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# EFFECTS OF THE IRRADIATION PROCESS ON THE PROPERTIES OF PVA HYDROGELS TO BE USED AS BIOMATERIAL

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## ABSTRACT

Hydrogels can be used as compliant surfaces in prosthesis of human synovial joints due to their biocompatible characteristics. In this work, hydrogels were prepared from two aqueous solutions of PVA (with 15 and 20% w/w) and using two different processes of irradiation under electron beam (EB), with radiation doses from 25 to 150kGy. Hydrogel samples were characterized by indentation creep tests, equilibrium water content (EWC) and Differential Scanning Calorimetry (DSC). The experimental results have shown some differences in the investigated properties of the samples as a function of the dose rate, beam current, line speed, and the number of irradiation steps.

## 1. INTRODUCTION

Hydrogels can be described as cross-linked hydrophilic polymeric networks that are water swollen but non-water soluble. Recently, an interest has increased in using the polyvinyl alcohol (PVA) hydrogels as synthetic articular cartilage due to their excellent biocompatibility, low friction coefficient, permeability to tissue metabolites for the cells (e.g. synovial liquid) and soft consistency [1]. However, these materials in the hydrated state are inadequate for biomedical applications when mechanical strength is required, as in the case of articular cartilage.

The physical properties of the polymer network of the hydrogels can be controlled. These properties are related with several factors, such as, polymer base (i.e. hydrophilic polymer), composition of blends or copolymers, cross-linking process, cross-linking density and the amount of absorbed water by the polymeric network [2]. These two last factors can be modified by changing the type or the concentration of the cross-linking agent, the cross-linking procedure, or by adding hydrophilic monomers or polymers [3-7]. In recent works, thermal and mechanical properties of PVA hydrogels obtained by chemical reactions with a cross-linking agent or by radiation induced reactions were compared. The results have shown an improvement of the mechanical properties of the hydrogels prepared by the combination of acetalization and electron beam irradiation, without decrease of their swelling properties [8,9]. The aim of this work was to investigate the influence of the dose rate, beam current, line speed, and the number of irradiation steps on the properties of PVA sheets produced by electron beam irradiation.

## 2. EXPERIMENTAL

### 2.1. Materials

The polymer used was polyvinyl alcohol (PVA) USA (Mw 89000-98000 g/mol and degree of hydrolysis of 99%) from Aldrich. The other chemical reagents used (Hydrochloric acid 37%, sulphuric acid, anhydrous sodium sulphate) were all commercial products from Merck.

### 2.2. Preparation and Irradiation of PVA Sheets

Aqueous solutions of PVA at concentrations of 15 and 20% (w/w) were prepared. The sheets were obtained by casting. The solutions were poured into round plates with diameter of 10 cm. After that, the samples were dried at room temperature for 170h. The dried sheets were acetalized by immersion in a bath containing formaldehyde, sulphuric acid, anhydrous sodium sulphate and water at 60°C. The acetalized PVA samples were put into hermetic metallic gadgets where nitrogen gas was introduced prior to irradiation to form an inert atmosphere. Then, the samples were irradiated with a Dynamitron Accelerator, E = 1.5 MeV to different radiation doses using two different irradiation processes. In the first process, named slow and discontinuous process (S-D), the samples were irradiated at a dose rate of 14.02 $kGy.s^{-1}$, with line speed of 3.35 $m.min^{-1}$ and current beam of 3.48 mA. The doses of 25, 50, 75, 100, 125 and 150 kGy were reached after 2, 4, 6, 8, 10 and 12 irradiation steps. In the second procedure, called fast and continuous process (F-C), the different radiation doses were obtained with only one irradiation step, by applying a dose rate of 28.04 $kGy.s^{-1}$, variable beam current from 6.96 to 10.44 mA and different line speeds.

**Table 1 - Conditions of radiation processes S1 and S2.**

| EB radiation doses (kGy) | S-D process | | | F-C process | |
|---|---|---|---|---|---|
| | Beam current (mA) | Line speed (m/min) | Steps | Beam current (mA) | Line speed (m/min) |
| 25 | 3.48 | 3.36 | 2 | 6.96 | 3.36 |
| 50 | 3.48 | 3.36 | 4 | 6.96 | 1.68 |
| 75 | 3.48 | 3.36 | 6 | 5.22 | 0.84 |
| 100 | 3.48 | 3.36 | 8 | 6.96 | 0.84 |
| 125 | 3.48 | 3.36 | 10 | 8.70 | 0.84 |
| 150 | 3.48 | 3.36 | 12 | 10.44 | 0.84 |

### 2.3. Equilibrium Water Content (EWC)

The capacity of absorption of water (EWC) of the hydrogels is one of the most important properties of these polymeric networks [10]. EWC is defined by equation 1.

$$EWC (\%) = [\text{swollen gel weight} - \text{dry gel weight}) / \text{swollen gel weight}] \times 100 \quad (1)$$

The swollen gel weight was measured allowing the hydrogels to reach equilibrium state in distilled water, which was indicated by their constant final weight.

### 2.4. Differential Scanning Calorimetry (DSC)

DSC measurements were carried out using a STA 409C of NETZCH equipment. The samples were previously dried at 80°C for 12 h. About 9 mg of dried samples were placed in aluminum pans and assayed in DSC to measure the glass transition temperature ($T_g$). These samples were heated from 25 to 150°C at a heating rate of 10°C.min$^{-1}$, then cooled to 25°C at a cooling rate of 5°C.min$^{-1}$ and later submitted to a second heating run in the temperature range of 24°C to 350°C at the same heating rate. The Tg values were taken as the temperatures of the midpoint of the base line variation in the DSC curves.

### 2.5. Indentation Creep Test

The Young's modules (E) of the samples were determined by indentation creep tests using a Material Test System (MTS- Teststar II). The indentation measurements were carried out on samples immersed in distilled water using a spherical tip with a diameter of 3.2 mm and a load of 0.5kgf during 180s.

## 3. RESULTS AND DISCUSSION

### 3.1. Equilibrium Water Content (EWC)

The water swelling (EWC) behavior of the hydrogels as a function of the radiation doses is presented in Fig. 1. In this figure, it can be observed that the samples submitted to the slow and discontinuous irradiation process (S-D process) show lower values of swelling than those hydrogels obtained by the fast and continuous irradiation process (F-C process).

These results show that the F-C process has induced lower degree of cross-linking in the studied hydrogels. The concentration of PVA in the aqueous solution has not shown any expressive effect on the swelling behavior of the samples when the F-C process was applied. However, samples originated from 15% polymeric aqueous solution presented higher EWC values than those generated from the solution with 20% of polymer, when irradiated under the F-C process. Under these facts, it can be concluded that the polymer concentration in the solution affects the cross-linking density of the obtained hydrogels.

Both hydrogels, with 15 and 20% of PVA, have presented a significant decrease in EWC % from 25 to 50kGy, remaining almost constant at higher doses. This result characterizes the significant increase of the cross-linked density with the increase of the radiation dose up to 50 kGy, in both irradiation processes.

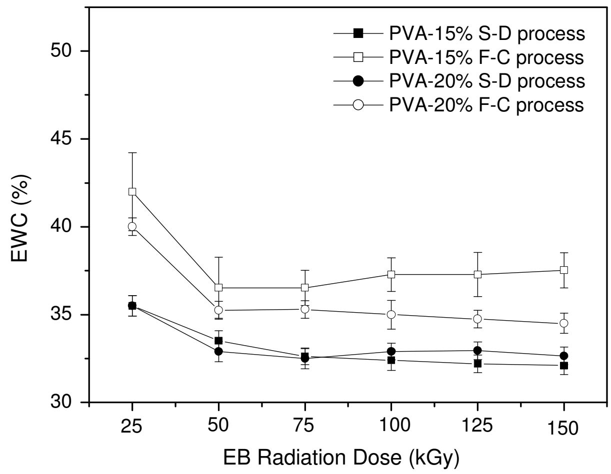



**Figure 1. Equilibrium water content (EWC %) behavior as a function of radiation dose for PVA-15 and PVA-20% hydrogels submitted to slow and discontinuous irradiation process (S-D process) or fast and continuous irradiation process (F-C process).**

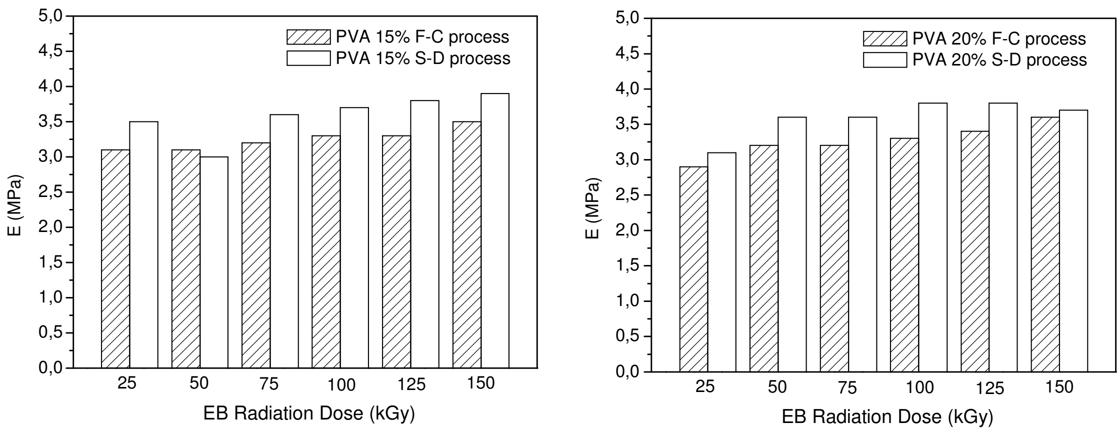
### 3.2. Glass Transition Temperature ($T_g$)

The S-D and F-C irradiation processes applied on samples with 15 and 20 % PVA have not shown any remarkable effect on the $T_g$ values of the hydrogels. However, as a function of the radiation doses, it was observed that the $T_g$ values of samples irradiated at 25 kGy are around 98°C, slightly lower than those of the hydrogels obtained with 50 kGy or higher doses. These results can be correlated with the lower degree of cross-linking reached by these samples, independently of the irradiation process or PVA concentration in the solution. Above 50 kGy, the $T_g$ remains almost constant at values of 104 ± 2 °C. This temperature is quite greater than the $T_g$ of 85°C of non-irradiated PVA samples. A high density of cross-linking reduces the flexibility of the chain, increasing the $T_g$. On the other hand, the plasticizer effect of the water reduces the value of the glass transition temperature causing an increase in its flexibility. Under these considerations, the $T_g$ determinations were carried out by DSC measurements using the second heating run, since the first heating run was used to eliminate the water retained in the polymeric cross-linked network.

### 3.3. Mechanical Properties – Young's Modulus (E)

Fig. 2 presents the values of Young's modulus (E) determined by creep indentation measurements.

In these figures, it was shown that the values of E are slightly greater for both samples -with 15 and 20% of PVA- irradiated by the S-D process than for the same samples irradiated by the F-C process. A small increase in the E values was also observed as a function of the radiation dose growth. This behavior was expected since the Young's modules have direct relationship with the cross-linking density of the sample. The observed difference in the degree of cross-linking as a function of the dose rate and number of steps of the irradiation process can be explained by the difference in the kinetic of the cross-linking reactions due to the different beam currents, line speed and dose rates.




(a) (b)

**Figure 2. Indentation creep modulus (E) for samples: (a) PVA-15% hydrogels, and (b) PVA-20%, submitted to slow and discontinuous irradiation process (S-D process) or fast and continuous irradiation process (F-C process).**

## 4. CONCLUSIONS

The slow and discontinuous process of irradiation has induced larger degrees of cross-linking in the PVA hydrogels investigated than the fast and continuous process. The used PVA concentrations have not shown any significant difference in the mechanical and swelling properties of the hydrogels obtained by the slow and discontinuous irradiation process. Therefore, the slow and discontinuous process has shown to be more convenient for the production of PVA hydrogels to be used as materials for compliant surfaces in prosthesis of human synovial joints due to their swelling and mechanical performance.

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