

Incorporation of organic acids in the crosslinking of polyvinyl alcohol hydrogels

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Abstract

This work studied the incorporation of organic acids as crosslinking agents and reaction time on the properties of poly(alcohol vinyl) (PVOH) hydrogels to act as scaffold systems to compounds incorporated into agriculture systems. PVOH hydrogels crosslinked with citric and L-malic acids were prepared, and the effects of heat-treatment time, and temperature on their swelling and hygroscopic performances were investigated by FTIR, thermal analysis and swelling. Both the swelling and rate of water uptake of hydrogels decreased with increasing heat-treatment time. While the swelling decreased with heat-treatment time, the chemical crosslinking shown in FTIR increased. DSC results indicated adsorbed water in the uncrosslinked PVOH and hydrogels, and the absorbed water changed the melting point and glass transition temperature. TGA analysis showed that the incorporation of organic acids brought thermal stability. The results obtained show effective crosslinking hydrogels by L-malic acids and possibilities to use in scaffold systems and controlled release.

Keywords: *PVOH hydrogels, chemical crosslinking, citric and malic acids.*

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1. Introduction

Poly(vinyl alcohol) (PVOH) is a synthetic, semi-crystalline polymer obtained by the hydrolysis of polyvinyl acetate. Its final physical properties are defined by its degree of hydrolysis, which changes its molecular mass and differentiates commercial grades. PVOH exhibits many important characteristics, as it is biodegradable, biocompatible, non-toxic, soluble in water, thermostable and has good chemical and adhesive resistance^[1-7]. However, the presence of hydroxyls in PVOH makes PVOH soluble, limiting its applicability^[2,3,8].

Physicochemical control of PVOH is possibly by crosslinking using various conventional crosslinking agents such as glutaraldehyde, boric acid, glycidyl methacrylate, genipin, microcrystalline cellulose, thermal crosslinking and photo-induced. In many of these cases, toxic solvents are commonly used, which are of concern for specific hydrogel applications^[2,5,7-10]. In this context, carboxylic acids are crosslinking agents for PVOH, and these acids are easily available, odourless, non-toxic, biodegradable, and also good chemical crosslinking agents^[2,5,9,11,12]. Chemical modification of hydroxyl groups of PVOH through crosslinking agents is simple, cost-effective and easily controlled; thus, opening up new fields of its applications in new materials^[2,7,8,13-15]. This molecular chain flexibility, biocompatibility and hydrophilicity is due to its large number of hydroxyl groups is used to form hydrogels with covalent bonds^[6].

Typically, the crosslinking of PVOH with organic acids is carried out by heating the PVOH in solution under stirring with a catalyst and elevated temperature^[2,11,14,16].

The literature search provides an option for preparing PVOH hydrogels with performance that is matched to the user's needs using an organic acid as a natural crosslinker^[2,12]. The most commonly used crosslinkers have problems of toxicity to living organisms. Citric and malic acids are dicarboxylic acids obtained from natural sources that can be used as a crosslinking agent and are non-toxic, easily available and low-cost^[2,12,15]. The effects of crosslinking, which is done by heating, on the swelling and hygroscopic performances of the PVOH hydrogels are studied and elucidated.

2. Materials and Methods

2.1 Materials

Poly(vinyl alcohol) (PVOH), with a molecular mass of $M_w = 105,000 \text{ g.mol}^{-1}$ and 87% hydrolyzed was obtained from Neon® (Brazil). Organic acids used were citric acid obtained from Neon® and malic acid supplied by Êxodo Científica® (Brazil). A hydrochloric acid catalyst (37% w/w) was obtained from Química Moderna® (Brazil). All solvents and reagents were used without further purification.

2.1.1 Hydrogel preparation

A solution of distilled water (~494.00 mL) and PVOH (~26.00 g) was solubilized under constant stirring at room temperature (30 min) and then at 85°C for 40 min.

For the synthesis of hydrogels by the casting method, the previously solubilized PVOH solution was mixed with ~114.00 g of distilled water and 1% (w/w) of specific organic acids (citric or malic) and hydrochloric acid (HCl) was used (1M, 4mL) as a catalyst^[16,17]. This mixture was stirred continuously for 20 min, 1, 2 or 3 h, following a previously published method^[11]. Subsequently, hydrogel solution (aliquots) was weighed and placed in Petri dishes and dried in an oven at 65°C for 24 h, removed for washing to remove residual HCl from the synthesis and dried again for 1 h in an oven at 65°C and stored in a desiccator for 6 days for the final curing process following an adapted methodology^[18]. The symbols of the previous PVOH (standard) and respective PVOH hydrogels, as prepared are presented in Table 1.

2.2 Hydrogels characterizations

2.2.1 Fourier transform infrared spectroscopy (FTIR)

Samples (90 × 35 × 0.4 mm³) were analyzed in an IR-Spectroscopy (Spectrum 1000, Perkin Elmer®, United Kingdom) with HATR system following ASTM E1252. 32 scans were averaged per spectrum over a wavenumber range from 600 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹. Subsequently, the baseline and HATR corrections (Savitzky-Golay, 5 points) were done using Origin® 2018 software. The chemical crosslinking of the PVOH hydrogels after incorporation of organic acids was characterized according to Awad and Khalaf^[19] to evaluate the degree of the crosslinking with changes in the carbonyl and hydroxyl groups showed by characteristic bands associated with carbonyl (1710 cm⁻¹), hydroxyl groups (3280 cm⁻¹) and compared with the vinyl standard group (1462 cm⁻¹), were calculated from the mathematically integrated areas (Equations 1 and 2) of the spectra using Origin® 2018 software, following the equations below.

$$\text{Carbonyl index (I}_{CO}) = \frac{I(1710)}{I(1462)} \quad (1)$$

$$\text{Hydroxyl index (I}_{OH}) = \frac{I(3280)}{I(1462)} \quad (2)$$

2.2.2 Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed according to ASTM E1131, on a thermobalance (TA Instruments®, Q50 model, United States). The samples were placed in a platinum crucible and heated in a temperature range from 25 and 900°C, under a dynamic nitrogen atmosphere with a flow rate of 90 mL/min and heating rate of 20°C/min.

2.2.3 Differential exploratory calorimetry (DSC)

PVOH and PVOH hydrogels were measured by differential scanning calorimetry (DSC) (TA Instruments®, Q20 model, United States) according to ASTM D3418. Samples sealed

in an aluminium pan were heated from 25 to 220°C at a heating rate of 10°C/min rate and were kept at 220°C heating isothermal for 1 min. The degree of crystallinity of the PVOH was calculated from the integration of the endothermic peak of the DSC curves using Equation 3, following a method applied by Yang et al.^[10] with the use of the TA Universal Analysis® software.

$$X_c \% = \frac{\Delta H}{\Delta H_c} \times 100 \quad (3)$$

Where: ΔH is the thermodynamic enthalpy of hydrogels and ΔH_c is the thermodynamic enthalpy of fusion of 100% crystalline PVOH (136.8 J g⁻¹)^[10].

2.2.4 Swelling

Swelling values of PVOH hydrogels were obtained following the method described by Sonker and Verma^[11]. 1.5 × 1.5 × 0.0325 cm³ hydrogel films were immersed in 50 mL of distilled water for 30 minutes, 2, 4, 6, 8 and 24 h at 25°C and weights were measured before and after water uptake. Swelling (S%) was calculated with the following Equation 4.

$$S \% = \frac{(M_f - M_i)}{M_i} \times 100 \quad (4)$$

2.2.5 Statistical analysis

The obtained results average (FTIR data, swelling) were subjected to one-way ANOVA tests and, whenever the null hypothesis was rejected, the averages were compared using Tukey–Kramer tests at a significance level of 5%.

3. Results and Discussions

3.1 Transform infrared spectroscopy (FTIR)

Figure 1 shows the spectra of PVOH and respectively of the hydrogels: citric acid (AC), and malic acid (AM), with reaction times of 20 min, 1, 2 and 3 h, presented in the range of 4000–600 cm⁻¹.

The characteristic peaks of PVOH and its interactions with citric acid (AC) are identified and presented as follows: The absorption bands at 3014–3680 cm⁻¹ are attributed to the stretching vibration of the hydroxyl groups (-OH) present in PVOH and free non-crosslinked AC molecules^[7,20-22]; characteristic bands at 2931 and 2853 cm⁻¹ are attributed to the asymmetric and symmetrical elongation of the C-H groups, respectively; a band at 1735 cm⁻¹ arising from residual carbonyl groups in PVOH (vinyl acetate)^[11] plus ester carbonyls in the crosslinked hydrogel; characteristic bands at 1426 cm⁻¹ are the result of in-plane deformation of the -CH₂- bonds; characteristic band at 1000–1180 cm⁻¹ can be attributed to C-O stretching of PVOH bonds; and the band at 842 cm⁻¹ is correlated with the vibrational stretching of C-C bonds^[20,22].

Table 1. Nomenclature of the PVOH hydrogels prepared by different crosslinking organic acids.

Organic acid	PVOH Hydrogels crosslinking time			
	20 min	1 h	2 h	3 h
Citric acid	PVOH-AC (-AC)	PVOH-AC1 (-AC1)	PVOH-AC2 (-AC2)	PVOH-AC3 (-AC3)
Malic acid	PVOH-AM (-AM)	PVOH-AM1 (-AM1)	PVOH-AM2 (-AM2)	PVOH-AM3 (-AM3)

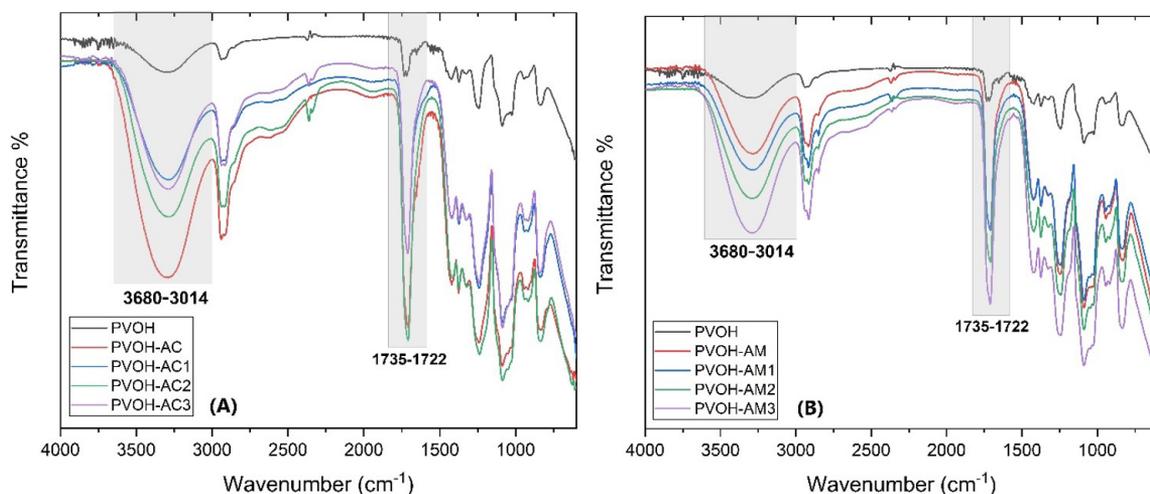


Figure 1. FTIR spectra of PVOH sample and PVOH-AC (A); PVOH-AM (B) hydrogels.

Sabzi et al.^[22] and Franco et al.^[21] state that the esterification reaction between PVOH and AC can be monitored by an absorption band close to 1722 cm^{-1} , attributed to the elongation of carboxylic acid groups (-COOH) due to unreacted AC in the heat treatment time indicative of an increasing percentage of AC in the hydrogel. This behaviour of the intense bands of carbonyls (C=O) and hydroxyls (-OH) with the reaction time of the hydrogel samples is also described in the literature and studied in carbonyl/hydroxyl indexes.

The main characteristic bands attributed to malic acid (AM) were described from the literature as stretching vibrations -OH at approximately 3400 cm^{-1} , derived from the hydroxyls present^[8,23]. As reaction time increased, there was an increase in the hydroxyl and carbonyl index in the samples^[8]. This behaviour of increasing the carbonyl index (C=O) is also observed by other authors. Three possibilities for esterification are presented (Figure 2): intermolecular crosslinks (type A), intramolecular crosslinks (type B) and uncrosslinked (type C). The chemical structures of the interaction among the respective organic acids and PVOH are described in the literature^[2,8,11,12,20].

Yang et al.^[10] studied the incorporation of tannic acid (TA) in PVOH-based hydrogels by FTIR, the results showed a band shift from 3408 cm^{-1} to 3373 cm^{-1} , which is attributed to the stretching bands of -OH, indicating that the intermolecular interactions between PVOH and TA via hydrogen bonds are formed, being characterized by the intermolecular types presented above and observed in the analysed spectra of -AM and its variations. Also, Zhang et al.^[17] when evaluating the behaviour of AM and AT acids, observed that the zeta potential increased slightly at the beginning of the titration and then decreased, while in the AT series, the surface energy decreased continuously, showing a strong influence of the interaction of hydrogen bonding in AM and showing a greater interaction with hydroxyl groups (-OH), presented under the chemical change in the polymeric chains of poly(2-vinyl pyridine).

3.1.1 Carbonyl (I_{CO}) and hydroxyl (I_{OH}) index

The carbonyl indices shown in Figure 3A revealed that the chemical reaction time for crosslink hydrogels is crucial for the increase in carbonyls (C=O) which indicates a higher concentration of organic acids esterified in the polymeric chain of PVOH (especially seen in the hydrogels of PVOH with AC) however, during the chemical reaction, this concentration of organic acids decreased due to a smaller chemical reaction for crosslinking by esterification during the separation of the aliquots over time (especially seen in hydrogels with AM, with the lowest values being with TA). Yang et al.^[10] described that it was also possible to verify that the intensity of bands at 1714 and 755 cm^{-1} (C=O) increased with increasing AT concentration, demonstrating that the diffusion of AT molecules in hydrogels is dependent on the final concentration or chemical reaction. Sonker and Verma^[11] state that PVOH, because it is a hydrolysis derivative of polyvinyl acetate (PVA), has remaining carbonyl bands (C=O) due to the remaining acetate groups. This behaviour can be observed in the PVOH compared to the other samples in FTIR spectrums (Figures 1 and 2) at 1735-1740 cm^{-1} .

The hydroxyl indices of samples shown in Figure 3B revealed that in addition to the esterification promoted by organic acids reducing the hydroxyls present in PVOH, there may also be an increase in the -OH indices due to the presence of hydrogen bonds and free hydroxyls between organic acids and PVOH^[21,22]. This behaviour is exhibited with citric acid (AC), which, because of the free hydroxyls of its chemical structure, had the highest average esterification percentage among all samples due to non-total esterification with PVOH, presenting unstable hydrogels and was not fully crosslinked, according to data presented in the topics of swelling, in addition to this AC having 4 hydroxyl groups (3 of them from -COOH groups) in its molecule. The -AM samples showed similar behaviour in terms of hydroxyl indices, which correspond to swelling tests in which the presence of a three-dimensional structure indirectly reduced the hydroxyl indices and increased the carbonyls.

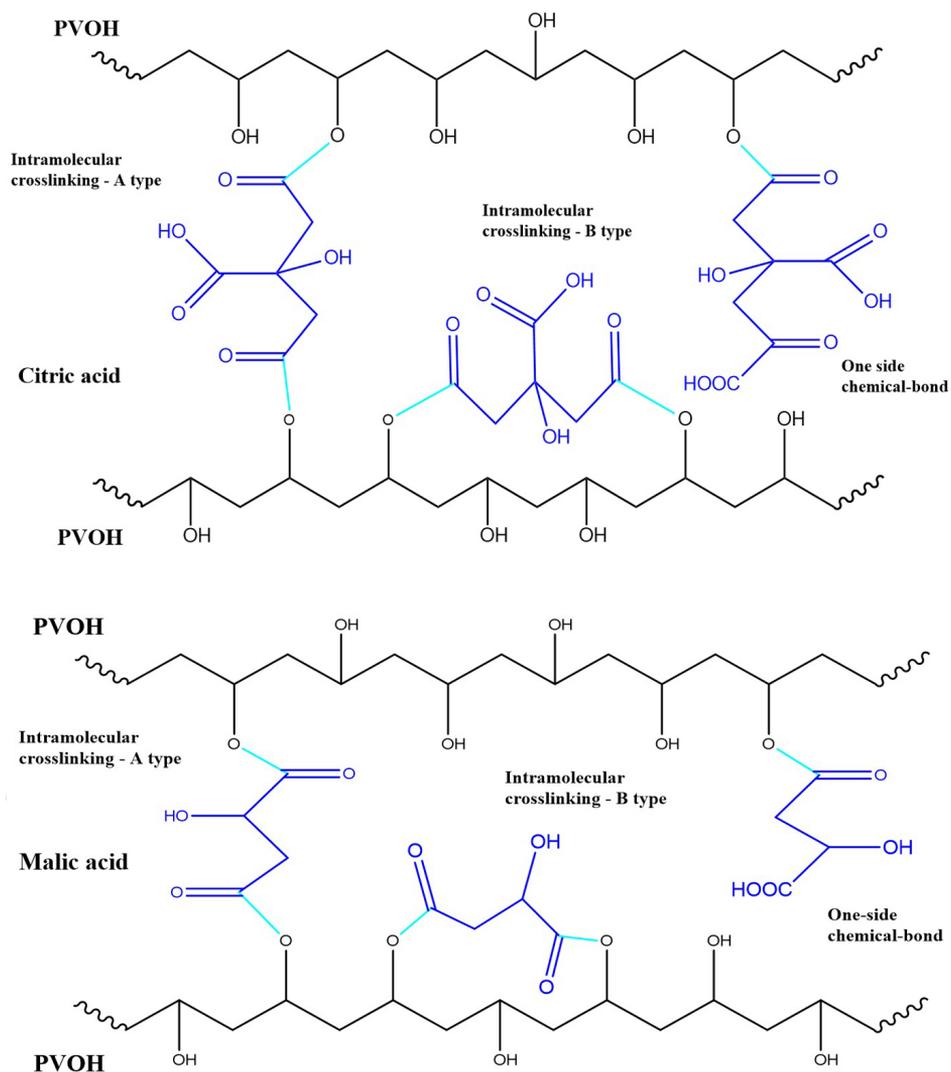


Figure 2. Esterification possibilities for PVOH-AC (up); PVOH-AM (below) hydrogels.

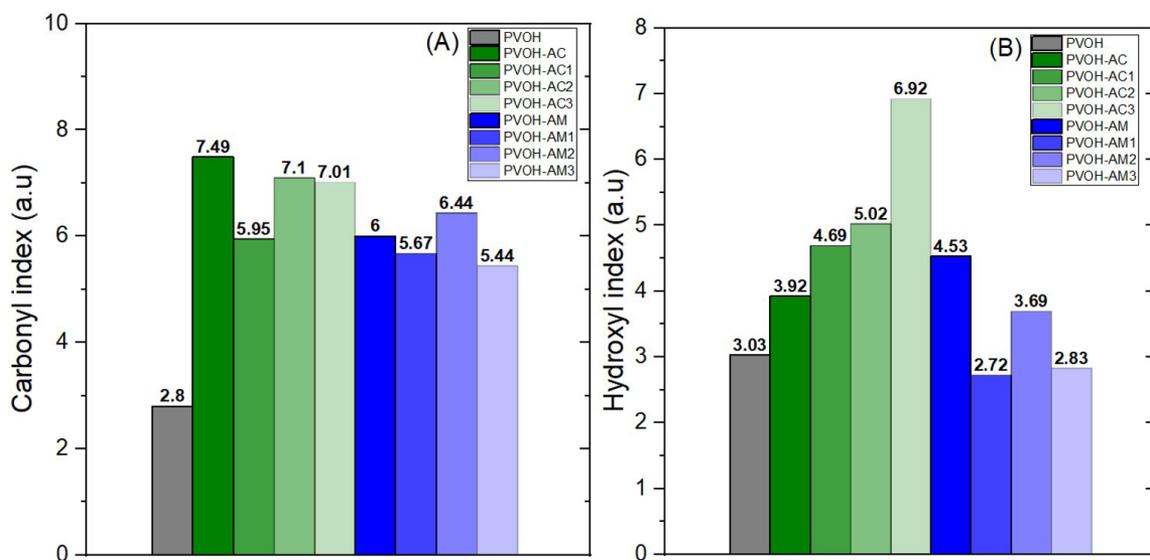


Figure 3. Carbonyl (A); hydroxyl (B) indexes of PVOH film, PVOH-AC and PVOH-AM hydrogels.

The statistical analysis from Figure 3 can be seen in Table S1 and Table S2 – Supplementary Material.

3.2 Thermogravimetric analysis (TGA)

Thermal analysis of PVOH film and their hydrogels (Figure 4) show significant mass loss in up to three (PVOH) and four stages (hydrogels), being studied from the second stage onwards. First, the weight loss up to 150°C was attributed to the loss of water present in the hydrogels^[11]. The first recorded temperature stage ranged from 150 to 320°C was due to the initial thermal decomposition of the chemical structure of PVOH, by low molecular weight compounds (including acetate groups) as well as the possible evaporation of water occluded within the hydrogel networks, while the second degradation process (320 - 400°C) has been associated with decomposition of the polymer backbone (C-C)^[24] and a third step between 400 and 500°C which may be associated with the decomposition of unsaturated macromolecules (products of PVOH decomposition) and the crosslinks of hydrogels. In the DTG curves, the temperatures corresponding to the maximum rate of weight loss of the second stage of degradation of PVOH (443.76°C); AC (350°C); -AC1 (366.24°C); -AC2 (364.35°C) and -AC3 (365.30°C) respectively. This behaviour implied lower thermal stability

of the hydrogels with the incorporation of citric acid, which was confirmed with the loss of mass (DTG) in the second stage due to the decomposition of the PVOH side chain^[24]. The thermal degradation temperature of the third stage (hydrogels) and the reaction times applied with the citric acid did not significantly change the TGA/DTG curves among the samples because the crosslinking reaction failed to change the structure of the PVOH main structure. Temperature data was used to compare differences in initial ($T_{10\%}$ and $T_{50\%}$) lost mass weight properties from Figures 4 and 5 can be seen in Table S3 – Supplementary Material.

The TGA and DSC curves of the PVOH film and malic acid (AM) hydrogels (Figure 5) show a significant mass loss in up to four stages in the hydrogels after the -AM incorporation, and having it studied from the second stage onwards, the mass loss up to 150°C was attributed to the loss of water present in the PVOH and in the hydrogels between 150°C and 200°C the remaining occluded water due to hydrogen bonds with the PVOH matrix^[8,24]. In the DTG curves, the temperatures corresponding to the maximum rate of weight loss of the second stage of degradation of PVOH (443.76°C), AM (360.57°C), -AM1 (356.79°C), -AM2 (353.95°C) and -AM3 (356.79°C) respectively. This behaviour implied lower thermal stability of the hydrogels

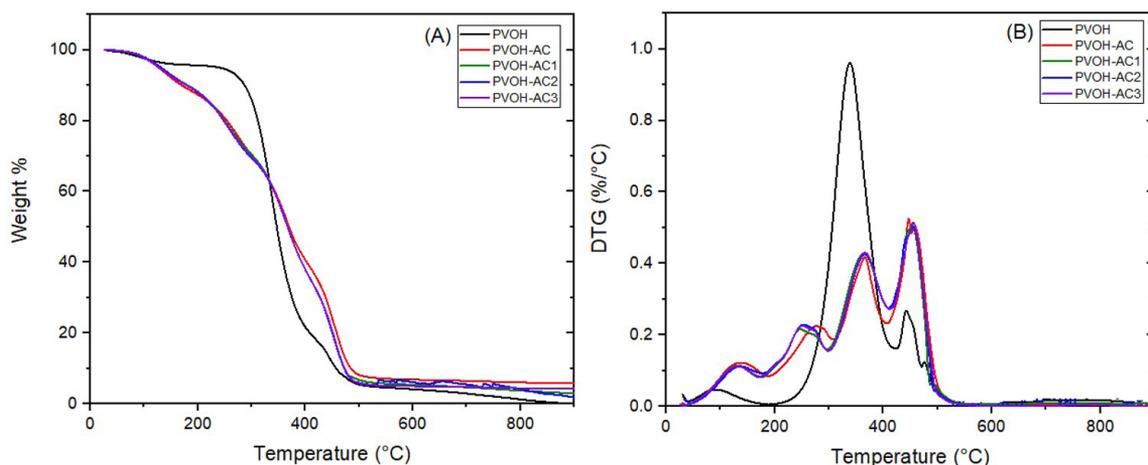


Figure 4. TGA (A); DTG (B) curves of PVOH film and PVOH-AC hydrogels.

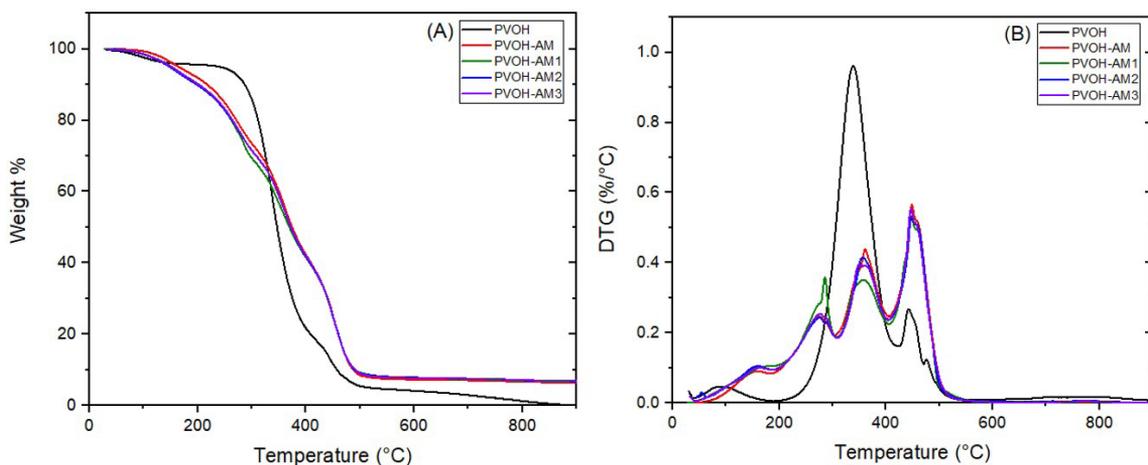


Figure 5. TGA (A); DTG (B) curves of PVOH film and PVOH-AM hydrogels.

with the incorporation of malic acid, which was confirmed with the loss of mass (DTG) of the hydrogels, in the second stage due to the decomposition of the PVOH side chain at around 440°C, and with a subsequent increase due to the chemical crosslinking process promoted by the degradation of AM together with PVOH, a similar behaviour was studied and evaluated with the incorporation of citric acid^[24]. In the third and fourth stages (440 – 500°C) the samples have a thermal change induced by the decomposition of the main polymer chain of PVOH (including acetate groups) and unsaturated bonds and crosslinked thermal among the organic acids used in hydrogels, making a new volatile compound^[24]. Above 600°C, the samples with AM in comparison to AC hydrogels incorporated, had greater thermal stability due to chemical crosslinking induced by thermal degradation.

3.3 Differential exploratory calorimetry (DSC)

The DSC curves of PVOH, -AC, -AC1, -AC2, -AC3 shown in Figure 6A observed that the PVOH film has a glass transition temperature (T_g) close to 60.1°C and a melting temperature (T_m) at 190.1°C. The incorporation of

the citric acid (AC) the chemical reaction time is observed for the samples, the PVOH-AC and -AC3 have a decrease in T_g , which cannot be observed, while the -AC1 and -AC2 samples exhibit a decrease in T_g to 38.5°C and 28.6°C respectively. This decrease in T_g is due to the addition of citric acid, which enabled partial crosslinking (esterification) of PVOH, through chemical interactions of esters and free hydroxyls (-OH) present in AC and facilitates the adsorbed water. This adsorbed and occluded water acted as a plasticizer for the hydrogel which resulted in a decrease in its T_g . This reaction behaviour is described by Yu et al.^[24] in which the incorporation of AC implies a lower thermal stability of the hydrogels, which is confirmed by the loss of mass in the second step due to the decomposition of the PVOH side chain.

For the DSC curves of PVOH, -AM, -AM1, -AM2, -AM3, (Figure 6B) it is observed that with the incorporation of malic acid (AM) the chemical reaction time for all samples, except for PVOH-AM3, has a decrease in T_g , around 30°C, while the -AM3 hydrogel sample showed a smaller decrease in T_g to 55.03°C. This decrease in T_g is due to the plasticization promoted by the adsorbed water and

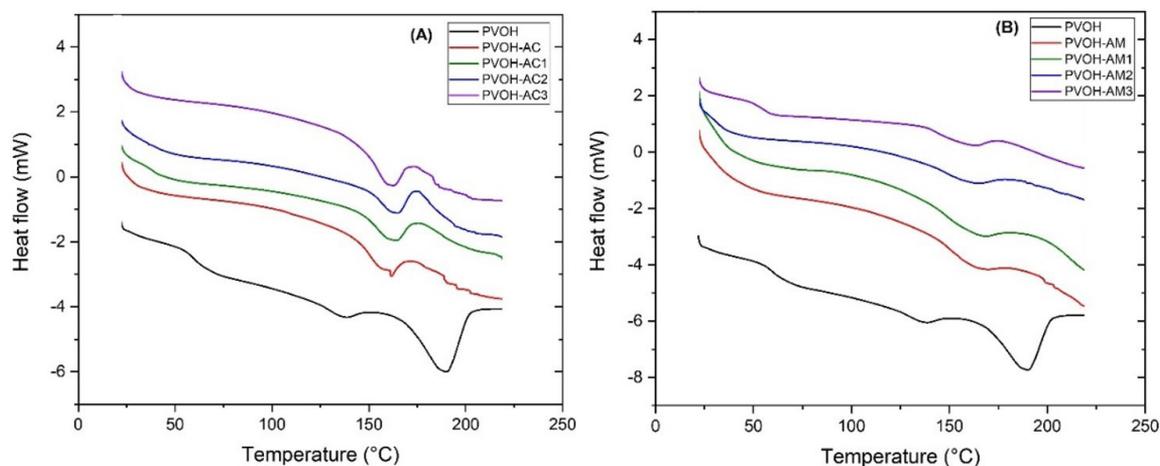


Figure 6. DSC curves of PVOH sample and PVOH-AC (A); PVOH-AM (B) hydrogels.

Table 2. DSC data of the evaluated PVOH film and hydrogels.

Samples	T_g (°C) ^{a)}	T_m (°C) ^{b)}	ΔH_f (J/g) ^{c)}	% Xc ^{d)}
PVOH	60.15	190.18	46.34	32.52
PVOH-AC	e)*	161.52	9.30	6.53
PVOH-AC1	38.52	162.03	13.87	9.73
PVOH-AC2	28.66	164.37	12.95	9.09
PVOH-AC3	e)*	159.72	12.06	8.46
PVOH-AM	30.40	163.06	10.74	7.54
PVOH-AM1	30.58	163.74	12.66	8.88
PVOH-AM2	31.27	161.82	8.88	6.23
PVOH-AM3	55.03	160.55	9.04	6.34

a) T_{max} : Glass transition temperature. b) T_m (°C): Melting temperature. c) ΔH_f (J/g): Enthalpy of fusion. d) % Xc: per cent crystallinity. e) *Non-measured.

incorporation of AM that rearranged the chemical chains of PVOH in a chemical behaviour previously observed with the PVOH/AC hydrogels. Kanmaz et al.^[25] described in their study that this T_g alteration is attributed to the incorporation of organic acid that promotes changes in the structural arrangement of PVOH molecules. Gao et al.^[8] state that water molecules, whether occluded or frozen, cannot bind directly to the hydrophilic groups of PVOH, thus being shown to be mass change.

To investigate the effect of the concentration of organic acids on the crystallization of hydrogels, in the DSC analysis in addition to the glass transition temperature (T_g), the melting temperature (T_m) the heat of fusion (ΔH_f) and the degree of crystallinity (X_c) were obtained from the curves of samples of PVOH hydrogels with citric (AC) and malic (AM) acids and their time variations are shown in Table 2.

The DSC curve for the PVOH film exhibits an endothermic peak at 190.18°C which is co-responding to the melting temperature of the PVOH crystalline phase^[10]. For hydrogels composed of PVOH/AC and -AM, as shown in Table 2, the melting point T_m of -AC, -AC1, -AC2, -AC3 and -AM, -AM1, -AM2, -AM3 are 161.52 °C to 164.37 °C and from 160.55°C to 163.74°C respectively, and all T_m points were shifted to a lower temperature as the concentration of organic acids increased, with similar behaviour for the -AC/-AM groups. This behaviour was also observed in a study by Yang et al.^[10] with the incorporation of tannic acid. Meanwhile, the X_c of composite hydrogels decreased from 32.52% to -AC (6.53%; 9.73%; 9.09% and 8.46%); -AM (7.54%; 8.88%; 6.23% and 6.34%) with the incorporation of organic acid in 1% by weight, indicating that the introduction of organic acids can chemically inhibit the crystallization of PVOH due to strong interaction of free hydrogen and -OH bonds formed between AC and AM in the polymeric chains of PVOH^[2].

3.4 Swelling

The water uptake capacity of the hydrogels was observed by measuring the degree of swelling ($S\%$) as a function of

time. The absorption/adsorption of water during swelling is due to a large number of hydroxyl groups (-OH) present in PVOH resulting in high swelling and therefore reducing its strength and final properties^[6,11]. Crosslinking not only reduces the active -OH groups but also covalently bonds the PVOH structure, reducing their interaction with water, and resulting in a reduced final swelling. In addition, the crosslinked structure of the hydrogel promoted by the organic acid confers better mechanical resistance in the presence of moisture between the interpenetrating chains, resulting from the formation of a chemical bond of ester between the chains of the matrix with the organic acids^[2,6,11]. Figure 7 shows the degree of swelling and its amplification for PVOH hydrogels with citric acid (-AC) and malic acid (-AM) for up to 24 h. The statistical analysis from Figure 7 can be seen in Table S4 – Supplementary Material.

For the swelling test, only PVOH-AC was different from the other samples. This is caused by the higher swelling of the hydrogel in comparison to other samples. This better stability in the time also promoted better crosslinking time properties in 2 h, increasing the time without disintegration. This thermal treatment in 3 h to -AC2 and -AC3, also promoted equal values for specific swelling, compared with PVOH-AC hydrogel had the most result obtained (485.38%). The AM hydrogels samples don't have statistical differences except for the PVOH-AM with more swelling in comparative the other samples with 236.15%.

Evaluating the swelling behaviour applied to the PVOH-AC hydrogel, a swelling speed up is observed up to the maximum limit of 680% in 1 hour of the swelling, for the 20 min reaction due to the low chemical interaction of citric acid (CA) with PVOH, the other samples of -AC1, -AC2 and -AC3 obtained longer-stability times during the test, however with relatively lower rates of swelling and with a gradual loss of mass. This behaviour is also the result of a decrease in the final dimensional strength of the hydrogel and its disintegration due to the high interaction with the hydrolysis promoted with water and acids, causing it to lose its shape and final dimension depending on the elaborated reaction kinetics and the time for hydrogel crosslinking^[11]. It is reported that the number of residual free carboxylic groups

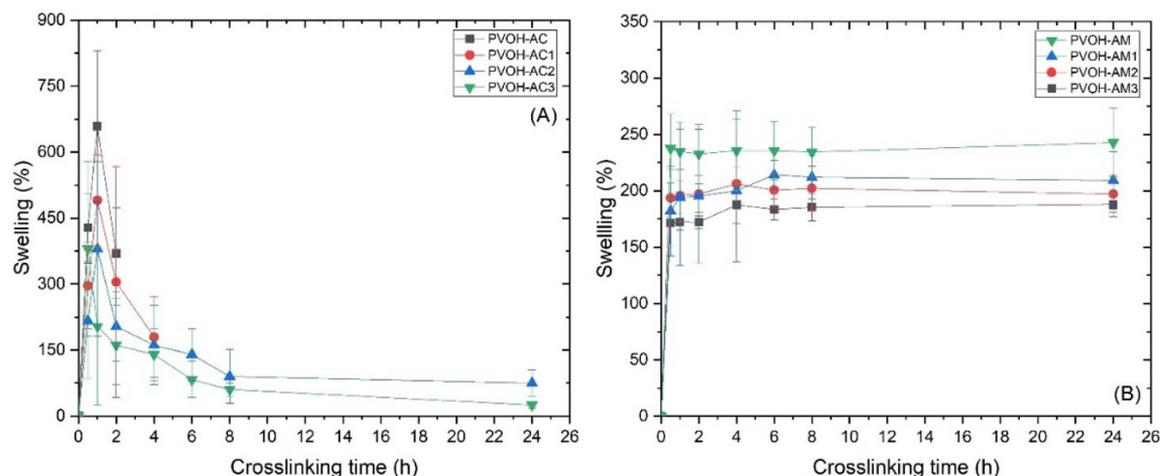


Figure 7. Swelling graphs of PVOH-AC (A); PVOH-AM (B) hydrogels.

(-COOH) increases with the CA content in the hydrogel^[22]. This theory is based on the concept of chemical synthesis and stability of hydrogels that was developed from the study of the literature^[2,6,11] that was addressed and presented in the topic discussion of FTIR [Figure 2] and had its method applied conceptually to the other organic acids in this study. Figure 8 shows a hydrogel made up of PVOH-AC (20 min) during the swelling tests up to the limit of two hours.

However, the PVOH-AC1, PVOH-AC2 and PVOH-AC3 hydrogels showed lower percentages of swelling due to increased crosslinking applied, but with a longer stability time when compared to PVOH-AC hydrogel; -AC2 and -AC3 hydrogels, on the other hand, had dimensional stability up to 24 h of testing, but with a gradual loss of mass over time due to hydrolyzation promoted by water in the hydrogel. This behaviour is because the longer the thermal reaction takes, the greater the percentage of cross-linking in the samples, promoting lower swellings but longer stability in liquids, respectively, but the crosslinking kinetics with citric acid does not favour chemical stability which is evidenced by the total hydrolysis of the hydrogel, which will be confirmed in the following topic of swelling kinetics. This behaviour has been studied and reported by several researchers^[2,22-27].

For the swelling of PVOH-AM, a decrease in the average percentage of swelling of the samples by 200% was observed, in which the PVOH-AM sample reached the maximum swelling value of 240%. Samples -AM1, -AM2 and -AM3 (Figure 9) had a swelling decrease with increasing reaction time, where sample -AM3 had the lowest swelling value of 180%, and all hydrogel samples had dimensional stability without disintegrating if up to 24 h. Gautam et al.^[2] describe that AM, because it has an additional hydroxyl group, is more hydrophilic, creating a strong interlocking of polymeric chains in PVOH, restricting its hydrophilicity, thus resulting in the formation of a more three-dimensionally

and stable crosslinked structure, resulting in lower swelling values in PVOH comparison with others. This behaviour is shown by the low swelling characteristic shown above in citric acid and its chemical crosslinking kinetics by esterification.

4. Conclusions

The effects of organic acids on hydrogels based on PVOH were studied by physio-chemical analysis, and the organic acids (citric and malic) modified the structure and physio-chemical properties of PVOH polymer with effectiveness. PVOH-AC hydrogels showed the highest swelling percentages but with shorter swelling times due to dimensional instability and their weak chemical interaction. The -AM samples obtained satisfactory results with crosslinking percentages and greater dimensional stability as compared to AC hydrogels. Consequently, this behaviour is attributed to chemical interactions promoted mainly by the type A (intermolecular) chemical reaction model for the -AM samples described in FTIR.

In the thermal analysis, the samples had similar degradation behaviour in all, where the -AC hydrogels were susceptible due to the percentage of absorbed and adsorbed water that promoted an initial decrease in the degradation temperature demonstrated in all samples as compared to PVOH film. The analysis of DTG curves showed characteristic and defined stages of degradation, in which the hydrogels of -AM followed by -AC presented the best results of resistance to degradation respectively.

It is concluded that organic acids can be used as crosslinking agents for hydrogels, however, the AC hydrogel does not meet the requirements through this applied methodology and the AM hydrogels are more promising for the development of hydrogels.

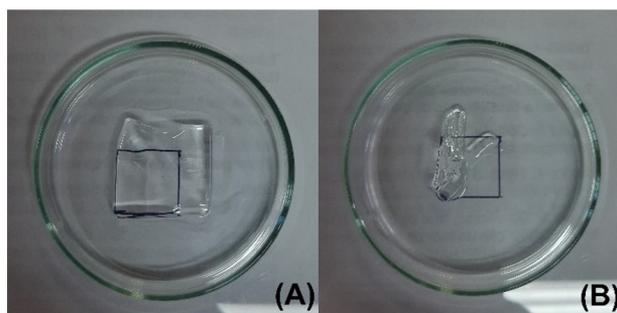


Figure 8. PVOH-AC hydrogel in swelling for 30 min (A); 2 h (B).

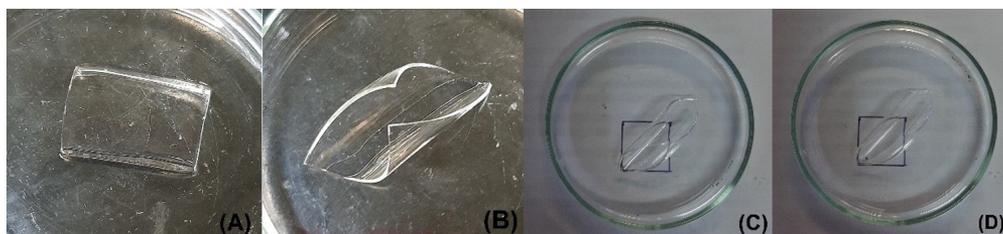


Figure 9. PVOH-AM hydrogels swelling after 24 h; -AM (A); -AM1 (B); -AM2 (C); and -AM3 (D).

5. Author's Contribution

- **Conceptualization** – Ruth Marlene Campomanes Santana; Dione Pereira de Castro; Vanessa Zimmer Kieffer.
- **Data curation** – Ruth Marlene Campomanes Santana; Dione Pereira de Castro.
- **Formal analysis** – Ruth Marlene Campomanes Santana; Dione Pereira de Castro.
- **Funding acquisition** – NA.
- **Investigation** – Dione Pereira de Castro.
- **Methodology** – Ruth Marlene Campomanes Santana; Dione Pereira de Castro; Vanessa Zimmer Kieffer.
- **Project administration** – Ruth Marlene Campomanes Santana; Dione Pereira de Castro; Vanessa Zimmer Kieffer.
- **Resources** – Ruth Marlene Campomanes Santana; Dione Pereira de Castro.
- **Software** – NA.
- **Supervision** – Ruth Marlene Campomanes Santana.
- **Validation** – Ruth Marlene Campomanes Santana; Dione Pereira de Castro.
- **Visualization** – Ruth Marlene Campomanes Santana; Dione Pereira de Castro; Vanessa Zimmer Kieffer.
- **Writing – original draft** – Ruth Marlene Campomanes Santana; Dione Pereira de Castro.
- **Writing – review & editing** – Ruth Marlene Campomanes Santana; Dione Pereira de Castro.

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Supplementary Material

Supplementary material accompanies this paper.

Table S1. Descriptive and inferential statistics averages were used to compare differences in carbonyl index averages for the PVOH film and hydrogels.

Table S2. Descriptive and inferential statistics averages were used to compare differences in hydroxyl index averages for the PVOH film and hydrogels.

Table S3. Temperature data was used to compare differences in initially lost mass weight properties for the PVOH film and hydrogels in 10 and 50%.

Table S4. Descriptive and inferential statistics averages were used to compare differences in swelling properties for the hydrogels.

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