

# **RADIATION AND CHEMICAL CROSSLINKING OF PVA/STARCH: A COMPARATIVE STUDY TO OBTAIN SUPERABSORBENT HYDROGELS**

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## **ABSTRACT**

In attainment of superabsorbent polymers (SAPs) based on PVA [poly (vinyl alcohol)] and starch, two different crosslinking processes were utilized: use of glutaraldehyde and gamma-radiation, aiming at evaluating the best alternative for the SAPs formation. Polymer mixtures from PVA aqueous solutions and starch suspensions were crosslinked chemically and by radiation apart. For that, the radiation absorbed dose and the proportion of crosslinker were kept fixed, varying only the amounts of PVA and starch at diverse proportions. It was observed experimentally that the irradiated samples showed a better reaction control and purity, but lower crosslinking degree than that of glutaraldehyde-crosslinked SAPs, thus resulting higher swellings for the former. The glutaraldehyde-crosslinked samples showed a higher range of degradability on TGA (thermogravimetric analysis) test due to the presence of residual HCl and glutaraldehyde in them. IR spectra absorption bands of the chemically obtained SAPs showed glutaraldehyde peaks, whereas these were absent in the irradiated materials. By these experiments, one concluded that increases of starch proportion lead to decreases of the SAPs swelling, probably due to higher hydrophobic characteristics of starch than those of PVA, despite some properties of the this having been improved.

## **1. INTRODUCTION**

Superabsorbent polymers (SAPs) are three-dimensional hydrophilic polymer networks exhibiting a significant swelling after absorbing water. The volumetric expansion mainly occurs through their porosity retaining the liquid within their structures is formed by crosslinks between the main chains of the polymer [1]. They are capable of absorbing large quantities of water and aqueous solutions without dissolving [2]. PVA is a polymer obtained from polymerization of vinyl acetate in an alcoholic solution [3], it is soluble in water, forming transparent solutions and films of various thicknesses. PVA has a simple chemical structure, macromolecule consisting of a long chain of carbon atoms reconnected to hydrogen atoms and hydroxyl (-OH) group. Its chemical formula is  $(C_2H_4O)_n$  [4] and its properties can vary depending on the degree of hydrolysis of its chain backbone. Cassava starch, in turn, is a carbohydrate consisting of two main polysaccharides, amylose and amylopectin and some minor components such as lipids and proteins [5]. PVA and starch processing always requires the presence of a plasticizer that decreases the  $T_g$  (glass transition temperature) of both, thus

minimizing their thermal degradation [6]. One can mix starch with other plasticizers, modify its chemical structure on existing hydroxyl groups, make mixtures of it with other products [7] to enable its commercial use in diverse applications. Starch also can be crosslinked in solution/suspension with other polymers and crosslinkers, such as, PVA and glutaraldehyde, respectively [8]. Glutaraldehyde consists of a simple molecule having five carbon atoms with an aldehyde group at each end, it is classified as an aliphatic dialdehyde. Gamma-radiation on aqueous polymer solutions induce radiolysis of both water and polymer, mainly forming free very reactive radicals such as H and OH. These radicals attack the polymer chain, binding to hydrogens and transferring the radical center to the chain [5]. Thus, crosslinking may occur by mutual recombination of macroradicals by means of covalent bonds without the use of crosslinkers and with advantages of producing a sterile and clean product. By using both crosslinking processes, SAPs obtained and several of their properties were evaluated [8].

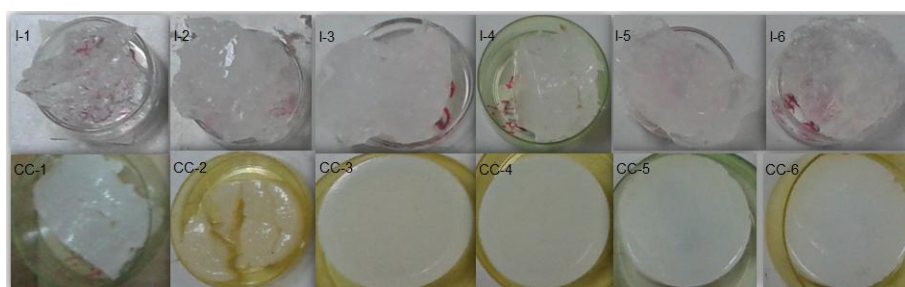
## 2. EXPERIMENTAL

### 2.1. PVA/Starch Crosslinking

Aqueous solution and suspension of PVA (Mowiol 40-88, Clariant) and manioc starch (Companhia Lorenz-PR), each at 8 % concentration, respectively, were prepared. From both, five mixture formulations were developed (Table 1). As plasticizer, 1 % (w/w) glycerol (Labsynth) was added to each mixture. Chemical crosslinking was performed adding to each mixture 1 % (v/w) of glutaraldehyde (25 % of Vetec) and 1 % of HCl 0,1 M solution (v/w) as catalyst, and all formulations were kept in oven for 1 h 30 min at 60 °C to complete crosslinking. Samples were coded as in Table 1 and Fig. 1.

**Table 1: Formulations PVA with Starch**

	Irradiated	With crosslinker
1	100 % PVA	100 % PVA
2	95 % PVA/ 5 % Starch	95 % PVA/ 5 % Starch
3	90 % PVA/ 10 % Starch	90 % PVA/ 10 % Starch
4	85 % PVA/ 15 % Starch	85 % PVA/ 15 % Starch
5	80 % PVA/ 20 % Starch	80 % PVA/ 20 % Starch
6	70 % PVA/ 30 % Starch	70 % PVA/ 30 % Starch



**Figure 1: Crosslinked samples: I (irradiated) and CC (chemically crosslinked).**

## 2.2. Gel fraction

The samples were dried in an oven at 60 °C until constant weight, weighed and packaged in metallic screens of 500 mesh. Next, they were immersed in 1000 ml of distilled water and brought to autoclave at 120 °C for 2 h. Subsequently, the samples were again dried, weighed, and the gel fraction was calculated in accordance with Eq. (1), with the final result obtained from the average of three samples of each hydrogel.

$$\text{Gel fraction (\%)} = \frac{M_S}{M} \times 100 \% \quad (1)$$

Where  $M_S$  is the mass of dry sample after removal of the sol fraction and  $M$  the mass of the dry sample before removal.

## 2.3. Swelling

The dried samples duly weighed and kept in their respective screens were immersed in distilled water, at a controlled temperature of 28 °C. At different time periods (30 min to 24 h), they were removed from the water and quickly dried by a paper towel in order to withdrawn water excess from their surfaces; next, they were weighed until already stabilized, that is, to constant weight. Water absorption was calculated in accordance with Eq. (2), and the final result was obtained by average of three samples from the crosslinked material.

$$\text{Swelling (\%)} = \frac{(M_I - M_S)}{M_S} \times 100 \% \quad (2)$$

where  $M_I$  is the mass of the swollen sample,  $M_S$  the mass of the dry sample after removing the sol fraction.

## 2.4. FT-IR-ATR

FT-IR-ATR (Attenuated Total Reflection) spectra were taken using a Perkin-Elmer Spectrum 100 spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT) with 64 scans.

## 2.5. TGA/DTGA

TGA/DTGA analysis (thermogravimetric analysis) performed on a Mettler-Toledo-TGA/SDTA 851 equipment with thermobalance under pure nitrogen atmosphere (flow rate of 50 ml.min<sup>-1</sup>) and in the range from 25 to 600 °C, with a heating rate of 10 °C.min<sup>-1</sup>. The samples (each weighing ca. 12 mg) were placed in alumina crucibles of 40 µL.

## 2.6. DSC

DSC tests (differential exploration calorimetry) were performed on the Mettler Toledo DSC 822 equipment under nitrogen atmosphere (50 mL.min<sup>-1</sup>). The heating was done at 25 to 250 °C at the rate of 10 °C.min<sup>-1</sup>, with the temperature maintained at 250 °C for five minutes. Samples were weighed between 10 and 15 mg ± 1 mg and packed in aluminum capsules and sealed. The crystallinity was calculated by Eq. (3) as follows:

$$Xc = p \times \frac{\Delta H_f \times 100}{\Delta H_0} \quad (3)$$

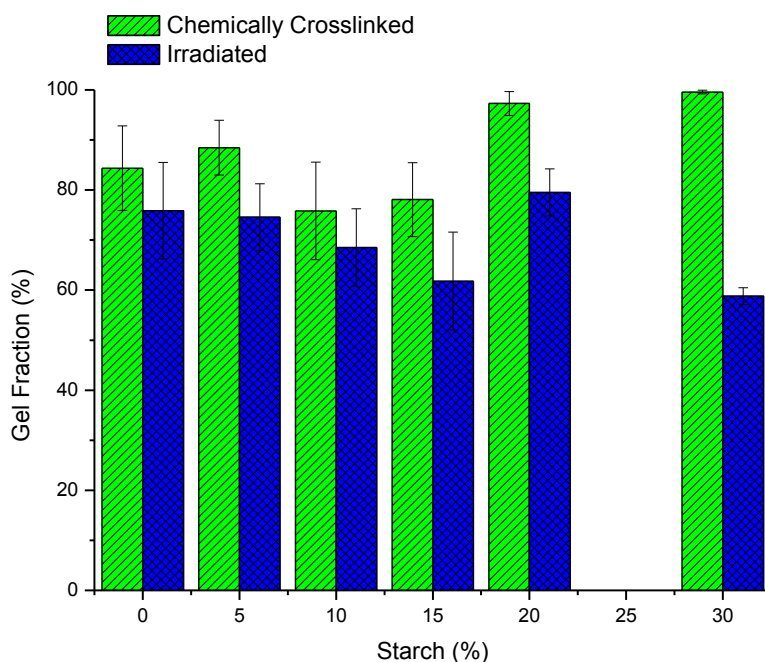
where  $\Delta H_f$  is the melting enthalpy and  $\Delta H_0$  is the melt enthalpy of the PVA, used at a value of approximately 73.3 J/g [9], where p is the amount of PVA in the sample.

## 2.7. SEM

SEM analysis (Scanning Electron Microscopy) the fracture morphology of the obtained materials was investigated in the Tabletop Hitachi TM 7000 electronic scanning electron microscope. For the analyzes, the samples were lyophilized by the Terroni® bench top freeze drier, enterprise line and cryogenically fractured in liquid nitrogen, and then covered with carbon.

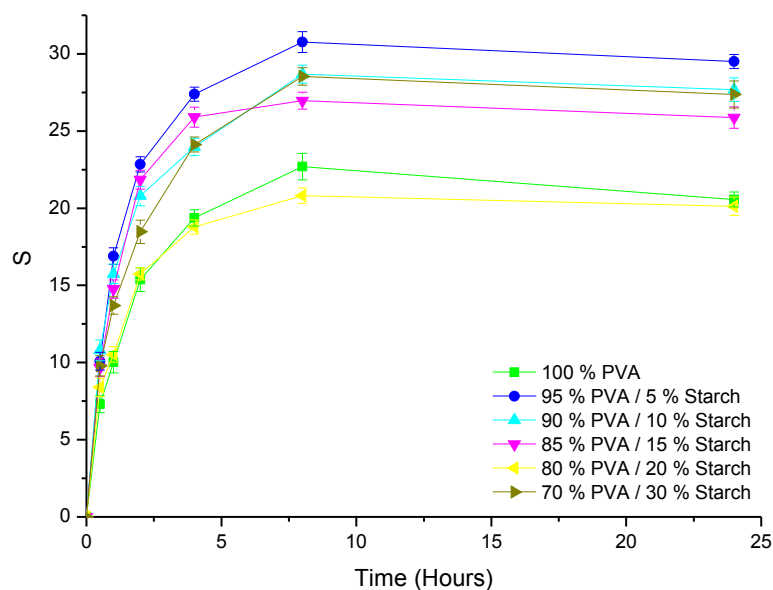
## 3. RESULTS AND DISCUSSION

Following are the results for comparison and analysis of hydrogels composed of PVA and PVA with starch, which were chemically crosslinked with only 1 % glutaraldehyde and those that were crosslinked only by irradiation with gamma-rays at a dose of 25 kGy. Fig. 2 shows the gel fraction results of the glutaraldehyde crosslinked hydrogels and of the crosslinked hydrogels only by gamma ray irradiation.



**Figure 2: Gel fraction of chemically crosslinked samples with only 1 % glutaraldehyde by weight and the crosslinked samples only by gamma-ray irradiation at a dose of 25 kGy.**

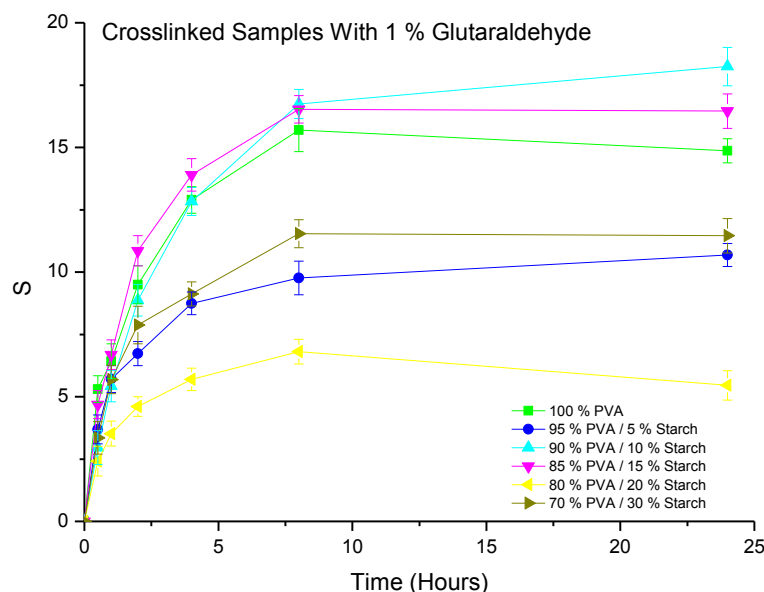
By the gel fraction values of Fig. 2, glutaraldehyde hydrogels presented higher values of gel fraction, more crosslinking the polymer. This happened due to the glutaraldehyde reticular with the free -OH groups of the polymer solution, both of the PVA and of the starch [1]. Irradiation presented lower values of gel fraction due to the breakdown of the starch molecules by the dose applied in the irradiation, leaving the hydrogel by the sun fraction [8]. In Fig. 3 is the swell in distilled water over time of the irradiated samples.



**Figure 3: Swelling (S) in distilled water over time of gamma-ray irradiated hydrogels at the dose of 25 KGy.**

By the swelling curves of the irradiated hydrogels, it was observed that the higher values were of the samples that had lower values of gel fraction, with the samples with 5, 10, 15 and 30 % of starch by weight presenting a greater swelling in relation to the samples with 20 % starch and with pure PVA. With the starch added in small amount to the solution, the liquid retention capacity of the hydrogel has been considerably improved as it is a highly hygroscopic polymer. When used in higher amounts in the solution, it swelled less reaching the close value of the pure PVA hydrogel, because gamma-radiation reached its polymer chains further and thus degraded its monomers during irradiation. The solution with 30 % starch swelled more than 20 % due to low crosslinking of the hydrogel PVA during irradiation, with more hydrogen bridges free for retention of the water molecules [6].

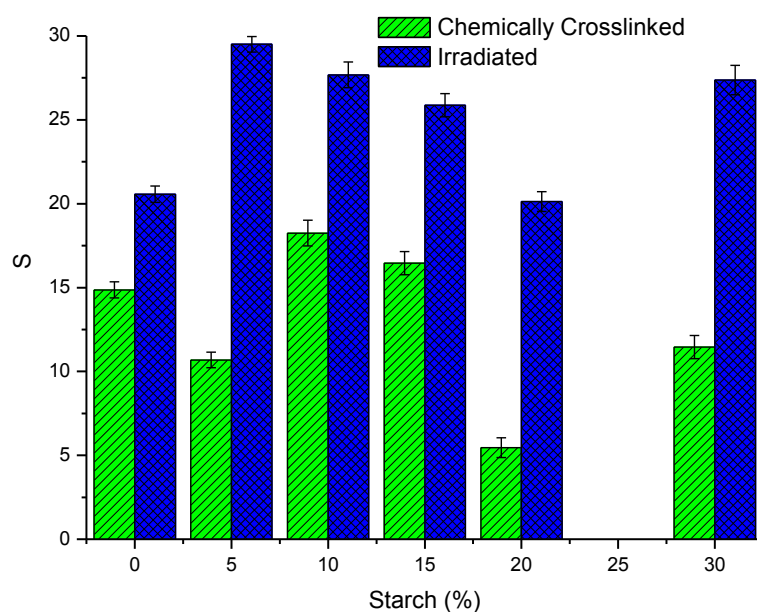
In Fig. 4 has the swelling curves of the chemically crosslinked hydrogels with 1 % by weight glutaraldehyde.



**Figure 4: Swelling (S) in distilled water over time of the hydrogels crosslinked with 1 % glutaraldehyde.**

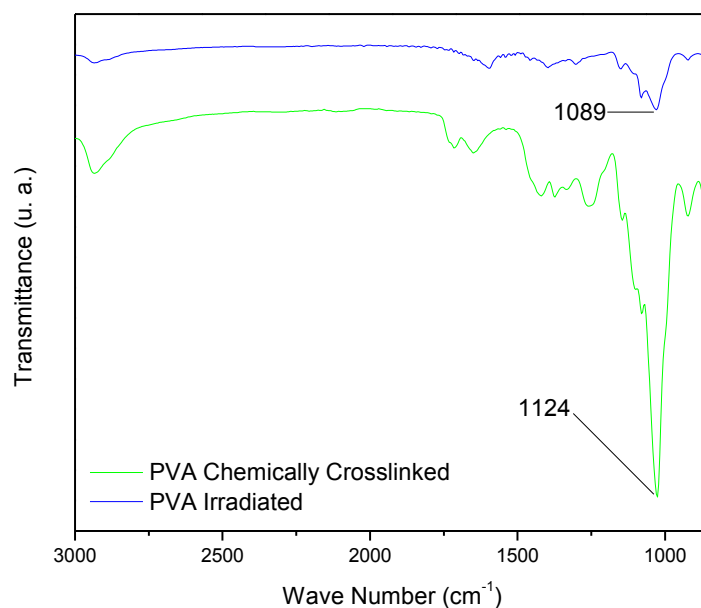
Starch-free hydrogels with 10 and 15 % starch became more swollen because they presented lower values of gel fraction, having greater flexibility in their chains for the retention of distilled water. The hydrogels with 5, 20 and 30 % of starch presented smaller swelling because they had more crosslinking, according to their gel fraction values, being able to have samples that varied in the maximum values of gel fraction due to the standard deviation that they presented by the swelling was made in triplicate of each hydrogel.

The swelling values after 24 hours of the hydrogels crosslinked only with glutaraldehyde and of the hydrogels crosslinked only by gamma radiation are in Fig. 5.



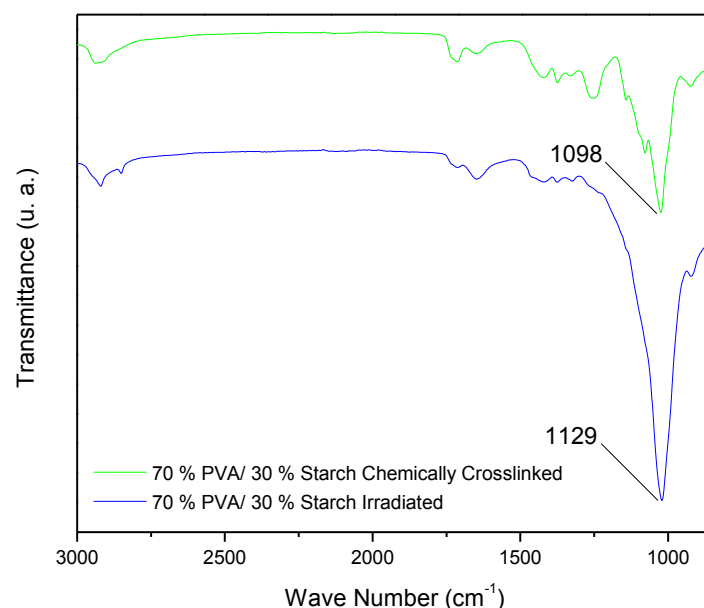
**Figure 5: Comparison between the swelling (S) of the chemically crosslinked samples and irradiated after 24 hours immersed in distilled water.**

Samples irradiated with gamma rays have been found to swell more than those chemically crosslinked with glutaraldehyde, owing to the different forms of crosslinking. For the amounts of 30, 20 and 5 % starch in the hydrogels, the swellings of the irradiated samples were considerably larger than the chemically crosslinked ones, with those of zero and 10 % starch being partially larger. This difference in swelling values was due to the high gel fraction values of the samples with glutaraldehyde, crosslinking the PVA and starch molecules through the -OH [9] groups. In the irradiation, the carbon crosslinking of the PVA occurred and the degradation of the greater part of the starch, swelling more by the creation of the hydrogen bonds [10]. In Fig. 6 has the ATR (FT-IR) curves of the chemically crosslinked and purely irradiated pure PVA hydrogels.



**Figure 6: ATR (FT-IR) of hydrogels composed of PVA, with one of them crosslinked with only 1 % glutaraldehyde and the other only by irradiation with gamma-rays at a dose of 25 kGy.**

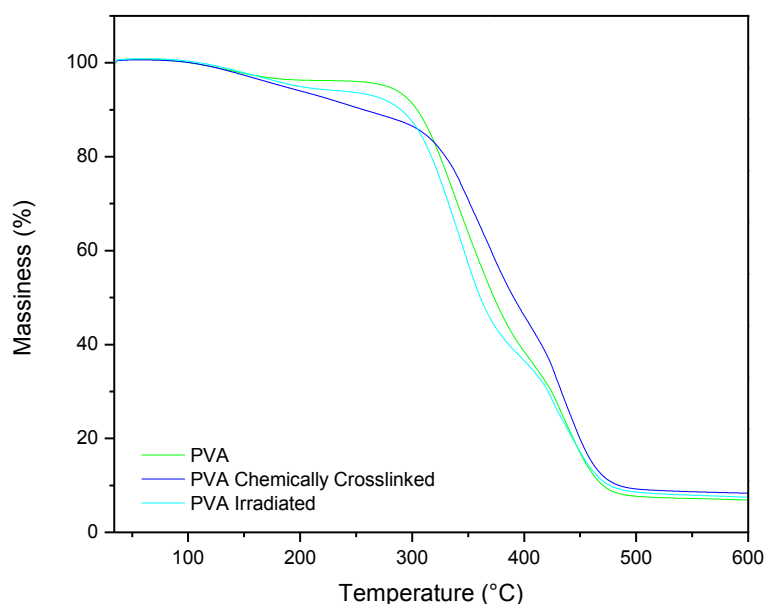
In the hydrogel with pure PVA, it was observed that the chemically crosslinked pure PVA hydrogel created an O-C-O stretch band of the acetal group which vibrated between 1000 and 1250  $\text{cm}^{-1}$ , not creating the same band on the polymer irradiated by reticular in a different way. In Fig. 7 are the ATRs (FT-IR) of the hydrogels composed of 70 % PVA and 30 % starch, one of them being crosslinked with glutaraldehyde and the other irradiated. The ATR (FT-IR) curves of the other formulations showed similar curves for both chemically and irradiated crosslinked hydrogels.



**Figure 7: ATR (FT-IR) of the hydrogels composed of 70 % PVA and 30 % starch, one of them crosslinked with 1 % glutaraldehyde and the other irradiated with gamma-rays at a dose of 25 kGy.**

By adding starch in the formulation, the pyran groups existing in their chains which also have O-C-O groups vibrated at wavelengths between 1085 and 1150  $\text{cm}^{-1}$  in the two hydrogels, becoming larger in the irradiated hydrogel because of the thickness of the sample used for the characterization to have been greater than that of the chemically crosslinked.

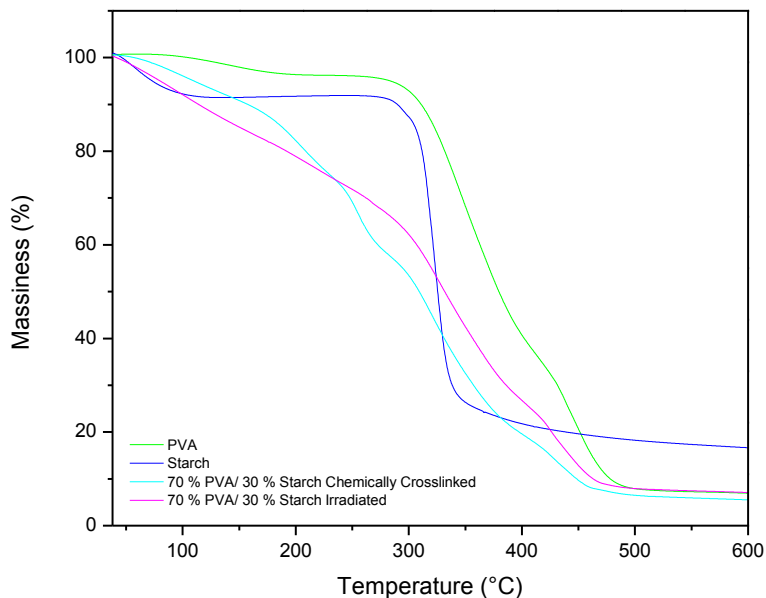
In Fig. 8 are the thermal degradations of the pure PVA, the PVA with 1 % glutaraldehyde and the PVA which was irradiated with gamma-rays at a dose of 25 kGy.



**Figure 8: TG of PVA and PVA hydrogels, one being chemically crosslinked only with 1 % glutaraldehyde and the other only crosslinked by irradiation with gamma-rays at a dose of 25 kGy.**



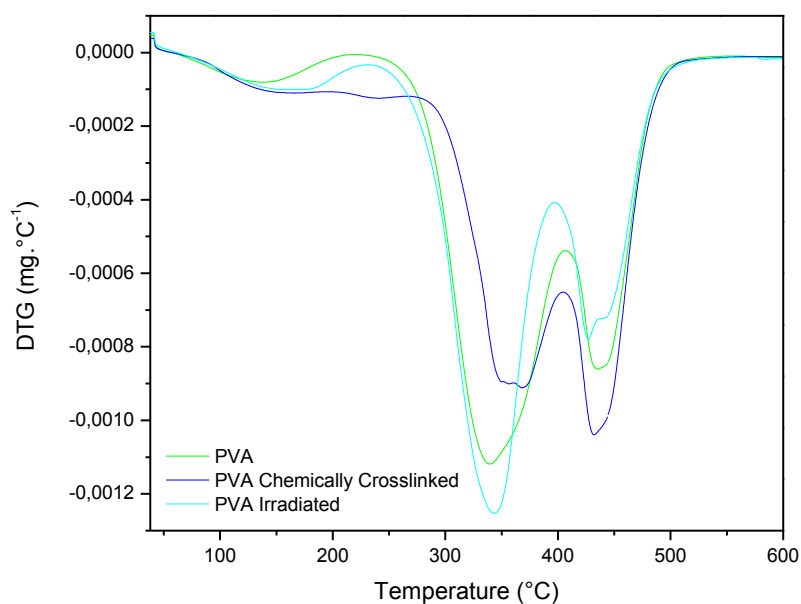
In Fig. 9 is the thermal degradation of PVA, starch and the solution of 70 % PVA and 30 % starch, one chemically crosslinked with only 1 % glutaraldehyde and the other irradiated only with gamma rays at a dose of 25 kGy. The other glutaraldehyde chemically crosslinked hydrogels showed TG data similar to those plotted in Fig. 5, the same happening with the gamma ray irradiated hydrogels.



**Figure 9: TG of PVA, starch and hydrogels with 70 % PVA and 30 % starch, one being chemically crosslinked with 1 % glutaraldehyde and the other only crosslinked by gamma-ray irradiation at a dose of 25 kGy.**

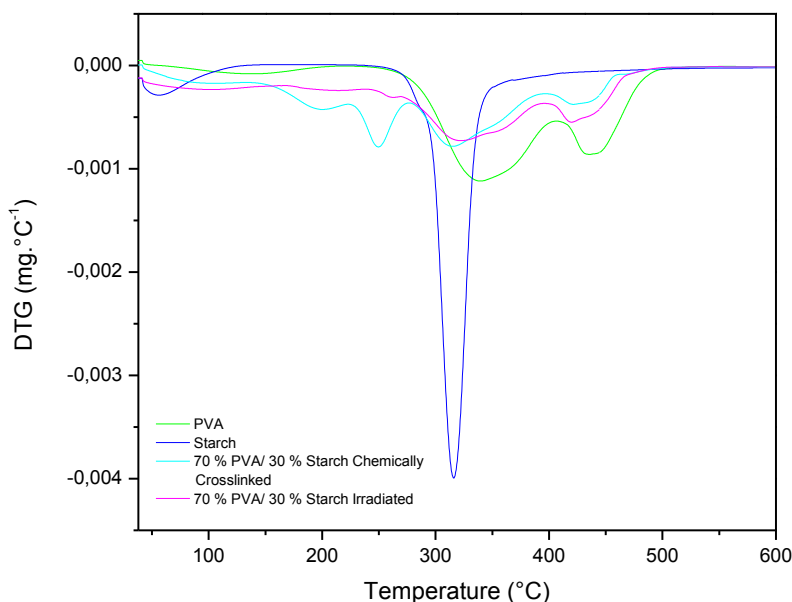
The degradation started by the loss of water and the -OH groups from the mixture to the temperature of 100 °C, followed by glutaraldehyde in the only chemically crosslinked hydrogel and the major chain breakdown, having average degradation at temperatures between 300 and 350 °C and carbonizing completely at a temperature close to 450 °C. The hydrogels with PVA alone crosslinked with glutaraldehyde and crosslinked only by gamma-ray irradiation presented degradation curves similar to pure PVA, thus showing that the polymer maintains its properties in the two forms of crosslinking. In the hydrogel curves composed of 70 % PVA and 30 % starch the good quality of the mixtures was observed, presenting average degradation temperature close to the pure PVA and starch, adhering to the properties of the polymers.

In Fig. 10 are the DTG curves of the pure PVA, the only chemically crosslinked PVA and the only irradiated PVA.



**Figure 10: DTG of PVA and hydrogels with 70 % PVA and 30 % starch, one being chemically crosslinked only with 1 % glutaraldehyde and the other only crosslinked by gamma-ray irradiation at a dose of 25 kGy.**

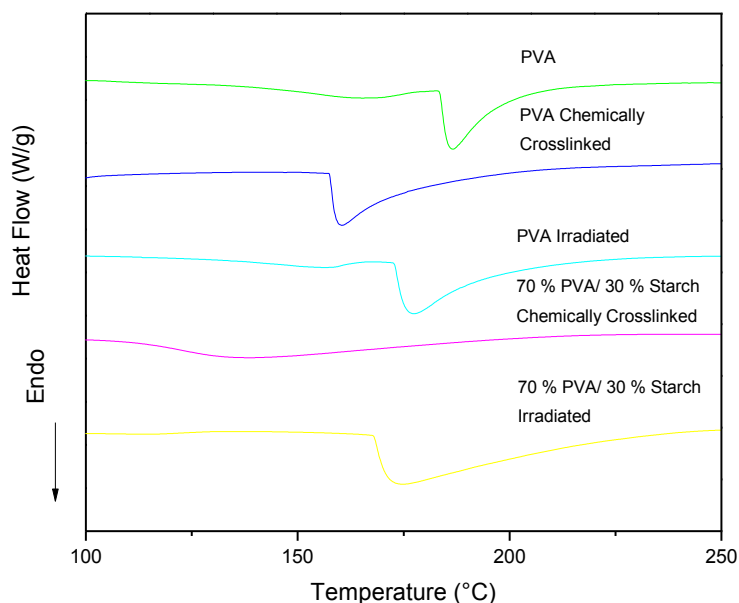
In Fig. 11 are to DTG curves of PVA without crosslinker, starch without crosslinker and hydrogels with 70 % PVA and 30 % starch, one being crosslinked only with 1 % glutaraldehyde and the other only crosslinked by gamma-ray irradiation at one dose of 25 kGy. Other formulations of the PVA hydrogels with starch presented similar curves.



**Figure 11: DTG of PVA, starch and hydrogels with 70 % PVA and 30 % starch, one being chemically crosslinked only with 1 % glutaraldehyde and the other only crosslinked by gamma-ray irradiation at a dose of 25 kGy.**

DTGs showed degradation peaks that resulted in their TG curves, showing average degradation in the two forms of crosslinking at temperatures between 300 and 350 °C, being

close to the pure polymers. The DTG of the PVA only hydrogels presented similar curves, degrading at the same temperatures. When adding starch in the solution, there was a slight alteration and acceleration in the degradation, especially in the irradiated one, which in the form of crosslinking, caused in the degradation of the starch due to the applied dose of 25 kGy, crosslinking less than the hydrogels with glutaraldehyde, as observed in the values of gel fraction of Fig. 2, degrading faster than the hydrogel crosslinked with glutaraldehyde alone. Fig. 12 shows the PVA DSC without crosslinking agent, of the hydrogels composed only of PVA and of the hydrogels composed of 70 % PVA and 30 % starch, which were only chemically crosslinked with 1 % glutaraldehyde and only irradiated with gamma-rays at a dose of 25 kGy.



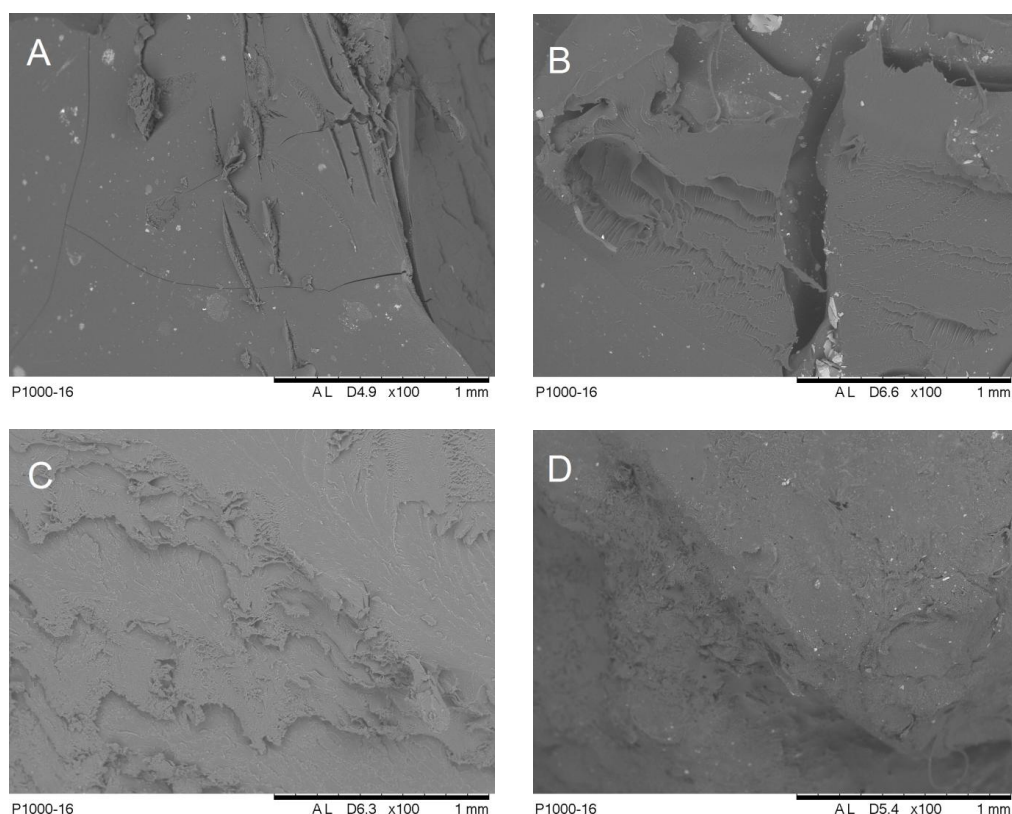
**Figure 12: DSC of PVA without crosslinker, of hydrogels composed only of PVA and of hydrogels composed of 70 % of PVA and 30 % of starch, with each having two forms of crosslinking, which were the crosslinking with only 1 % glutaraldehyde and crosslinking only by irradiation with gamma-rays at a dose of 25 kGy.**

The results of crystallization temperature, melt temperature and crystallinity are in the Table 2.

**Table 2: Values of crystallization temperature ( $T_c$ ), melt temperature ( $T_m$ ) and crystallinity ( $X_c$ ) obtained by DSC for the PVA without crosslinking agent, of the hydrogels composed only of PVA and of the hydrogels composed of 70 % PVA and 30 % starch having two different crosslinking forms, which were crosslinking with only 1 % glutaraldehyde and crosslinking only by gamma-ray irradiation at a dose of 25 kGy.**

Samples	$T_c$ (°C)	$T_m$ (°C)	$X_c$ (%)
PVA	103,32	186,34	75,14
PVA Chemically Crosslinked	89,32	160,43	23,67
PVA Irradiated	62,58	177,23	24,72
70 % PVA/ 30 % Starch Chemically Crosslinked	68,47	132,58	26,78
70 % PVA/ 30 % Starch Irradiated	87,38	174,42	21,43

With the data obtained from the pure PVA curve, it was observed that the melt temperature of the PVA which was only crosslinked with glutaraldehyde was lower than that which was only irradiated, due to the first being crosslinked with the -OH groups of the polymer and the second being reticulated with the carbon of its major chains, creating stronger bonds. Even though the two hydrogels showed proximity at their melting temperatures [3]. The hydrogel of the PVA blends with the starch that was crosslinked only with glutaraldehyde showed a decrease in the melting temperature due to the incorporation and crosslinking of the molecules with the starch, which caused in decreasing the melt temperature of the PVA which formed part of the composition of the material. The DSC temperature of the PVA blend hydrogel with the irradiated crosslinked starch presented practically the same temperature of the hydrogel composed only of PVA that was only irradiated because gamma radiation broke most of the starch molecules with the dose applied of 25 kGy, not crosslinking with the starch and hindering the crosslinking with the PVA. The crystallinities of the Table 2 materials were close to 25 %, despite the difference in  $T_c$  and  $T_m$  between the hydrogels and the pure PVA, thus demonstrating that the PVA reacted well in the two cross-linking forms, showing little loss of  $T_c$  and  $T_m$ , despite the considerable loss of crystallinity that demonstrated the high solubilization of PVA with the starch. Fig. 13 shows the SEM of the hydrogels composed only of PVA and of the hydrogels composed of 70 % of PVA and 30 % of starch, which were chemically crosslinked and irradiated, with a magnification of 100 times.



**Figure 13: SEM of the hydrogels composed of 100 % of PVA and of the hydrogels composed of 70 % of PVA and 30 % of starch. The sample (A) was the 100 % PVA hydrogel that was crosslinked with only 1 % glutaraldehyde, (B) the hydrogel with 100 % PVA which was crosslinked only by irradiation with gamma-rays at a dose of 25 kGy, (C) the hydrogel composed of 70 % PVA and 30 % starch which was crosslinked with only 1 % glutaraldehyde and to (D) the hydrogel composed of 70 % PVA and 30 % starch which was crosslinked only by gamma ray irradiation at a dose of 25 kGy.**

In the chemically crosslinked hydrogels, the PVA only compound presented higher porosity compared to the hydrogel formed by PVA and starch. Thus, it crosslinked less and swelled more, as shown in Fig. 50 sample (A) and Fig. 50 sample (C). In the irradiated hydrogels, the PVA only compound also had higher porosity than the hydrogel formed by 70 % PVA and 30 % starch, but because the irradiation degraded the starch molecules, it crosslinked more and swelled less. In the pure PVAs, the irradiated presented large cracks in the obtained SEM, due to the degradation of the material with the applied dose, unlike the PVA crosslinked with glutaraldehyde. In the hydrogels with 70 % of PVA and 30 % of starch, the only irradiated presented higher porosity, due to the degraded starch that did not adhere to the solution. The glutaraldehyde crosslinked alone presented good solubilization and formation of the hydrogel, presenting lower porosity and greater uniformity of the polymer chains because it had more crosslinking.

#### 4. CONCLUSIONS

In this work a new SAP of PVA with manioc starch was obtained. The crosslinking of the solutions of these polymers by casting with glutaraldehyde and only by irradiation with gamma-rays reached optimum values, and the solutions with glutaraldehyde were the ones that crosslinked the most. The swelling tests showed the good liquid retention properties of the blends, with the only irradiated hydrogels swelling more. In the ATR (FT-IR) the O-C-O stretch bands of the glutaraldehyde acetal were identified by crosslinking with the -OH groups of the two polymers. TG tests have shown that glutaraldehyde hydrogels degrade faster than gamma-ray irradiated, because the two forms of crosslinking are different. It has been found that the two forms of crosslinking are feasible for obtaining the SAP, can be exploited in other situations for a better understanding of the polymer, such as, for example, changing the proportions of PVA and starch, verifying the influence of these variations on the gel fraction and swelling, irradiating gamma-rays of the PVA blends with starch at different doses, observing the starch degradation and also performing swelling tests in buffer solutions with different pH.

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#### REFERENCES

1. S. K. Saxena, "PVA (Poly (Vinyl Alcohol))", *CTA (Chemical and Technical Assessment)*, 61, pp 3-7 (2004).
2. P. F. Halley, R. Smith, "Biodegradable Polymers for Industrial Application", *Woodhead Publishing*, Cambridge (2005).
3. M. Scholten, S. Selifonov, N. Zhou, "Degradable Superabsorbent Polymers", *Patent WO2012006278A2*, Reluceo (2011).
4. B. S. Chiou, G. M. Glenn, S. H. Imam, M. K. Inglesby, D. F. Wood, W. J. Orts, A. K. Mohanty, M. Misra, L. T. Drzal, "Natural Fibers, Biopolymers, and Biocomposites", *Starch Polymers: Chemistry, Engineering, and Novel Products*, Boca Raton: Taylor & Francis (2005).

5. M. Zhai, F. Yoshii, T. Kume, K. Hashim, "Syntheses of PVA/Starch Grafted Hydrogels by Irradiation", *Carbohydrate Polymers*, Vol. 50, pp 295-303 (2002).
6. H. R. Fiscer, J. J. De Vlieger, "Biodegradable Polymer Blends and Composites From Renewable Resources, Starch-Based Nanocomposites Using Layered Minerals", *John Wiley & Sons* (2009).
7. S. H. Gehrke, P. I. Lee, "Hydrogels For Drug Delivery Systems", *Specialized Drug Delivery Systems*, v. 41, pp. 333-392 (1990).
8. M. T. S. Alcântara, A. J. C. Brant, D. R. Giannin, J. O. C. P. Pessoa, A. B. Lugão, "Influence of Dissolution Processing of PVA Blends on the Characteristics of Their Hydrogels Synthesized by Radiation-Part I: Gel Fraction, Swelling, and Mechanical Properties", *Radiat. Phys. Chem*, v. 819, pp. 1465 (2012).
9. H. S. Mansur, C. M. Sadahira, A. N. Souza, A. A. P. Mansur; "FTIR Spectroscopy Characterization of Poly (Vinyl Alcohol) Hydrogel with Different Hydrolysis Degree and Chemically Crosslinked with Glutaraldehyde", *Science Direct* (2007).
10. M. Zhai, F. Yoshii, T. Kume, K. Hashim, "Syntheses of PVA/Starch Grafted Hydrogels by Irradiation", *Carbohydrate Polymers*, v. 50, pp. 295-303 (2002).