m_m). These parameters have a physical meaning in terms of the sorption process and different from the BET model and its fitting range is between 0 and 1 water activity.

The GAB equation expressed as follows:

$$m = \frac{k \cdot a_w \cdot m_m \cdot C_{GAB}}{(1 - k \cdot a_w) \cdot (1 - k \cdot a_w + C_{GAB} \cdot k \cdot a_w)} \quad \dots(2)$$

$$C_{GAB} = D \cdot e^{(H_1 - H_m) / RT} \quad \dots(3)$$

$$k = B \cdot e^{(H_L - H_m) / RT} \quad \dots(4)$$

Where, m is the grams of water per gram of PVA, m_m is the monolayer capacity or weight of water when the surface of one gram

of PVA is covered by a monolayer (g/g), a_w is the water activity. C_{GAB} and k are energy constants. B and D are constants, usually taken as 1. H_1 is the heat of sorption of water in the first layer (kJ/mol). H_m is the heat of sorption of water in the multilayers (kJ/mol). H_L is the heat of liquefaction (J/mol). R is the universal gas constant (8.3145 J/molK) and T is the absolute temperature. The fitting procedure was performed using the Statgraphic software vs XV (Warrenton, VA). A non-linear regression was then applied with the principle of least squares.

Contact angle analysis

Rectangular dry films (10x5 mm) of 1 mm thickness were used for the analysis. Contact angles were determined on a goniometer (4003, Bausch & Lomb, Tokyo, JP) according to the sessile drop method. A digital camera (DCR-SX45, Sony, Tokyo, Japan) was used for the data analysis. A droplet of ~25 μ L was put carefully onto the upper surface of the film and the contact angle was reported after 0.5 s of spreading.

Physical properties

The true density of films was measured on ~2 g of sample employing a Helium pycnometer (AccupycII 1340, Micromeritics, USA). Moisture content was determined on a Shimadzu infrared moisture analyzer (MOC63U, MA, USA) loaded with ~0.5 g of sample and operated at 110°C for 10 min. Bulk density was obtained by taking the dimensions of cubic films previously weighed in an analytical scale. Porosity was determined as reported previously [11].

Statistical analysis

The analyses were performed by a completely randomized design. Data were tested by the analysis of variance (ANOVA) using the Design Expert® software 8.04 (Stat-Easy Inc., Minneapolis). The results were considered to be statistically significant when $\alpha \leq 0.05$.

RESULTS AND DISCUSSION

Cross linking reactions and FT-IR characterization

The original PVA is not adequate as a film coating material due to its high stickiness and hygroscopicity and low plasticity requiring the addition of plasticizers and other additives. Fortunately, PVA can be cross linked with GA to improve its film forming properties. For instance, hydroxyl groups of PVA react with the aldehyde groups via acetal linkage formation. This reaction occurs twice for each aldehyde group present. For example, there are three different ways GA could cross link PVA [12]. The first one implies an intermolecular cross linking and occurs between different polymer chains leading to a high gelation propensity. The second way is an intramolecular cross linking and happens internally in a single polymer chain leading to a more fluid polymer due to contraction of the polymer coils. The third way is described as an incomplete intramolecular cross linking of a single polymer chain (fig. 1).

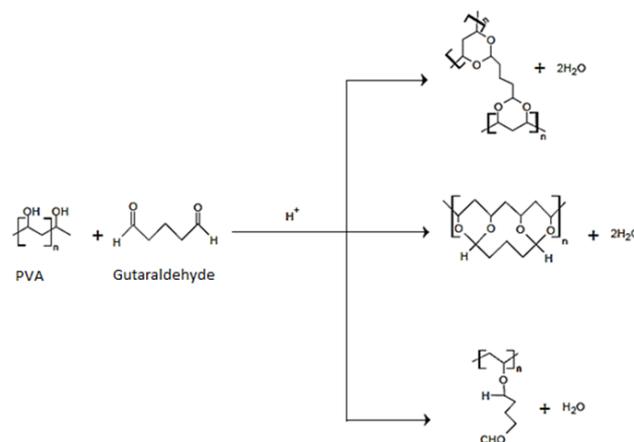


Fig. 1: Different types of Cross linking reactions with GA. A. Intermolecular. B. Intra molecular C. Incomplete or pendant from one chain

GA easily cross linked PVA, especially at a low pHs forming a white gel. Thus, at a pH of 2.5 a gel was formed immediately, whereas at a pH of 2.6, 3, 4 and 5 it took 5, 10, 45 minutes and 5 h to form a gel, respectively, which upon drying become a film. The FT-IR spectra of these reactions are shown in fig. 2. Even though an excess of GA (25 % v/v) with respect to polymer (2.5 or 5%, w/w) was employed, at

pHs from 2.5 to 4.0 a band typical of aldehydes was shown at 2750 cm^{-1} indicating a free aldehyde moiety was still present in the single polymer chain due to an incomplete intra molecular Cross linking besides the intermolecular Cross linking that also took place. However, at a pH of 5.5 only intermolecular Cross linking was expected to occur due to the absence of this band.

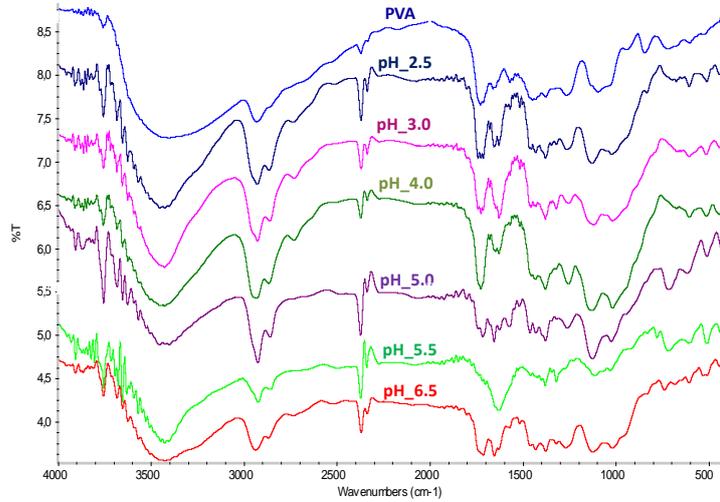


Fig. 2: FT-IR spectra showing the effect of pH on the progression of Cross linking reaction with glutaraldehyde

The most characteristic bands of PVA and their respective assignments are observed between 3550 and 3200 cm^{-1} and are ascribed to the O-H stretching from the intermolecular and intra molecular hydrogen bonds. The absorption band at 2930 cm^{-1} and a shoulder at 2860 cm^{-1} correspond to the stretching of $-\text{CH}_2-$ and $-\text{CH}-$, respectively. Further, the band at 1730 cm^{-1} and the shoulder at 1660 cm^{-1} correspond to the unhydrolyzed acetate groups. The band at 1730 cm^{-1} is from carbonyl group stretching of acetate ion and a shoulder at 1660 cm^{-1} is from C-O associated with carbonyl group of unhydrolyzed acetate. Moreover, the bands shown at 1570 cm^{-1} and 1266 cm^{-1} are due to the presence of some carbonyl groups from acetate (CH_3CO). The band at 1450 cm^{-1} is attributed to $-\text{CH}_2-$ bending. The band at 1097 cm^{-1} corresponds to C-O unbounded and it could be associated with PVA crystallinity. The band at 850 cm^{-1} is attributable to rocking vibration of the methylene groups ($-\text{CH}_2-$) [13].

Several changes occurred in the FT-IR spectra as a result of the Cross linking reaction at pHs of 5.5 and 6.5 (Figs. 3,4). The magnitude of the band at 3402 cm^{-1} appeared reduced and became less wide and sharp indicating a reduced interaction of hydroxyl groups via hydrogen bonding with incoming water molecules. These results suggest that hydrogen bonding becomes weaker in cross linked PVA products compared to pure PVA because most of the initial OH groups were transformed to acetal linkages. As a result, a partial removal of the hydroxyl groups by the ether moieties was attributable to the formation of acetal bridges, coming from two vicinal hydroxyl groups of the parent PVA. As a consequence, the original inter and intra hydrogen bonding network was disrupted rendering a tight polymer structure due to the formation of GA bridges between the chains via acetal bond formation.

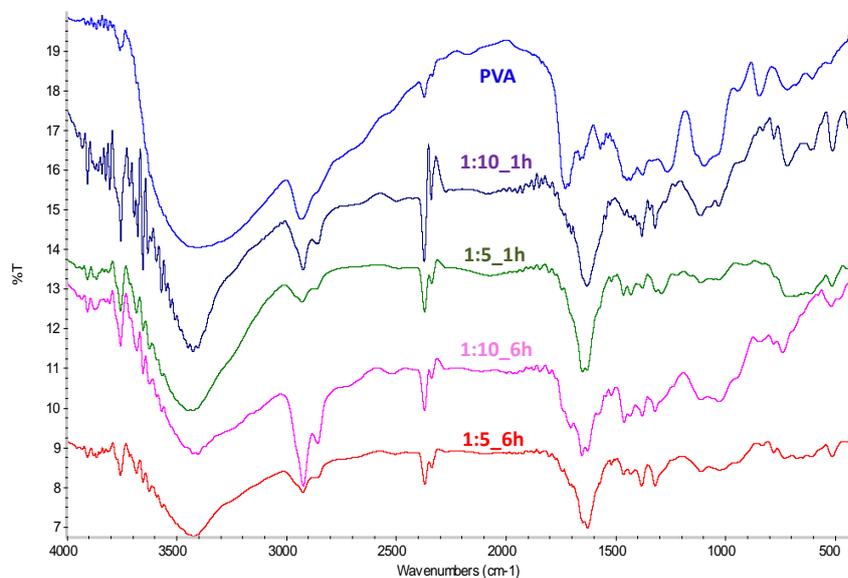


Fig. 3: FT-IR spectra showing the effect of PVA: GA ratio and reaction time on the progression of Cross linking reaction at a pH of 5.5

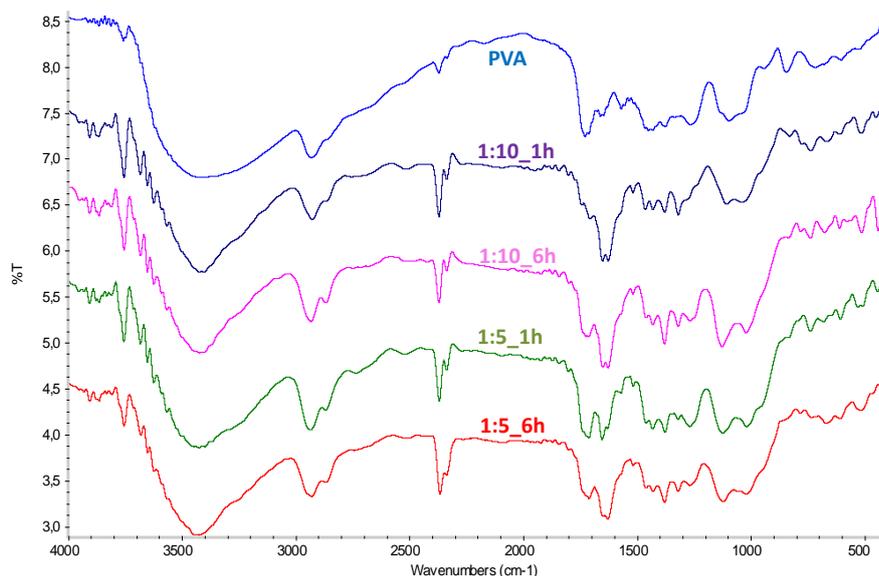


Fig. 4: FT-IR spectra showing the effect of PVA: GA ratio and reaction time on the progression of Cross linking reaction at a pH of 6.5

This new dense chemical network is defined by the intensification of the band at 2860 cm^{-1} corresponding to the symmetric CH stretching. Further, a shoulder at 2750 cm^{-1} could be attributed to C-H asymmetric stretching of the methyl group in the aldehyde moiety and was present only in materials produced at very low pHs (pH 2.5-4.0). This might suggest the formation of intra molecular crosslinking leaving one of GA free. At the same time, the bands at 1460 cm^{-1} and 850 cm^{-1} decreased and almost disappeared since CH and CH_2 groups are now participating in the acetal bonds. Further, the band at 1730 cm^{-1} corresponding to C=O from the residual acetal disappeared as the Cross linking reaction evolved. The complete disappearance of this band occurred at pH of 5.5 and also indicated that most of the aldehyde groups of GA were used in the Cross linking reaction with O-H groups of PVA chains. In fact, at this pH independent of the reaction time and amount of PVA a complete Cross linking was observed (fig. 3). The decrease of the CO peak on those samples is also explained by the possible hydrolysis of acetate groups at acid pH with the progression of Cross linking reaction with GA. In general, a tight polymer network induced by Cross linking was promoted by pH rather than time and the amount of PVA used. On the other hand, the largest change observed in the FT-IR spectra corresponded to the formation of an intense band at 1660 cm^{-1} . Moreover, the band at 1097 cm^{-1} of the parent PVA attributable to C-O appears reduced and a new small band emerged at 1030 cm^{-1} . This could indicate a reduction of crystallinity and hence, a decrease of the hydrogen bonded in the crystalline regions. The peak at 1380 cm^{-1} correspond to the bending vibration of CH and the disappearance of the band at 1097 cm^{-1} and emergence of a band at 1113 cm^{-1} suggests that the backbone structure of PVA was also altered upon Cross linking.

Although it is accepted that acid media favors Cross linking with GA, results indicate that a complete reaction is not favored at pH <5.5 and could be even uncompleted at a pH >5.5 . This could be explained by the continue formation and destruction of acetal bonds during the acid catalysis. On the other hand, at pH of 6.5 the slightly neutral environment does not favor the acid catalysis, especially at long reaction times (6h). The degree of Cross linking associated to the formation of acetal bridges could be calculated as a percentage from the absorption of the CO band at 1660 cm^{-1} with respect to the absorption of CO band at 1730 cm^{-1} . Further, the hydroxyl band on each cross linked material was evaluated against the initial hydroxyl band of PVA by using a baseline integration method. These results are listed in table 2 and showed a large Cross linking degree and reduction of hydrogen bonding in reactions conducted at a pH of 5.5 independent of the PVA amount and reaction time employed. Thus, is clear that reactions conducted at a pH of 5.5 resulted in higher degree of Cross linking and consequently, a large reduction of available hydroxyl groups.

In a complete reaction, four hydroxyl groups from PVA would react with one molecule of GA leading to intermolecular Cross linking. The amount of GA in respect to PVA ranged from 5 to 10 fold to achieve a complete intermolecular Cross linking. However, the degree of Cross linking varied and did not depend on the initial amount of PVA (2.5 or 5 g) or the reaction time (1 or 6h). The un reacted PVA and GA were not present in the final products since they are highly hydrophilic and water soluble, and hence, their excess was eliminated during the subsequent neutralization and washing steps. On the other hand, yield or product mass improved with long reaction times.

Table 2: Physical properties of PVA and glutaraldehyde-cross linked films

Reaction conditions	Hydroxyl groups reduction (%)	Cross linking degree (%)	MC (%)	Product mass (g)	DC (%)
pH5.5_1:10_1h	65.8	98.6	0.08	3.7	34.3
pH5.5_1:10_6h	53.5	93.2	0.92	4.4	39.9
pH5.5_1:5_1h	30.8	98.9	0.61	2.5	39.1
pH5.5_1:5_6h	44.6	96.1	0.12	3.9	37.2
pH6.5_1:10_1h	55.8	93.1	2.12	2.7	32.7
pH6.5_1:10_6h	50.5	84.3	0.52	4.2	39.6
pH6.5_1:5_1h	49	44.8	0.41	3.7	34.0
pH6.5_1:5_6h	19.7	70.6	0.55	3.5	39.0
PVA	0	0	2.9	N.A	74.5
			<i>p-value</i>	0.86	0.50

MC: Moisture content; DC: degree of crystallinity

XRD and thermal characterization

As discussed previously, the decrease of crystallinity was observed from the reduction of the intensity of C-O stretching at 1097 cm^{-1} . The intensity of this peak is influenced by the crystalline portion of the polymeric chains in the region of the chain where an intra molecular hydrogen bond is formed between two vicinal OH groups of the carbon chain. The crystalline region was also dependent on the number of OH groups of PVA and decreased by Cross linking as seen

by the reduction of the intensity of the bands at 3400 cm^{-1} . These results were confirmed by the diffraction patterns of the cross linked materials which revealed the absence of the main peak exhibited by the PVA precursor ($19.4^\circ 2\theta$). The degrees of crystallinity are listed on table 2 and indicate that acetal bridges induced a significant reduction of crystallinity to less than 40% restricting the mobility of PVA chains promoting amorphization due to the hydrogen bonding reduction. Other minor crystalline peaks of PVA were observed at 11.6 and $40.5^\circ 2\theta$ and disappeared in the cross linked products.

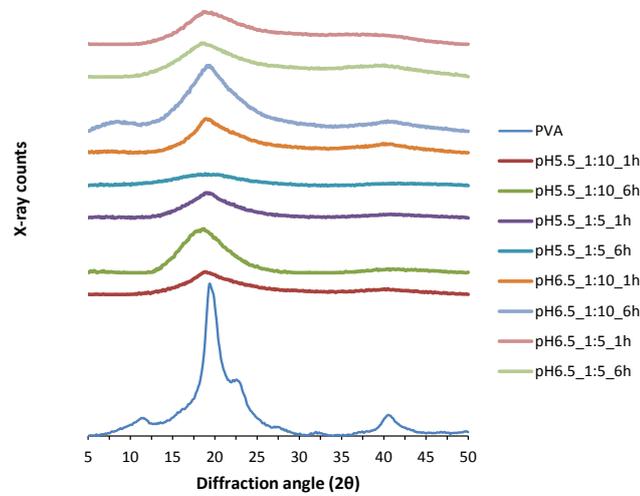


Fig. 5: X-Ray diffractograms of PVA and cross linked films

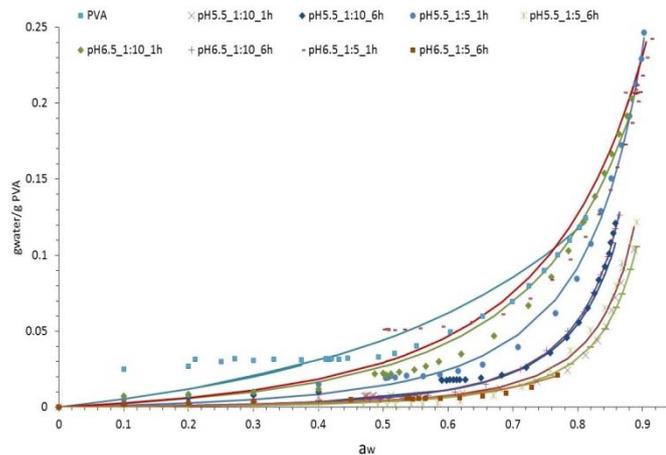


Fig. 6: Water sorption isotherms of PVA and cross linked films

Water sorption analysis

Water sorption isotherms of PVA and cross linked materials are shown in fig. 6. All samples exhibited a typical type III isotherm indicating weak polymer-water interactions showing a characteristic low uptake at low water activity and a strong increase in sorption at higher water activity [14, 15]. The initial PVA had a crystallinity degree of 74.5% showing a high hydrophilic character due to the hydroxyl groups and the 5% acetate moieties still present in the polymer. As a result, a strong hydrogen bonding interaction between the hydroxyl groups of PVA and incoming water molecules is expected to occur. These hydroxyl groups play a crucial role in relation to water molecules. The resulting parameters from the GAB model are listed in table 3 and data fitted well to this model ($r^2 \geq 0.90$).

The monolayer capacity (m_m) value expresses the amount of water that is sufficient to form a layer of water molecules of one molecule thickness on the polymer surface. The monolayer capacity indicates

that PVA had the highest hydrophilicity and hence, affinity for water. Conversely, cross linked materials showed lower monolayer capacities. This might be explained by their limited hydrogen bonding capacity compared to that of PVA because of the formation of hydrophobic acetal bonds. PVA also had the highest enthalpy for the multilayer sorption indicating that the formation of secondary sites is more favorable even before the monolayer is complete and as a result, water molecules are expected to pile up because of the low enthalpy requirement. Further, in all cases the energetic of monolayer adsorption (c) was lower than the energetic of multilayer (k). Except for PVA, in most materials k values ranged from 0.8-1.0 and hence, it is expected no distinction between multilayer molecules and liquid water and as a result, the multilayer molecules are not completely structured in layers but have some characteristics as the liquid.

On the other hand, for PVA water molecules in the multilayer are strongly structured and differed considerably from the bulk liquid

water due to its low k value (~ 0.6). PVA also had the largest monolayer sorption capacity followed by two samples produced at pH of 6.5 (labeled as pH6.5_1:5_1h and pH6.5_1:10_6h). This means that the primary sorption sites, especially for PVA are capable of more hydrogen bonding formation than cross linked materials.

In cross linked materials, the primary sites for sorption are already taken in the acetal linkages leaving few hydroxyl groups in the

polymer chain available for bonding water molecules. As cross linked products become less hydrophilic, water molecules are sorbed more tightly in the active sites and thus, the formation of a monolayer is energetically more favored than the formation of a multilayer. Moreover, cross linked products had the lowest multilayer sorption enthalpy indicating that the formation of a monolayer is more likely to occur and remain in this state than forming secondary and ongoing water layers.

Table 3: Water sorption properties and GAB parameters of PVA and its cross linked films

Reaction conditions	Contact angle (degrees)	Porosity (%)	k	m_m	c	H_m-H_L	H_1-H_m	r^2
						(kJ/mol)	(kJ/mol)	
pH6.5_1:10_1h	52.6 ± 4.3	31.3±0.2	0.83	0.29	0.08	0.46	-6.3	0.989
pH6.5_1:10_6h	51.0 ± 5.2	40.5±0.1	0.99	0.35	0.01	0.02	-11.7	0.999
PVA	25.7 ± 6.6	22.2±0.7	0.57	0.91	0.09	1.39	-6.0	0.903
pH6.5_1:5_6h	30.9 ± 5.9	68.3±0.2	1.00	0.01	0.27	0.00	-3.2	0.984
pH5.5_1:10_1h	75.8±1.4 ± 1.4	51.5±0.5	1.00	0.07	0.03	0.00	-8.7	0.981
pH6.5_1:5_1h	63.2 ± 6.0	53.3±0.1	0.81	0.53	0.05	0.52	-7.4	0.987
pH5.5_1:5_6h	59.9 ± 7.0	49.2±0.1	0.99	0.18	0.01	0.02	-11.4	0.992
pH 5.5_1:10_6h	64.2 ± 10.8	26.8±0.1	0.99	0.16	0.02	0.02	-9.7	0.996
pH5.5_1:5_1h	41.4 ± 2.6	58.7±0.3	0.93	0.25	0.04	0.18	-8.2	0.980
p - value	0.17	0.77	0.17	0.18	0.19	0.19	0.17	N. A.

k : Energetic of multilayer sorption; m_m : monolayer capacity; c : energetic of monolayer sorption; H_m-H_L : enthalpy difference of multilayer formation; H_1-H_m : enthalpy difference of monolayer formation.

Wetting and swelling studies

Wetting results from intermolecular interactions when water and a film surface are brought together. In all cases, a partial wetting was achieved since water drops spread on top of the films with time from its initial non-zero contact angle moving towards its limiting equilibrium. Table 3 shows the contact angles of PVA and cross linked materials. PVA films exhibited more wettability than cross linked materials. Thus, contact angles of cross linked materials were larger than 30 degrees and appear to increase with the Cross linking reaction conditions employed. This phenomenon suggests that the new tight chain network restricted wettability of the polymer due to the reduction of the hydrogen bonding environment as discussed previously.

Swelling ratio of the materials at 37 °C is shown in fig. 7. The large swelling in water is attributed to the relaxation of amorphous zones, especially in cross linked products. It is also expected that, Cross linking makes chains less ionic because the acetate residues of PVA are eliminated and as a result, there was no repulsion in the chains decreasing swelling ratio. Further, the smooth film surface produced by Cross linking also prevented water from penetrating the core of the films reducing swelling. On the contrary, PVA swelled first and then dissolved due to the disappearance of physical bonding.

Compared to PVA, cross linked films showed some resistant to swelling. A decrease in the hydroxyl groups resulted in a loss of the polar nature of PVA and as a result, the solubility of cross linked materials in water decreased, except for two materials produced at a pH of 6.5 for 1h (labeled as pH6.5_1:10_1h and pH6.5_1:5_1h) which showed a minimum swelling and dissolved within 3 h. This could be due to a weak Cross linking that caused a minimum swelling and a rapid erosion of the tiny hydrogels.

In general, Cross linking caused insolubilization due to the formation of cross links. The presence of acetal bridges weakened both intra and intermolecular hydrogen bonding interactions between vicinal hydroxyl groups. In solution, the PVA inter chain separation distance decreased with increasing degree of Cross linking causing a competition between PVA-water and PVA-PVA interactions and as a result, cross linked materials become more water insoluble.

In most cases, the equilibrium swelling ratio was reached within 5 h showing $\sim 150\%$ increase in the initial weight due to water sorption of the polymer matrix. On the other hand, PVA showed a 450% increase in weight due to the absorption of water. Nevertheless, after 3 h the hydrogel formed started to erode and dissolved slowly at a rate of 1.4%/h.

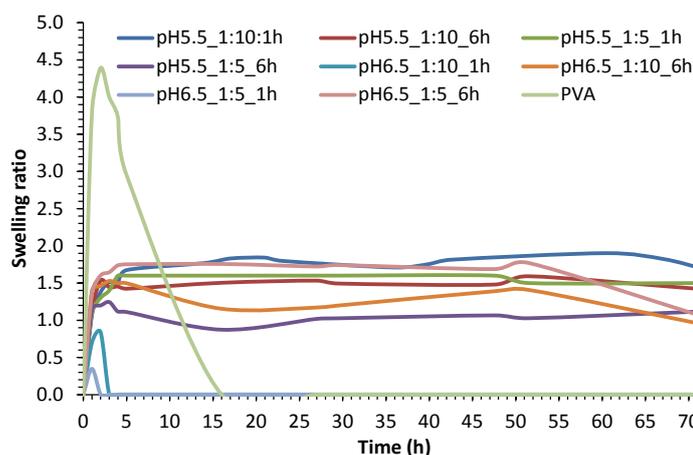


Fig. 7: Swelling ratio of PVA and cross linked films

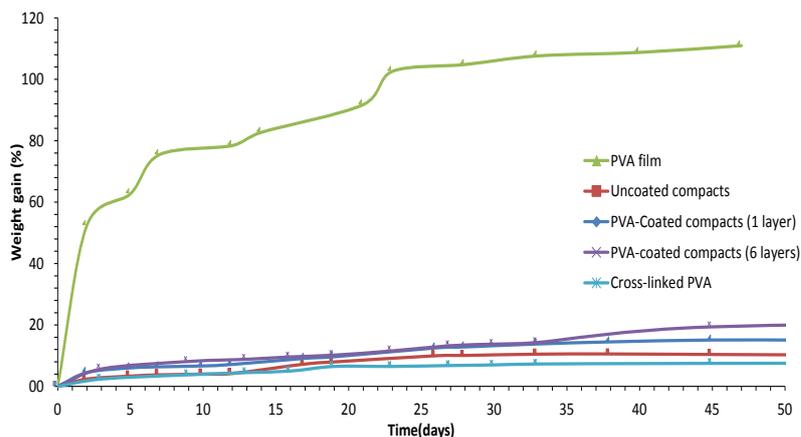


Fig. 8: Water uptake of compacts coated with PVA and cross linked products

Enhanced water proof properties

A material having a high Cross linking degree retarded the sorption of water when films are exposed to a 100% relative humidity. Thus, cross linked films produced a physical barrier for water molecules to penetrate the core of tablets. On the other hand, compacts having 6 layers of 10% of w/v PVA film solution failed to waterproof the tablets and hence, these cores absorbed most of the water from the environment (100% RH) (fig. 8).

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CONCLUSION

Chemical cross link by GA has modified the original PVA polymer chain by reducing their wettability, water sorption and aqueous solubility due to the formation of several acetal bonds. Cross linked films were also more amorphous due to the reduction of the hydroxyl network, which in turn, was responsible for crystallinity and water interaction.

CONFLICT OF INTEREST

Declared None

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