EVALUATION OF THE EFFECT OF CITRIC ACID ON THE CROSSLINKING OF PVA THROUGH SWELLING AND THERMAL ANALYSES

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Abstract - Hydrogels are crosslinked polymeric structures that can retain a big quantity of fluids. The grade of reticulations influences the final properties of the material and it depends on various factors, such as the nature of the monomer and reticulation method. According to it, this study aimed to evaluate, through swelling and thermal analyses, the influence of the citric acid (AC) content on poly (vinyl alcohol) (PVA) chain reticulation. Swelling analysis shows that increasing the AC content increases the network crosslinking. Through DSC analysis, it was possible to verify that the secondary event related to the glass transition of the samples shifted to higher values as the AC content was increased, which implies the crosslinking of the polymer network suffered a positive influence with the acid content increase. TGA analysis has showed that the stability with 5% of loss of mass of the non-crosslinked polymer is less than that of crosslinked polymer.

Keywords: *Hydrogels, PVA, citric acid, chemical reticulation, thermal analysis.*

Introduction

Hydrogels are crosslinked polymeric structures that can retain a big quantity of water or other fluids, until a physical-chemical equilibrium occurs, without losing their shape (1-4). Their capacity to absorb and retain big amounts of water is due to the presence of hydrophilic functional groups linked to the polymer chain, while resistance to dissolution is the result of their crosslinks between network chains, once the hydrophilic matrix is water-soluble. These materials can be prepared by modification of their naturals structures, by synthetics monomers, or by a blend of both materials – over the past few decades, natural materials have been gradually replaced by synthetics ones. They can be crosslinked in several ways: chemical methods – using crosslinking agents and reaction initiators or incidence of ionizing radiation, or physical methods (4,5). Among the most widely used synthetic polymers, poly(vinyl alcohol) (PVA) stands out, due to its properties like biocompatibility, excellent thermal and chemical stability, and atoxicity (6,7).

The properties of the materials must be known to determine their performance in a particular application. Swelling analysis measures the water absorption capacity of hydrogels. Thermoanalytical analyses are a large group of analyses capable of determining various physical properties of different types of materials. Among these techniques, TGA and DSC stood out. TGA monitors the loss and/or gain of mass of a sample as a function of time or temperature, allowing the decomposition of compounds to be visualized. This technique is important to determine the thermal stability of the materials. DSC, on the other hand, monitors the enthalpy variations of a sample concerning a reference material, which makes it possible to check the temperatures where the thermal events occur, such a glass transition temperature (T_g), cristallization (T_c) and melting (T_m), in addition to quantitive measurements of specif heat, melting, crystallization and reaction heat (8).

Reffering to it, the present study brings swelling analysis to evaluate de water absortion, and TGA and DSC analyses to evaluate the influence of the concentration of CA in the properties of the studied materials.

Experimental
Materials
For the production of hydrogel films, poly(vinyl alcohol) (PVA) with a hydrolysis degree of 87-89% and a molar mass of 104500g/mol, anhydrous citric acid with a molar mass of 192.12g /mol, and hydrochloric acid (1M HCl) was used.

Synthesis of crosslinked PVA hydrogels with different citric acid contents
Initially, a 5%wt PVA solution was prepared by dissolving the granulated polymer in deionized and distilled water, at room temperature and under shaking. The system was heated to 80 ±5ºC and kept at that temperature until the polymer was completely dissolved. After the solution was cooled, the evaporated solvent was compensated. Then, the hydrogel was prepared with the addition of different concentrations of citric acid to the PVA solution, using 1M HCl as a chemical catalyst, under heating of 85 ±5ºC, for 20 minutes. The material was processed via casting, dried on a stove (60º by 16h). After drying, the hydrogels were washed with distilled and deionized water to remove the acids remaining on the surface and replaced in the stove for another hour, under the same drying conditions. Fig. 1 shows the representation of the method used to obtain the hydrogels. The process of obtaining the hydrogels was extensively tested before being standardized, and from this, all samples used in this study were obtained. Table 1 shows the hydrogel formulations.
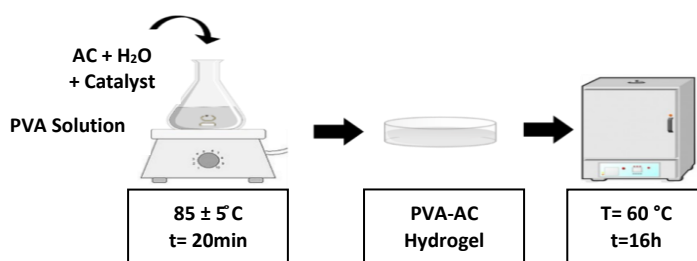

Figure 1: Schematic representation of the synthesis and processing of hydrogel samples.

Table 1: Formulation of the different hydrogel samples.

Samples	PVA solution (wt%)	Citric Acid (wt%)	HCl 1M (mL/50g solution)
PVA	4	-	-
AC0.4	4	0.4	1
AC1.2	4	1.2	1
AC2.8	4	2.8	1
AC3.6	4	3.6	1

Methods
Swelling
Specimens of each hydrogel composition were subjected to swelling in recipients containing distilled and deionized water, and measurements were taken at predetermined time intervals.

Thermogravimetric Analysis (TGA)
To perform the analyzes in the hydrogel samples, the TGA equipment [TGA 4000, Perkin Elmer] programmed in the temperature range of 30 to 950°C was used with a heating rate of 40°C/min, under an atmosphere of N_2.

Differential Scanning Calorimetry (DSC)
DSC analyzes were performed on a Perkin Elmer DSC 600 calorimeter, with two cycles of heating in a nitrogen atmosphere, with a heating rate of 20ºC/min, from room temperature to 220ºC.

Results and Discussion
Swelling
Fig. 2 shows the sample swelling profiles. It can be seen that increasing the level of AC caused an increase in crosslinking as the degree of swelling decreased. It is also possible to observe that the swelling reaches a plateau after approximately 0.5h for samples AC0.4 and AC1.2 and after 4h for samples AC2.8 and AC3.6, suggesting that the materials reached their maximum water absorption.
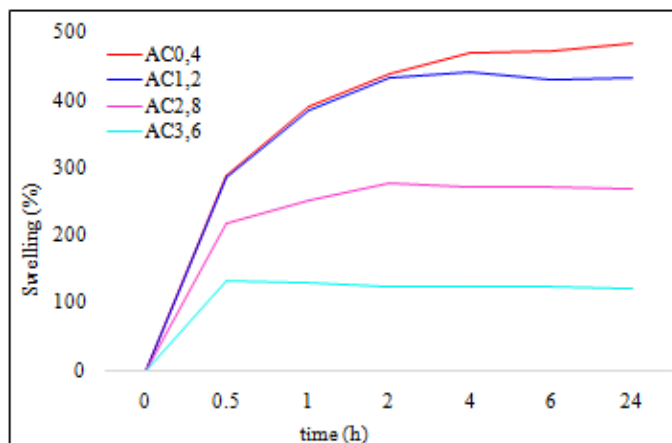

Figure 2: Sample swelling profiles.

Thermogravimetric Analysis
TG analyzes were performed for PVA and hydrogels with different citric acid contents. Fig. 3 (a) shows the thermogravimetric curves (TG) for these materials, where the initial thermal stability was evidenced by data between 100 and 200ºC, and 3 (b), the derivative of these curves. Table 2 shows the temperatures in some mass loss ranges and DTG peak temperatures of the main thermal events presented by the materials during the analysis.
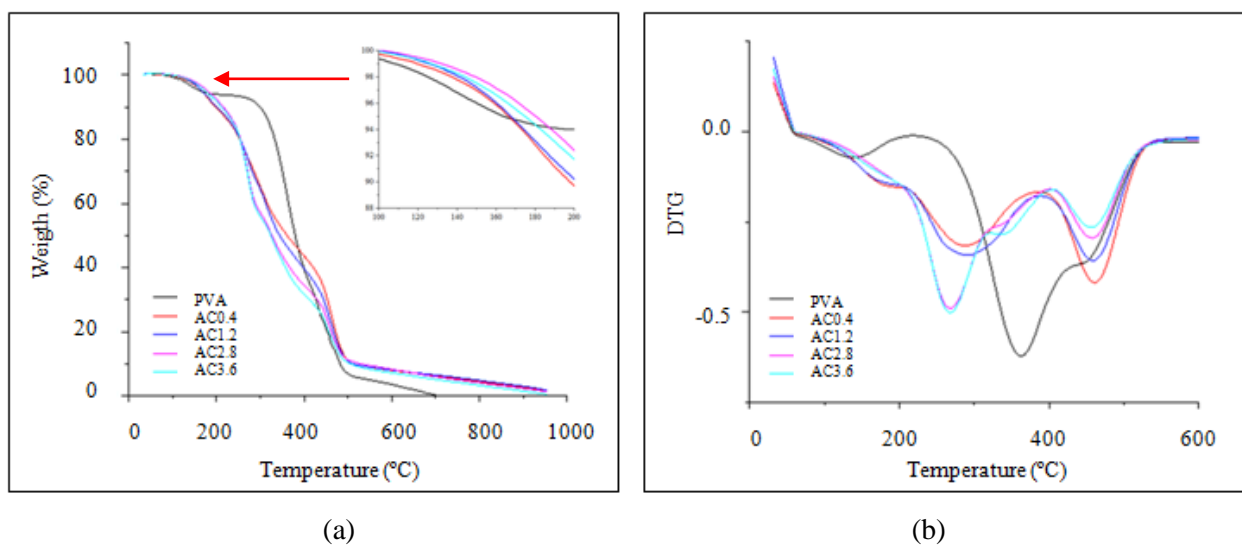

(a)   (b)

Figure 3: Thermal curves for the pure PVA film and with the addition of different levels of AC: (a) TG and (b) DTG.

Table 2: temperatures in ranges of mass loss and ash content, in addition to maximum decomposition kinetics temperatures of samples of pure PVA and hydrogels obtained from the thermogravimetric analysis.

Samples	TG				DTG	
	T (ºC) 5% loss	T (ºC) 10% loss	T (ºC) 20% loss	Ash content (%)	1º T_p (ºC)	2º T_p (ºC)
PVA	163.4	299.9	332.5	0	363	-
AC0.4	166.2	197.4	252.7	1.52	287	461
AC1.2	167.7	201.5	254.2	1.57	290	459
AC2.8	180.5	215.8	254.3	1.32	268	458
AC3.6	174.8	211.9	253.0	0.02	268	456

The first process observed in PVA, between 100 and 200ºC, can be associated with the loss of residual water from the film drying process, representing about 6% by weight of the material. After this temperature, a huge loss was observed, between 245 and 550ºC, with maximum decomposition kinetics at 363ºC, which can be associated with the decomposition of the polymeric chain, representing 95% of lost mass. In the decomposition of PVA, water vapor is formed, which generates unsaturation in the polymeric chain, causing a shift to the right shoulder in the decomposition curve, as the energy to break unsaturated bonds in the polymeric chain tends to be greater. At the end of the analysis, no residual mass was observed.

Samples AC0.4 and AC1.2 (with 0.4 and 1.2%wt of ac, respectively), showed similar curves. In both cases, the presence of an initial event is noted, between temperatures 150 and 200ºC with a loss of approximately 10% of the mass, which can be associated with the loss of water occluded in the sample network. There was a second event, between 220 and 380ºC, with a peak temperature of 287 and 290ºC, which can be associated with the decomposition of polymer chains, with a residual mass of 43%. After 400ºC, a third thermal event can be observed, which the decomposition of the unsaturation and crosslinking of the polymeric chain occurs, and it requires more energy than the saturated bonds of the PVA chain to decompose.

In samples AC2.8 and AC3.6 (with 2.8 and 3.6% wt of ac, respectively), it was not possible to evaluate the initial process of water loss, it can be justified by the greater difficulty of water diffusing through the reticulated chain. The first event observed had a maximum decomposition rate at the temperature of 268°C, for both samples, showing, as in the pure PVA sample, decomposition shoulders of unsaturations generated in the water chain generated by the release of H_2O molecules from the OH functional group present in the matrix of the material and the capture of hydrogen from the saturated chain. After the first decomposition, a second event is noted, with a maximum kinetic temperature of 457ºC for the two samples, where the unsaturation and crosslinking of the polymeric network occurs. At the end of the analysis, all hydrogel samples had ash content, resulting from the non-decomposed crosslinking of their polymer chains.

Differential Scanning Calorimetry (DSC)
Through the DSC it was possible to verify the influence of the crosslinking agent concentration in the variation of the thermal events of the samples. Crosslinking increases the rigidity of the macromolecular chain, causing the thermal events of the materials to be shifted to higher temperatures. Through fig. 4, where the DSC curve of the samples is presented, it is possible to perceive this effect in the increase of T_g for the samples with the addition of crosslinking agent, observing a displacement in the baseline for higher values.

The pure PVA sample, which does not have to crosslink in its network, presented a T_g of 73ºC. Meanwhile, samples containing 0.4 and 1.2% wt of AC have showed an increase in that temperature: 89.3 and 98ºC, respectively. The effect of crosslinking on samples with a content of 2.8 and 3.6% wt of AC made the identification of the T_g of the samples impossible since the change

in the baseline was broad, and it was not possible to determine where the beginning and the end of the thermal event occurred. It is possible to infer, through analysis, that the crosslinking agent added to the pure material promoted the crosslinking of the samples, provided that it caused an increase in the transition temperature of the materials, as their composition was increased. In the analysis, it was not possible to verify the T_m of the materials, as the test was carried out to observe crosslinking through the change in T_g.
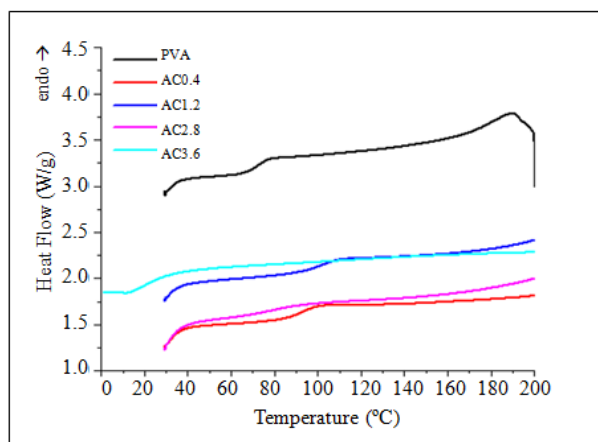

Figure 4: DSC curve for PVA film and hydrogels samples.

Conclusions
In the swelling analysis, the influence of CA on the crosslinking of the PVA network was evident. The results obtained through the DSC analysis proved, through the displacement of the secondary thermal event (glass transition temperature) to higher values, that the addition of AC increased the rigidity of the chain, giving evidence of greater crosslinking with the increase of its concentration. Through the TGA technique, it was possible to evidence an increase in the initial thermal stability of the PVA with the addition of the crosslinking agent, verified by the appearance of thermal events at higher temperatures for the materials with the addition of the AC, in addition to remaining material remaining at the end of the process. It is possible to affirm, through these analyses, that AC is effective as a crosslinking agent for PVA.

Acknowledgments

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