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Influence of Chemical Nature of Citric and Tartaric Acids on Reaction Time of the Crosslinking of Polyvinyl Alcohol Hydrogels

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Abstract: Poly(vinyl alcohol) (PVOH) is a water-soluble polymer having a hydroxyl group as a functional group contributing to excellent membrane-forming and mechanical performance. PVOH is obtained by the hydrolysis of polyvinyl acetate, and its physical properties are affected by its degree of hydrolysis, whether, partial or complete. In this study, PVOH hydrogels were synthesized by a solution under stirring and heating techniques with citric (AC) and tartaric acids (AT) crosslinker agents, with different time reactions of 20 min.; 1; 2, and 3 h were investigated. These samples were characterized by the kinetics of water uptake, gel fraction, thermal analysis, and physical-chemical analysis, and their structure was elucidated. The results obtained have shown chemical modification by organic acids and improved the properties to good thermal stability and swelling to AT hydrogels up to 900% water uptake. In the gel fraction, the samples' esterification was shown and verified by FTIR spectra. To AC hydrogels the chemical modification was low due to the steric hindrance, which caused disintegration of the hydrogel in swelling and gel fraction test, but with absorption in the moisture test performed. The incorporation and effects of citric and tartaric acids enable the development of new hydrogel systems, with specific properties.

Key words: PVOH hydrogels, chemical-crosslinking, citric and tartaric acids, scaffold systems.

INTRODUCTION

The hydrogels are three-dimensional crosslinked, water-swollen structures composed mainly of hydrophilic homo-polymers or copolymers utilized in various fields (Mishra et al. 2018). Chemical crosslinking is defined as the formation of chemical bonds between different polymeric chains of PVOH; however, they should swell and lose after they absorb a certain amount of water or moisture (Gao et al. 2017, Gautam et al. 2022). This physical-chemical modification of PVOH polymer can be changed by crosslinking the polymeric chains by classic methods which can be done with the use of conventional crosslinking agents, such as glutaraldehyde, boric acid, glycidyl methacrylate, genipin, microcrystalline cellulose, thermal crosslinking or photo-induced, where toxic solvents are typically used, which are of great concern for specific hydrogel applications (Gautam et al. 2022, Pei et al. 2021, Yang et al. 2021).

Various carboxylic acids such as di- and polycarboxylic acids and their derivatives are used as good crosslinking agents, as they have two or more reactive sites that help in the formation of a strong, stable, and high-density crosslinked network, which when reacting with the hydroxyl groups of PVOH (Gautam et al. 2022, Pei et al. 2021, Sonker & Verma 2018, Suganthi et al. 2020), give rise to esterification reactions and different forms of inter/intramolecular bonds in the polymer, improving the mechanical strength and thermal stability of PVOH (Awada & Daneault 2015, Gautam et al.

2022, Sanchez & Alvarez 2019). Hydrogels are a class of such crosslinked polymers that, due to their hydrophilic nature, can absorb large amounts of water (Karoyo & Wilson 2021; Kim et al. 2003, Liu et al. 2021, Omidian & Park 2010).

The structure of a particular type of hydrogel can be developed for a specific application from biomedicine, pharmaceuticals, removal of impurities, the environment, and even biocompatibility, by selecting the raw materials of interest and product synthesis technique (Karoyo & Wilson 2021, Kim et al. 2003, Omidian & Park 2010). Typically, the crosslinking of PVOH with a crosslinking agent is carried out by heating the PVOH in solution under stirring and temperature (Sanchez & Alvarez 2019, Sonker & Verma 2018). Citric and tartaric acids are natural organic acids extracted from citrus fruits and can actively participate in hydrogen bonding interactions with polymeric networks due to their carboxylic (−COOH) and hydroxyl groups (−OH) presents (Salihu et al. 2021, Ukaji & Soeta 2012). Organics acids are often used as poly-functional modifiers to transform OH-polymers into reactive functional polymers, through crosslinking reactions (Gautam et al. 2022, Sabzi et al. 2020, Salihu et al. 2021).

Usually, the crosslinking of PVOH films with crosslinker is performed by heating polymer-crosslinker solid films (physical mixture) in a hot air oven, including the tartaric acid (Sonker & Verma 2018, Suganthi et al. 2020). The advantages and limitations of different carboxylic acids as PVOH crosslinkers are also summarized for various fields such as engineering, dressing, scaffolds, drug delivery, pervaporation, desalination, and food packaging (Gautam et al. 2022, Kim et al. 2003, Liu et al. 2021, Suganthi et al. 2020). With this approach, the object of this work is to synthesize the hydrogels and study the effects of the chemical crosslinking processes on the chemical-kinetics performances of PVOH hydrogels with citric and tartaric organic acids.

MATERIALS AND METHODS

Materials

Poly(vinyl alcohol) (PVOH) (M_w = 105,000 g/mol; 87% hydrolyzed) and citric acid (M_w = 192,12 g/mol) were supplied from Neon®; tartaric acid (M_w = 150,09 g/mol) was obtained from Synth® and hydrochloric acid catalyst (HCl) (37% w/w) was obtained from Química Moderna®. All chemicals were used as received without further purification.

Synthesis of hydrogels

The hydrogels are prepared in two steps using a casting method. Initially, a solution of distilled water (494 mL) and PVOH (26g) was solubilized at 85°C for 40 minutes. For the synthesis of hydrogels, the solubilized PVOH solution was mixed with 114g of distilled water and 1% (w/w) total volume of specific organic acids (citric or tartaric) and HCl was used (1M, 4mL) as a catalyst (Dlamini et al. 2014, Kim et al. 2003, Zhang et al. 2022). The mixture was stirred continuously for 20 min., 1 h, 2 h, and 3 h, following a previous method (Sonker & Verma 2018). 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 (Omidian & Park 2010). Also, a film containing only PVOH without a catalyst was synthesized as a control sample. The symbols of the previous PVOH (standard) and PVOH hydrogels, as prepared, are presented in Table I.

Table I. Nomenclature of the PVOH hydrogels and reaction times used.

Organic acid	PVOH Hydrogels crosslinking time			
	20 minutes	**1 hour**	**2 hours**	**3 hours**
Citric acid	PVOH-AC (-AC)	PVOH-AC1 (-AC1)	PVOH-AC2 (-AC2)	PVOH-AC3 (-AC3)
Tartaric acid	PVOH-AT (-AT)	PVOH-AT1 (-AT1)	PVOH-AT2 (-AT2)	PVOH-AT3 (-AT3)

Characterization technique of hydrogels

Fourier transform infrared spectroscopy (FTIR)

PVOH film and hydrogels were performed using a Perkin Elmer® Spectrum 1000 Spectrometer in the 4000–600 cm^{-1} range with 32 scans and the HATR system method (ASTM E1252). Following the spectra, the degree of crosslinking for each hydrogel with changes in the carbonyl and hydroxyl groups showed by the characteristic bands associated with carbonyl (1710 cm^{-1}), hydroxyl groups (3280 cm^{-1}) and vinyl's (1462 cm^{-1}) were calculated from the mathematically integrated areas (Equations 1 and 2) using the Origin® 2018 software, following a method applied by Castro et al. (2023).

$$Carbonyl\ index\ (I_{CO}) = \frac{I\ (1710)}{I\ (1462)} \tag{1}$$

$$Hydroxyl\ index\ (I_{OH}) = \frac{I\ (3280)}{I\ (1462)} \tag{2}$$

Thermogravimetric analysis (TGA)

The TGA analyses were carried out using the Thermogravimetric Analyzer (TA Instruments®, Q50 model). 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.

Differential scanning calorimetry (DSC)

PVOH film and PVOH hydrogels were measured (TA Instruments®, Q20 model) according to ASTM D3418. Samples sealed in an aluminum 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. (2021) with the use of the TA Universal Analysis® software.

$$X_c\% = \frac{\Delta H}{\Delta H_c}\ x\ 100 \tag{3}$$

Where ΔH_c is the thermodynamic enthalpy of hydrogels and ΔH_c is the thermodynamic enthalpy of fusion of 100% crystalline PVOH (136.8 J g^{-1}) (Yang et al. 2021).

Swelling and moisture test

Swelling values and uptake to PVOH films and PVOH hydrogels were obtained following the method described by Sonker & Verma (2018) and Kim et al. (2003). 1.5 x 1.5 x 0.0325 cm^3 hydrogel films were immersed in 50 mL of distilled water for 30 minutes, 2, 4, 6, 8, and 24 hours at 25°C, and weights were measured before and after water uptake. Swelling (S%) was calculated with the following equation:

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

Where M_f is the final swollen mass; Mi is the initial dry mass.

Relative moisture absorption at 75% (*WA%*) was performed following ASTM D5229 and ASTM E104. The samples were dried in an oven at 65°C for 24 h and then placed in a closed vessel with a saturated salt solution at 27.5°C. The samples were weighed at times of 30 min., 2, 4, 6, 8, and 24 h. The test was performed in quintuplicate for each formulation and the results were divided into two categories, using kinetics water absorption (Eq. 5) and Peleg law (Eq. 6), The calculation was done with the following equations:

$$WA\% = \frac{\left(M_2 - M_1\right)}{M1} \times 100 \tag{5}$$

Where M_1 is the dry sample weight and M_2 is the final weight after exposure to moisture.

The data obtained from equation 6 were adjusted according to the mathematical model proposed by Peleg (Peleg 1988), for absorption kinetics of the samples.

$$M_{(t)} = M_0 + \left[\frac{t}{\left(k_1 + k_2 t\right)}\right] \tag{6}$$

Where $M(t)$ is the defined moisture at time t, M_0 is the initial moisture, k_1 is the velocity constant (h/(water/dry)) and k_2 is the capacity constant (dry/water).

Sol-gel rate

PVOH hydrogels were put into the Soxhlet system in water reflux for 24 h following the method described by Yang et al. (2021). The sol-gel ratio was calculated using the equations:

$$Fs\% = \left(\frac{M_g}{M_0}\right) \times 100 \tag{7}$$

$$Fg\% = 100 - Fs\% \tag{8}$$

Where M_o and M_g are the mass of the dry sample and after the test.

Statistical analysis

The obtained results averaged including the FTIR data, swelling, and moisture analysis were subjected to one-way ANOVA tests. Whenever the null hypothesis was rejected, the averages were compared using Tukey–Kramer tests at a significance level of 5%.

RESULTS AND DISCUSSION

Transform infrared spectroscopy (FTIR)

Figure 1 shows the spectra of PVOH and hydrogels respectively: citric acid (AC), and tartaric acid (AT), with reaction times of 20 min., 1, 2, and 3 h, in the range of 4000-600 cm^{-1}.

The characteristic peaks of PVOH polymer and its chemical interactions with citric acid (AC) are identified and presented follows: The absorption bands at 3014–3680 cm^{-1} are attributed to the stretching vibration of hydroxyl groups (-OH) present in PVOH film and free non-crosslinked AC molecules (Franco et al. 2021, Hrabalikova et al. 2016, Sabzi et al. 2020, Suganthi et al. 2020, Xu et al. 2018); the characteristic bands at 2931 cm^{-1} and 2853 cm^{-1} are attributed to the asymmetric and
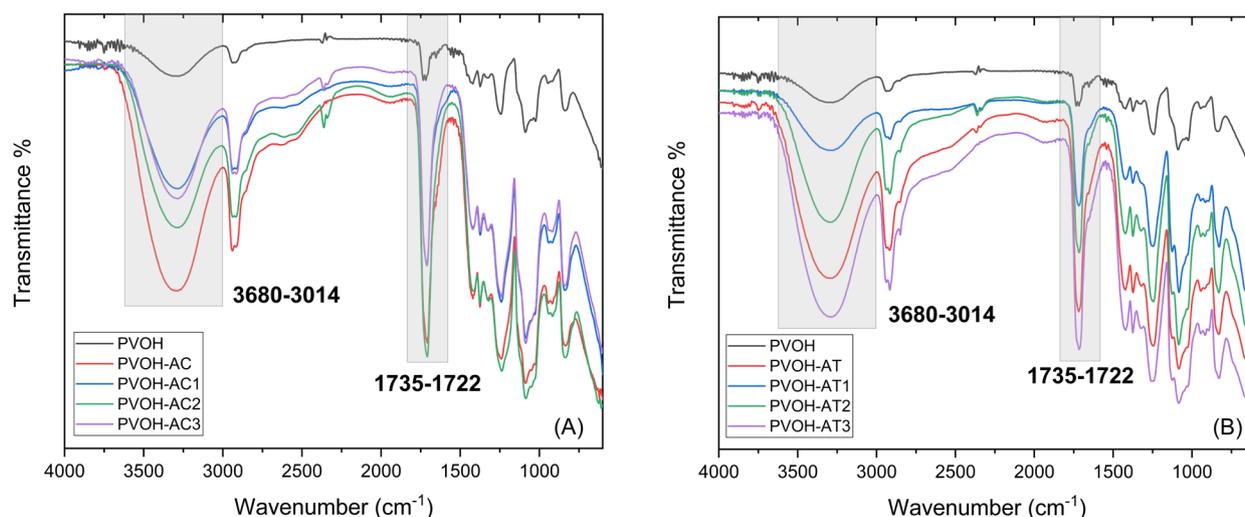
Figure 1. FTIR spectra of PVOH sample, PVOH-AC (A), and PVOH-AT (B) hydrogels.

symmetrical elongation of the C-H groups, respectively; a band at 1735 cm^{-1} arising from residual carbonyl groups (C=O) in the molecular chains of PVOH (Franco et al. 2021, Suganthi et al. 2020, Xu et al. 2018); characteristic bands at 1426 cm^{-1} are the result of in-plane deformation of the -CH_2- 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 (Franco et al. 2021).

Sabzi et al. (2020) and Franco et al. (2021) claim that the esterification reaction between PVOH and AC is also justified by the occurrence of an absorption band close to 1722 cm^{-1}, attributed to the elongation of carbonyls and carboxylic acid groups (-COOH) remaining in the AC and increased with increasing percentage of AC in the hydrogel. This behavior of intense bands of carbonyls (C=O) and consequently of the hydroxyls (-OH) along with the reaction time of hydrogel samples, is also described in the literature.

The spectra of the PVOH sample and PVOH-AT hydrogels and their variables confirm the evidence of crosslinking between PVOH and tartaric acid (AT). The characteristic absorption bands corresponding to the -OH stretch (3200-3400 cm^{-1}) originated from the intra- and intermolecular hydrogen bonds of organic acids and PVOH (Yang et al. 2021); -CH stretch (2940 cm^{-1}); adsorbed water (1640 cm^{-1}) present in AT and PVOH; molecular twist (1435 cm^{-1}); -C-O stretch associated with PVOH (1095 cm^{-1}) are shown and analyzed (Sonker & Verma 2018). As PVOH is obtained from the partial hydrolysis of poly(vinyl acetate) (PVA), it has a characteristic small absorption carbonyl band (C=O) peak due to unhydrolyzed acetate groups (Sonker et al. 2019).

The characteristic crosslinking of hydrogels is shown in the spectra, resulting from the reduction of hydroxyls (-OH) with conversion to new ester bonds (Sanchez & Alvarez 2019) in the hydrogel, due to the stretching and increasing of carbonyl region (C=O) at 1735-1740 cm^{-1} originating from the interaction with the tartaric acid and others organic acids (Awad & Khalaf 2020, Hrabalikova et al. 2016, Sonker et al. 2019, Sonker & Verma 2018, Suganthi et al. 2020, Xu et al. 2018). Yang et al. (2021) studied the treatment of different concentrations of tannic acid (TA), in which new absorption bands in PVOH/TA hydrogels appeared at 1714 cm^{-1}, 1027 cm^{-1}, and 755 cm^{-1}, which correspond to the characteristic bands of TA, proving the incorporation of TA in the PVOH hydrogel. This behavior can

be observed by the reason of the peaks (C=O/-OH) that are obtained through the spectra that confirm the interaction of AT with PVOH; this mathematical calculation was performed using the spectra using equations 1 and 2.

Three theoretical possibilities for esterification (Gao et al. 2017, Gautam et al. 2022, Hrabalikova et al. 2016, Sonker & Verma 2018) of the PVOH matrix to citric acid (AC) and tartaric acid (AT) are presented (Figure 2), which are divided into intermolecular crosslinks (type A), intramolecular crosslinks (type B), uncrosslinked (type C). Sonker & Verma (2018), described that depending on the chemical orientation
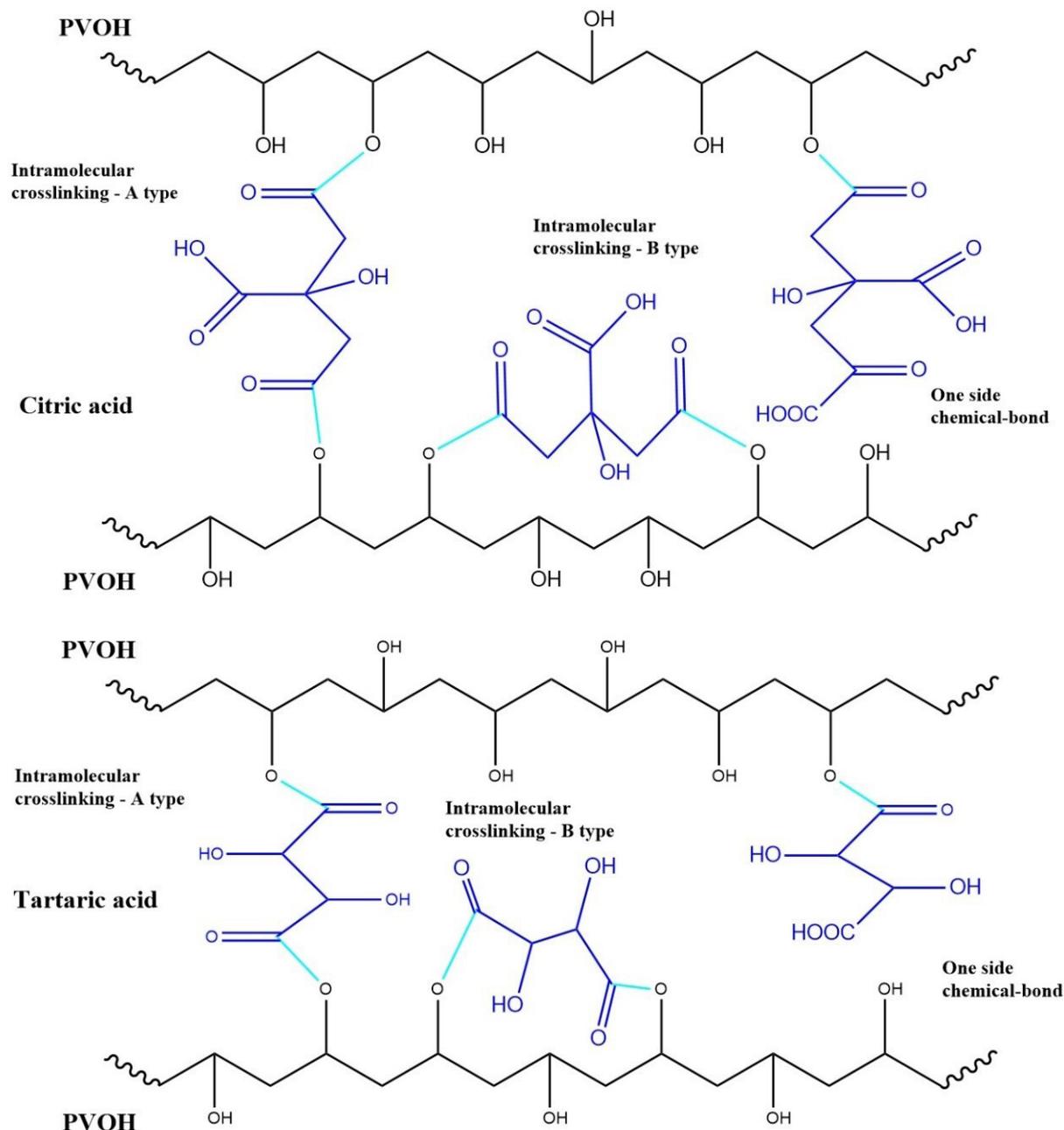
Figure 2. Esterification possibilities for PVOH-AC (up) and PVOH-AT (below) hydrogels.

of PVOH and AT, crosslinking can occur in types A, B, or one side chemical bond. Furthermore, it is also possible that only one end of the organic acid reacts with PVOH, giving rise to partial esterification without chemical reactivity at the other carboxylic group (unilateral crosslinking) as presented in the literature (Gao et al. 2017, Gautam et al. 2022, Sonker et al. 2019, Sonker & Verma 2018).

Sonker & Verma (2018) describe that the intensity ratio (C=O/-OH) measured experimentally for the PVOH/TA hydrogel increases with the degree of crosslinking and reaches 0.5 to 35% w/w TA- CLPVA.

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

The carbonyl indices of the samples show that the chemical reaction time for crosslinking the 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 (Figure 3), where the steric hindrance configuration did not react chemical esterification with PVOH, causing your disintegration, observed in swelling test and studied previously in literature (Gautam et al. 2022, Castro et al. 2023). However, during the chemical reaction, this concentration of organic acid decreased due to a smaller chemical reaction for crosslinking by esterification during the separation of the aliquots over time (especially seen in hydrogels with AT). Yang et al. (2021) described that it is possible to verify that the intensity of the bands at 1714 cm^{-1} and 755 cm^{-1} (C=O) which increases with increasing AT concentration, demonstrating that the incorporation of tartaric acid molecules in hydrogels is dependent on final concentration or chemical reaction during their formation. Sonker & Verma (2018) 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 behavior can be observed in the PVOH hydrogels compared to the other samples in the FTIR spectrum (Figure 1) at 1735-1740 m^{-1}.
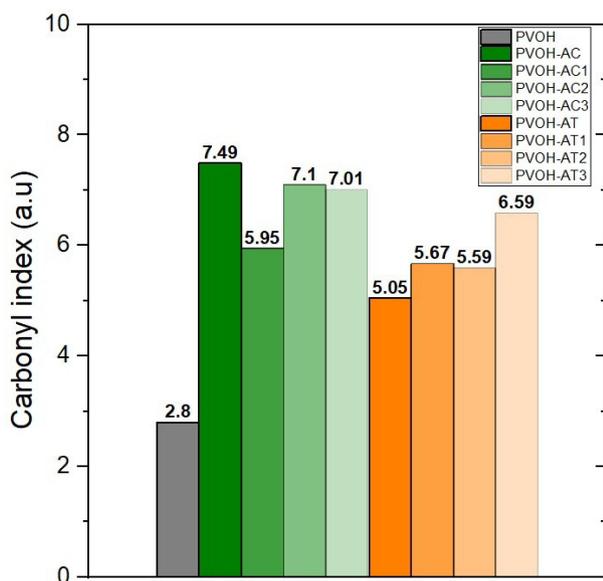

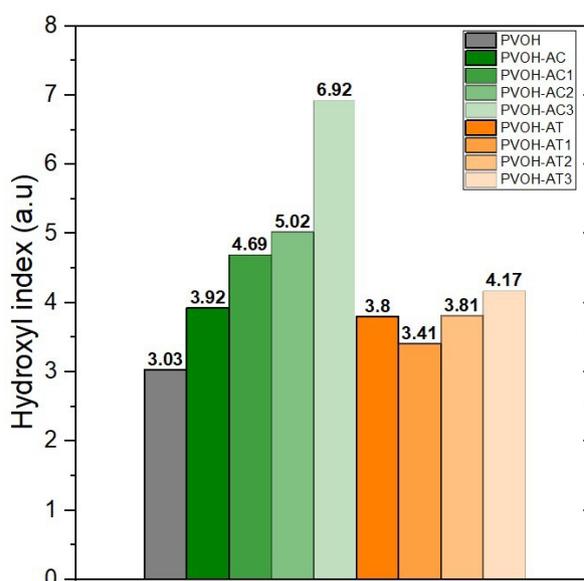**Figure 3.** Carbonyl index of PVOH sample, PVOH-AC, and PVOH-AT hydrogels.

Figure 4. Hydroxyl index of PVOH sample, PVOH-AC, and PVOH-AT hydrogels.

Inferential statistics was used to separately verify differences in quantitative results from the carboxyl index using as factors the PVOH film and crosslinking time from Figure 3, and statistical analysis can be seen in Table SI – Supplementary Material.

The statistics test doesn't show the differences among the samples, and the F value (0.98), non-represent differences in similarity among the hydrogel groups analyzed, show the same carboxyl properties comparable.

The hydroxyl indices of the samples show that, in addition to esterification, they also show an increase in the organic indices as -OH, due to the presence of hydrogen and hydroxyl bonds between the organics and PVOH (Franco et al. 2021, Sabzi et al. 2020). This is the citric acid that presents free hydroxyls of its largest structure, it had the percentage of all projected structures and non-total esterification with PVOH matrix presenting hydrogels with insulated and non-crosslinked with presentation according to data presented in the details of swelling behavior and this is their sol-gel groups in addition to hydroxyl possess (4 hydroxyl being 3 groups of -COOH) (Gautam et al. 2022). However, the tartaric acid hydrogel samples showed similar behavior in terms of hydroxyl indices, which correspond to the swelling, sol-gel fraction, and moisture tests in which the presence of a three-dimensional structure indirectly reduced the hydroxyl indices and increased the carbonyls. Figure 4 shows the hydroxyl index of PVOH-AC and PVOH-AT hydrogels.

Inferential statistics was used to separately verify differences in quantitative results from hydroxyl index averages using as factors the PVOH film and crosslinking time from Figure 4, and statistical analysis can be seen in Table SII.

The statistics test shows the differences among the samples composed by PVOH-AC in the time synthesis of 20 minutes and 3 hours. To the -AT hydrogels the samples can be comparable with the similarity with the -AC group with the Tukey-Kramer test showing proximity the all groups except to the -AT3 hours group ([AB]). F value (1.54) represents statistical differences among the hydrogel's groups -AC and -AT analyzed, showing the hydroxyl properties comparable ever with your statistical differences.

Thermogravimetric analysis (TGA)

Thermal analysis of PVOH and its hydrogels (Figure 5) shows significant mass loss in up to four stages, 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 (Sonker et al. 2019, Sonker & Verma 2018, Yu et al. 2021). The first recorded temperature stage ranged from 200°C to 350°C was due to the initial thermal decomposition of the chemical structure of PVOH, by low molecular weight compounds, while the second degradation process (400°C-500°C) has been associated with the decomposition of the polymer backbone (Sonker et al. 2019, Suganthi et al. 2020, Yu et al. 2021). In the DTG curves, the temperatures corresponding to the maximum rate of weight loss of the second stage of degradation of the PVOH sample, -AC, -AC1, -AC2, and -AC3 were 443.76°C; 366.24°C; 364.35°C and 365.30°C respectively. This behavior implied lower thermal stability of the hydrogels with the incorporation of citric acid, which was confirmed by the loss of mass in the second step due to the decomposition of the PVOH side chain (Hrabalikova et al. 2016, Suganthi et al. 2020, Yu et al. 2021). The thermal degradation temperature of the third stage and the reaction times applied with AC did not significantly change the TGA/DTG curves because the crosslinking reaction failed to change the PVOH backbone structure.
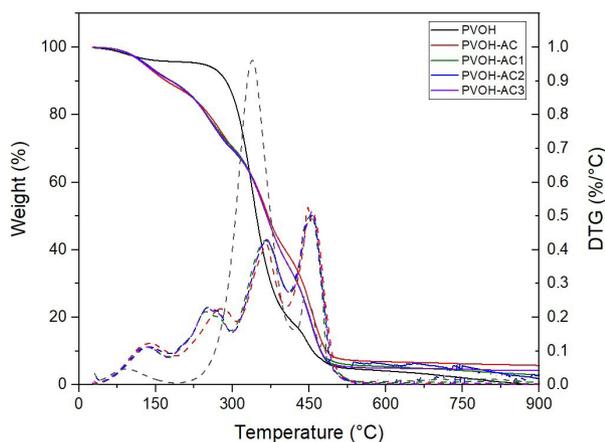
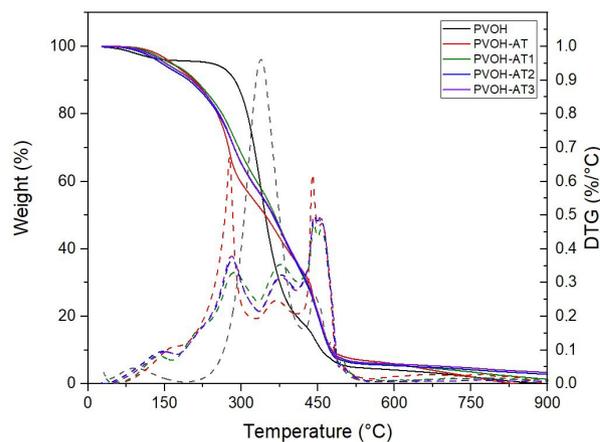**Figure 5.** TGA and DTG curves of PVOH film and PVOH-AC hydrogels.

Figure 6. TGA and DTG curves of PVOH film and PVOH-AT hydrogels.
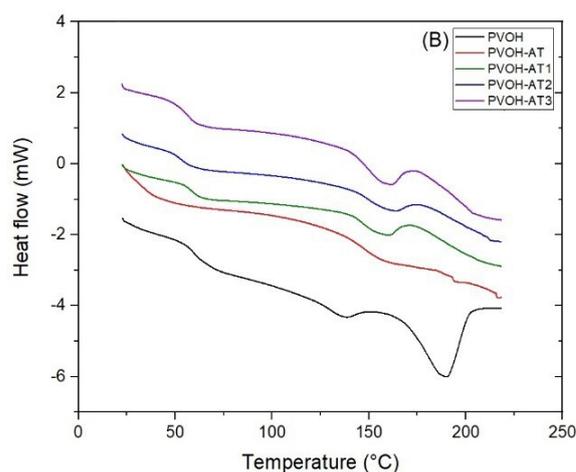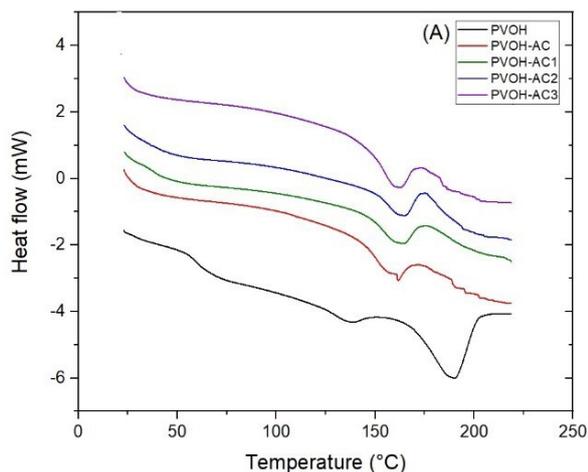

Figure 7. DSC curves of PVOH sample, PVOH-AC (A), and PVOH-AT (B) hydrogels.

TGA curves of the PVOH film sample and -AT hydrogels (Figure 6) show a similar weight loss trend across four temperature ranges, as reported by Sonker & Verma (2018) and Yang et al. (2021). The temperature ranges from 80°C to 200°C corresponds to the mass loss caused by the absorbed and adsorbed water content in the hydrogel structure. The difference in this region may be due to the presence of a greater amount of adsorbed water in the crosslinked PVOH films. The first degradation region corresponds to the maximum mass loss from 200°C to 450°C, recording a slower degradation of PVOH crosslinked with organic acids compared to pure PVOH sample (Suganthi et al. 2020); something also observed through the progress during the thermal degradation up to 450°C (Sonker et al. 2019). In this region, mass loss is observed due to chain scission and degradation of the PVOH backbone. The crosslinking of PVOH with organic acids modifies its chemical structure, forming a chemically crosslinked intra- and intermolecular structure (Gautam et al. 2022, Hrabalikova et al. 2016, Suganthi et al. 2020).

Table II. DSC data of the evaluated hydrogels.

Samples	Tg (°C)[a]	Tm (°C)[b]	ΔHf (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-AT	29.67	155.46	4.73	3.32
PVOH-AT1	58.10	158.04	9.87	6.93
PVOH-AT2	53.35	161.05	8.07	5.66
PVOH-AT3	56.43	157.79	9.89	6.94

Where: [a] T_{max}: Glass transition temperature; [b] T_m (°C): Melting temperature; [c] ΔHf (J/g): Enthalpy of fusion; [d] % Xc: percent crystallinity; [e] * non-measured.

Differential scanning calorimetry (DSC)

The DSC curves of the PVOH film sample, -AC, -AC1, -AC2, -AC3 shown in Figure 7 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 (Sanchez & Alvarez, 2019). The incorporation of citric acid (AC) in the chemical reaction time is observed for the hydrogel 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 behavior is described by Yu et al. (2021) 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 composed by -AT, -AT1, -AT2, -AT3 shown in Figure 7, it is observed that with the incorporation of tartaric acid (AT) the chemical reaction time for all samples, except for PVOH-AT, did not have a significant decrease in its T_g, staying around 53°C to 58°C, while the -AT sample showed a greater decrease in Tg to 29.6°C. Compared with the PVOH film sample (T_g = 60.15°C) the maximum range of T_g difference from tartaric acid to PVOH is 30.5°C. Yang et al. (2021), state in their study that the degree of crystallinity (% Xc) of hydrogels with tannic acid (TA) decreased from 46.7% to 8.7% with increasing concentration from 0 to 0.5% in mass, indicating that the incorporation of AT reduces the crystallization of PVOH due to the strong hydrogen bond formed between AT and its polymeric chains.

To investigate the effects 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 (Xc) were obtained from the curves of samples of PVOH hydrogels with citric (AC) and tartaric (AT) acid and their time variations are shown in Table II.

The DSC curve for the PVOH film exhibits an endothermic peak at 190.18°C which corresponds to the melting temperature of the PVOH crystalline phase (Yang et al. 2021). For hydrogels composed of PVOH-AC and -AT, as shown in Table 4, the melting point T_m of -AC, -AC1, -AC2, -AC3 and -AT, -AT1, -AT2,
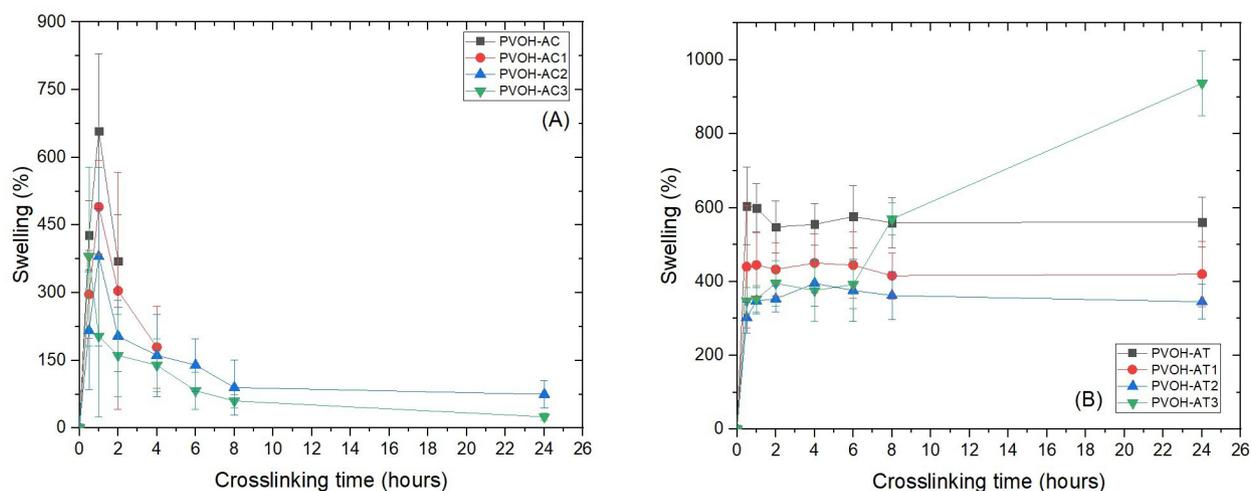
Figure 8. Swelling graphs of PVOH-AC (A) and PVOH-AT (B) hydrogels.

-AT3 is 161.52°C to 159.72°C and from 155.46 °C to 157.79°C respectively, and all T_m points were shifted to a lower temperature as the concentration of organic acids increased, with similar behavior for the -AT group. This behavior was also observed in a study by Yang et al. (2021) with the incorporation of tannic acid. Meanwhile, the Xc of composite hydrogels decreased from 32.52% to 3.32%; 6.93%; 5.66%, and 6.94% with the tartaric acid. The incorporation of organic acid in 1% by weight, indicates that the introduction of organic acids can chemically inhibit the crystallization of PVOH due to the strong interaction of free hydrogen and -OH bonds formed between AC and AT respectively the polymeric chains of PVOH (Gautam et al. 2022). The DSC curves in Figure 7 also show that the T_m values of all crosslinked PVOH hydrogels are lower than that of pure PVOH film (T_m = 190.1°C) and follow an average order of PVOH > PVOH-AC > PVOH-AT hydrogels, which should again be due to the lower rigidity and weakened intermolecular hydrogen bonding among polymeric chains in the crosslinked PVOH film. This thermal behavior was also observed and studied (Xu et al. 2018).

Swelling test

The swelling capacity (S%) of the hydrogels was observed by measuring the degree of function of test time. The uptake of water during swelling is due to a large number of hydroxyl groups (-OH) present in PVOH and the organic acids, resulting in high swelling and therefore reducing its strength and final properties in the hydrogels (Sonker & Verma 2018). The cross-linking in addition to reducing the active -OH groups, also covalently bonds the PVOH chemical structure, reducing their interaction with water, and resulting in final swelling (Gautam et al. 2022, Sonker & Verma 2018). Hrabalikova et al. (2016) studied that an increase in the crosslinking degree leads to a significant decrease in the S% of the examined samples. Figure 8 shows the degree of swelling for PVOH hydrogels with citric acid (-AC) and tartaric acid (-AT) for up to 24 hours.

Inferential statistics was used to separately verify differences in swelling properties using as factors the used crosslinking time to PVOH-AC hydrogels, and statistical analysis can be seen in Table SIII.

For the swelling test, only PVOH-AC was different from the PVOH-AT samples, which is caused by the higher swelling of the -AC hydrogels in comparison to the other samples composed of tartaric
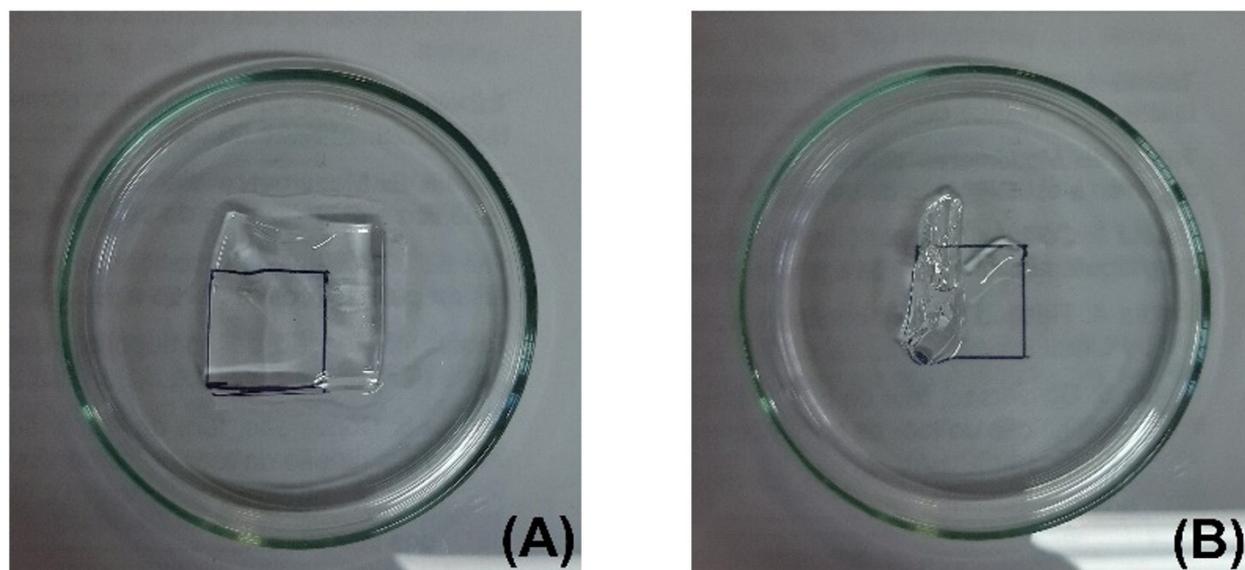
Figure 9. PVOH-AC hydrogel in swelling for 30 minutes (A) and 2 hours (B).

acid (-AT). This better stability in the time also promoted better crosslinking time properties in 2 hours, increasing the time without disintegration. This thermal treatment in 3 hours to -AC2 and -AC3, also promoted equal values for specific swelling, with PVOH polymer crosslinking and citric acid due to the more time of the synthesis in comparison with PVOH-AC hydrogel had the most results. The AT hydrogel samples have a statistical difference with the PVOH-AT3 having more swelling in comparison to the other samples.

Evaluating the swelling 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 minutes reaction due to the low chemical interaction of citric acid (AC) with PVOH, the other samples of -AC1, -AC2 and -AC3 obtained longer-stability times during the test (Castro et al. 2023), however with lower relative rates of swelling and with gradual loss of mass until the final of the perform. Kim et al. (2003) observed in their study a maximum swelling of 400% in 2h for PVOH-based hydrogels. This behavior 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 (Sonker & Verma 2018). It is reported that the number of residual free carboxylic groups (-COOH) increases with the AC content in the hydrogel (Gautam et al. 2022, Sabzi et al. 2020). This chemical theory is based on the concept of chemical synthesis and stability of hydrogels that was developed from the study of the literature (Gautam et al. 2022, Sonker & Verma 2018) that will be addressed and presented in the FTIR section and the method applied conceptually to the other organic acids in this study. Figure 9 shows a hydrogel made up of PVOH-AC (30 minutes) after the swelling tests up in a Petri dish to the limit of two hours. Illustrative images of PVOH-AC, -AC1, -AC2, and -AC3 to compare the same time in the swelling test up to 2h can be seen in Figure S1.

However, the -AC1, -AC2, and -AC3 hydrogels showed lower percentages of swelling due to the increased crosslinking applied, but with a longer stability time when compared to the -AC; -AC2 and
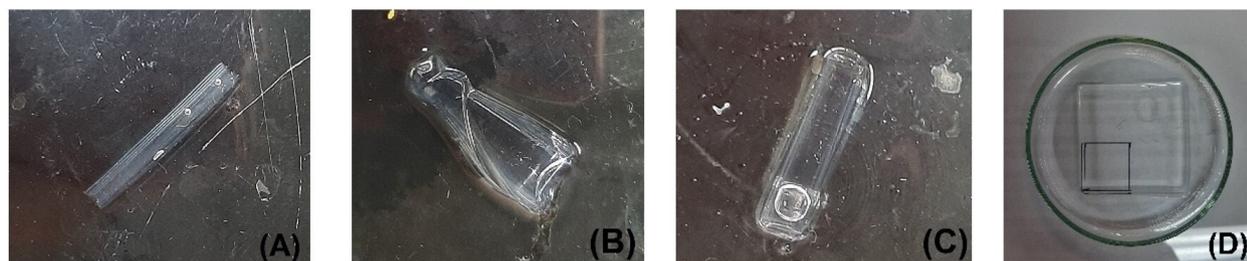
Figure 10. PVOH-AT hydrogels swelling after 24 hours; -AT (A); -AT1 (B); -AT2 (C) and -AT3 (D).

-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 hydrogels. This behavior is because the longer the thermal reaction takes, the greater the percentage of crosslinking in the samples, promoting lower swellings but longer stability in liquids, respectively, but the crosslinking kinetics with citric acid does not favor chemical stability which is evidenced by the total hydrolysis of the hydrogel, which will be confirmed in the following topic of swelling kinetics. This behavior has been studied and reported by several researchers (Gautam et al. 2022, Castro et al. 2023).

For the swelling of PVOH-AT, a decrease in the average percentage of swelling of the samples by 50% was observed, in which the PVOH-AT3 sample reached the maximum swelling value of 900% provided by the unwinding and linearization of the hydrogel, allowing a greater dimensional expansion. Sonker & Verma (2018) describe that the maximum mean swelling for -AT was 180% for 30 minutes and 150% for 2 hours with the addition of at least 5% AT, and swelling was reduced with an increasing volume percentage of AT added to the hydrogel. This value is also presented for the reaction obtained in 2 hours (PVOH-AT2) with the value of 380% on average, taking into account the percentage difference of AT used for the synthesis of 1% vs 5%. Samples -AT1, and -AT2 (Figure 10) had a swelling decrease with increasing reaction time, where sample -AT2 had the lowest swelling value of 350%, and all hydrogel samples had dimensional stability without disintegrating up to 24 h. Furthermore, the swelling percentage can be controlled either by the concentration of AT or its crosslinking time, as well as the crosslinking kinetics can be altered by intra- or intermolecular crosslinking which is described in the FTIR discussion (Sonker & Verma 2018). Gautam et al. (2022) describe that tartaric acid (AT), 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 behavior is shown by the low swelling characteristic shown above in citric acid and its chemical crosslinking kinetics by esterification. Figure 10 shows the samples of hydrogels with AT and their variables after 24 h of swelling test.

Moisture absorption

The samples of hydrogels with citric acid (-AC) obtained the maximum moisture value for the 20 minutes reaction (PVOH-AC) with an average value of 14.50%; and the PVOH-AC3 sample obtained good swelling rates with an average final of 13%. Moisture absorption is directly linked to the reaction chemistry of citric acid (AC), which, due to its low chemical interaction and having free (-OH) and
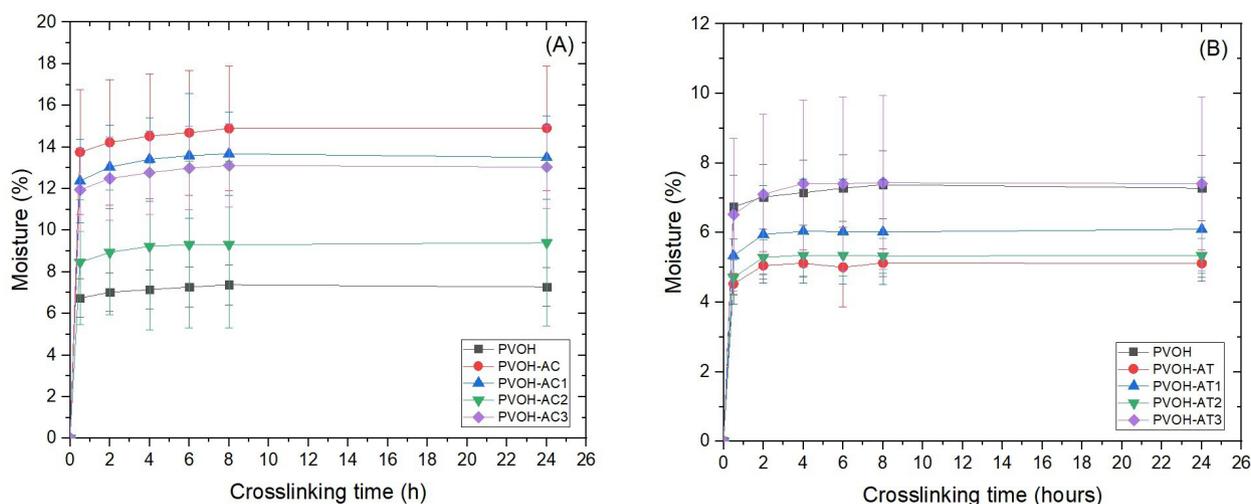
Figure 11. Moisture graphs of PVOH sample, PVOH-AC (A), and PVOH-AT (B) hydrogels.

available hydroxyl groups, transmits a more hydrophilic character to the sample, providing higher percentages of absorption through hydrogen bonds (Liu et al. 2021, Sabzi et al. 2020). It is observed that the PVOH sample obtained the lowest percentage of moisture absorption with 7% characterized by its hydrophilic characteristic and chemical structure that, after the initial adsorption, prevents greater absorption of moisture compared to the incorporated samples of AC by presenting hydroxyl groups free (-COOH) on its surface (Uyanga & Daoud 2021). Liu et al. (2021) studied the polymer chains and the surrounding water molecules, where the researchers tried to elucidate such interactions with defined water states: free water, intermediate water, and bound water. For the hydrogels constituted by PVOH-AT, the values are the lowest concerning the performed samples composed by -AC, having a maximum of 7.50% and observed and addressed in other recent studies involving hydrogels and carboxylic acids, in which how much the greater the crosslinked density of the hydrogel, the lower the water absorption, lower the degree of final swelling of the hydrogel on its surface (Uyanga & Daoud 2021). This parameter is in agreement with the sol-gel fraction results. Figure 11 shows a hydrogel made up of PVOH-AC and PVOH-AT during the moisture tests up to the limit of 24 hours.

Inferential statistics was used to separately verify differences in moisture properties in PVOH-AC and PVOH-AT hydrogels, as factors the used crosslinking time, and statistical analysis can be seen in Table SIV.

For the moisture test performed, only PVOH-AC1 and -AC3 were different from the other samples in the statistical test, and the citric acid had better results obtained in comparison to the PVOH-AT samples. This is caused by the higher swelling of the hydrogel in comparison to other samples and PVOH film. This better moisture in the time also is due to the crosslinking time properties until 20 minutes to PVOH-AC, promoted by hydroxyl groups free (-COOH) shown previously in Figure 11. The thermal-synthesis treatment applied to -AC2 and -AC3, also promoted equal values for specific swelling, compared with PVOH-AC hydrogel which had the most result obtained (14.50%). The PVOH-AT1 and -AT2 samples, had the better results obtained by statistical data, promoted by the chemical interaction of the tartaric acid and PVOH polymer. The PVOH-AC and PVOH-AT hydrogels results obtained through the moisture experiment were analyzed using a mathematical model of moisture

Table III. Peleg constants k_1 and k_2 of the analyzed hydrogels.

Samples	k_1	k_2
PVOH	0.193	6.643
PVOH-AC	0.307	13.607
PVOH-AC1	0.447	12.147
PVOH-AC2	0.320	8.300
PVOH-AC3	0.367	11.757
PVOH-AT	0.353	4.353
PVOH-AT1	0.407	5.137
PVOH-AT2	0.387	4.517
PVOH-AT3	0.393	6.323
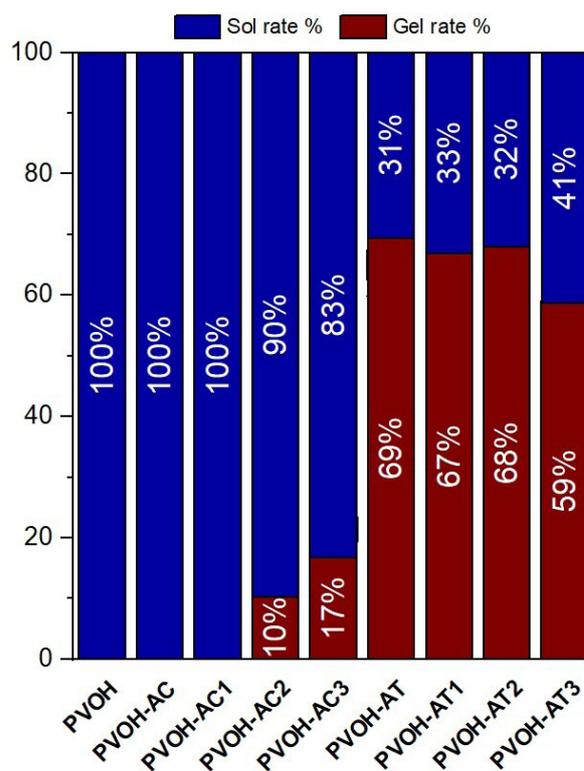
Figure 12. Sol-gel rate graphs of PVOH film sample, PVOH-AC, and PVOH -AT hydrogels.

absorption kinetics, widely used in foods and applicable to hydrogels, the Peleg model (El Sayed et al. 2021, Peleg 1988). Peleg's constants (k_1 and k_2) for the analyzed hydrogels are presented in Table III. The symbol k_1 represents the mass transfer (water) in the samples. Thus, the lower the value of k_1, the higher the initial absorption rate of the hydrogel. The value of k_2 represents the maximum absorption capacity. Where, the higher the value of k_2, the lower the absorption capacity of the hydrogel.

It can be observed that the PVOH-AC and PVOH-AT hydrogels and their variations showed higher constants k_1 and k_2 concerning the PVOH film sample (neat), indicating that the hydrogels had lower initial absorption and lower absorption capacity total, which is presented in the swelling and moisture tests. It is observed that the values of the constants increased from PVOH film sample to PVOH-AC and PVOH-AC3 (where k_1 and k_2 reached their maximum value for -AC) and decreased again in the PVOH-AT all samples in k_2, which due to the high k_2 value for the -AC hydrogels, they suffer from moisture hydrolysis and consequently swelling and disintegration, a phenomenon observed by the moisture and swelling tests.

Sabzi et al. (2020) describe that this phenomenon is due to the free hydroxyl groups of citric acid, which provide high moisture absorption. Uyanga & Daoud (2021) and Gautam et al. (2022) state that the higher the crosslinking rate in the hydrogels, the lower the percentage of absorbed moisture. It is also noted that all samples had k_1 and k_2 values higher than those of PVOH, which indicates that change in the absorption behavior with the inclusion of organic acids and that the initial average

absorption rate is higher than that of PVOH neat. El Sayed et al. (2021), describe that the affinity of hydrogels for swelling/water absorption is maximum when the swelling process starts, the affinity decreases as the hydrogel becomes saturated.

Sol-gel rate

For the interpretation of the analyses in sol-gel rate (Figure 12), the PVOH film sample was defined as the standard because it is soluble (sol rate) for all samples incorporated with citric and tartaric acids. The samples constituted by -AC3 had the highest sol fraction rate (83%), attributed to the low kinetics of chemical crosslinking of citric acid, which hydrolyzes easily causing its disintegration in the testing. It is also described in the literature (Gautam et al. 2022) that the dimensional stability of tartaric acid favors stable interlocking structures that are conditioned to its high degree of crosslinking in comparison to the PVOH-AC samples. Pei et al. (2021) and Yang et al. (2021), describe in their sol-gel results that the interaction of hydrogen bonds can improve the crosslinking density of the hydrogel network to form a dense network structure, but with less swelling, shown by the incorporation of organic (tannic) acid into their hydrogels. Xu et al. (2018) describe that the gel content increases with the organic acid content, indicating the increasing crosslinking degree can be associated with higher consumption of hydroxyl groups and therefore a higher crosslinking degree.

CONCLUSIONS

The effects of citric and tartaric organic acids on hydrogels based on PVOH polymer were studied successfully. In physic-chemical analysis, the PVOH-AC hydrogels showed the highest swelling percentages, but with shorter swelling times due to dimensional instability and their weak chemical interaction promoted between AC and PVOH characterized by type B and C (intramolecular) chemical-reaction presented in FTIR, it was also observed through sol-gel analysis that -AC did not interact effectively for hydrogel crosslinking, with the lowest indices calculated for samples with 2 and 3 hours. The tartaric acid (-AT) hydrogels obtained satisfactory swelling results with good cross-linking percentages that promoted good moisture absorption, sol-gel, and FTIR properties, and the -AT hydrogels had greater dimensional stability in compared to citric acid hydrogels. Thus, this behavior is attributed to chemical interactions promoted mainly by the majority of the type A (intermolecular) chemical reaction model for the -AT hydrogels samples described in FTIR, and calculated carbonyl/hydroxyl data.

For samples of -AC and -AT hydrogels, the behavior for moisture absorption calculated using absorption kinetics laws, shows values to k_1 for all samples, and all hydrogel values were higher than the PVOH film sample, which shows the interaction of organic acids with the absorbed and adsorbed water, and the k_2 was higher for the samples with citric acid, resulting from the chemical bonds present in the hydroxyl functional groups of organic acids. The behavior of k_1 is also similarly described in the swelling and diffusion kinetics with their values nearest to the trend values of the chemical reactions of hydrogels over time. In the thermal analysis, the samples had similar degradation behavior 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 in comparison to the PVOH film sample. The analysis of DTG curves shows characteristic and defined stages of degradation, in which the hydrogels of -AT followed by -AC presented the best results of resistance to degradation, respectively. Regarding the proposed and analyzed reaction times, it is observed that for the AC hydrogels, the best reaction time was 3 h, and for the AT-incorporated hydrogels, the best time observed was 1 h, considering the potential of swelling of the samples versus the time crosslinking. It is concluded that organic acids can be used as crosslinking agents for hydrogels citric and tartaric-based, however, the AC hydrogel samples still do not meet the requirements through this applied methodology and the hydrogel samples constituted by tartaric acid are more promising to the development of hydrogels.

Acknowledgments

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Dione Pereira de Castro; performed the experiments analyzed the data and wrote the paper. Ruth Marlene Campomanes Santana; conceived the project, analyzed the data, and revised the paper.

SUPPLEMENTARY MATERIAL

Tables SI - SIV.

Figure S1.