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# Microstructural Evaluation of Poly(vinyl alcohol)-Based Hydrogels Obtained by Freezing-Thawing Technique: Thermal Analysis and Positron Annihilation

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**ABSTRACT:** In this work, semi-interpenetrating polymer network (s-IPN) hydrogels of poly(vinyl alcohol) (PVA) with different contents of water-soluble sulfonated polyester (PES) were obtained by freezing and thawing cycles. The samples were characterized by positron annihilation lifetime spectroscopy (PALS) and differential scanning calorimetry (DSC). PALS was used to determine the average free volume radius through lifetime measures of the *ortho*-positronium (*o*-Ps). Degree of crystallinity of the PVA/PES hydrogels was evaluated using the melting enthalpy ratios between the samples and the 100% crystalline PVA. The

results show that an increase on the PES content leads to a decrease on the degree of crystallinity of the samples, reflecting an increase on the lifetimes ( $\tau_3$ ). These structural changes could be interpreted as a result of different polymer-polymer interactions between PVA and PES in the hydrogels. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 899–902, 2007

**Key words:** differential scanning calorimetry (DSC); free volume; hydrogel; positron lifetime; water-soluble polymers; polymer–polymer interactions

## INTRODUCTION

Hydrogels can be defined as three-dimensional polymeric networks of hydrophilic or partially hydrophilic polymers that swell in contact with water without dissolving.<sup>1</sup> Because of their water uptake capacity, hydrogels show such interesting characteristics as biocompatibility, biodegradability, and good mechanical properties and chemical resistance.<sup>2,3</sup>

Volumetric transitions in hydrogels can occur under certain physicochemical stimulus, including pH, temperature, ionic strength, electrical field, and so forth. These materials have attracted several research groups, especially in the development of

biomedical and pharmaceutical devices as well as contact lenses and human scaffolds.<sup>4</sup>

Poly(vinyl alcohol) (PVA) is a hydrophilic polymer used in several applications because of easy handling, good chemical resistance, and physical properties, and complete biodegradability.<sup>5</sup> Aqueous solutions of PVA form strong hydrogels when submitted to freezing and thawing cycles. These cycles allow the formation of fine crystalline domains that act as crosslinking sites, leading to the insolubility of hydrogels into the water. An advantage of this technique when compared with other chemical-based hydrogels' preparation is the nontoxicity behavior of these hydrogels, once it is free of residual chemical from the conventional crosslinker agents, besides an improvement of mechanical strength.<sup>6</sup>

PVA is a neutral polymer, whose environmental sensibility is very weak, especially under changes in pH and ionic strength. Chemical modifications of PVA chains or inserting a polyelectrolyte to form an interpenetrate polymer network (IPN) are used to leads a volumetric phase transition in PVA hydrogels.<sup>7–9</sup> However, it is necessary to obtain a complete understanding of these systems to determine the influence of these chemical modifications or the presence of a second polymer under the hydrogel

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behavior like transport process, diffusion and permeation of low molecular weight substances, and the stability over long periods of time.

Positron annihilation lifetime spectroscopy (PALS) has been used in the characterization of systems at molecular level. However, the number of papers focusing the use of PALS in the field of hydrogels obtained by freezing-thawing technique is small.

Tao<sup>10</sup> and Eldrup et al.<sup>11</sup> showed a preferential localization of *ortho*-positronium (*o*-Ps) into the free volume hole, based in the spherical potential well and the lifetime of the *o*-Ps ( $\tau_3$ ) is directly related to the free volume radius ( $R$ ). Assuming that the annihilation rate of the *o*-Ps inside the electron layer of width  $\Delta R$  at the internal surface is  $2 \text{ ns}^{-1}$ , we can use the following equations:

$$\tau_3 = \frac{1}{2} \left[ 1 - \frac{R}{R + R_0} + \frac{1}{2\pi} \sin 2\pi \frac{R}{R + R_0} \right]^{-1} \quad (1)$$

$$V_f = \frac{4}{3} \pi R^3 \quad (2)$$

where  $R_0$  is the width of the electron layer where the *o*-Ps annihilates and is equal to 1.66 Å.

The aim of this work was to study the morphological changes of PVA hydrogels obtained by freezing-thawing technique with different concentrations of a polyelectrolyte (PES) used as a model. Changes on the crystallinity degree of the hydrogel as a function of PES content also were analyzed. PALS was used to determine the average free volume radius. Results are discussed in terms of structural changes as a consequence of the different polymer–polymer interactions due to the presence of PES with different contents.

## EXPERIMENTAL

### Materials

PVA (degree of hydrolysis 99%;  $M_w$  86,000–146,000) was supplied by Aldrich. We have used a commercial water-soluble copolyester (Gerol 20<sup>®</sup>, Kemira) as a model of polyelectrolyte (PES). PES has 20% per mol of sulfonated groups. All materials were used as received.

### Hydrogels preparation

A 10% (w/v) PVA solution and a 2.5%, 5.0%, and 10.0% (w/v) PES solution were obtained by dissolving the components in distilled and deionized water under reflux during 4 h and at 60°C under mechanical stirring during 1 h, respectively. PVA/PES mixtures with 90/10, 75/25, and 50/50 (v/v) polymer ratio were prepared, being the various mixtures

dispensed into Petri dishes (2.5 mL/dish). The hydrogels were obtained after five cycles of freezing–thawing. Each cycle, with exception of the first one, consisted of 1 h at  $-22^\circ\text{C}$  and 30 min at room temperature. The first cycle differed from the others by having a longer standing time (17 h) at  $-22^\circ\text{C}$ . Samples were maintained under vacuum until it show constant weight.

### Thermal analysis

The degrees of crystallinity of PVA/PES hydrogels were measured with a differential scanning calorimetry (DSC, model 7, Perkin–Elmer) ranging from 40°C to 250°C at 10°C/min. A nitrogen purge was applied to maintain stable thermal environment. The degrees of crystallinity were obtained by:

$$\chi_c = \frac{\Delta H_m}{\Delta H_{m100\%}} 100\% \quad (3)$$

where,  $\Delta H_m$  is the heat required for melting the sample and  $\Delta H_f = 138.6 \text{ J g}^{-1}$  is the 100% crystalline melting heat of PVA.<sup>12</sup>

### Positron annihilation lifetime spectroscopy

The lifetime spectra were obtained using a conventional ORTEC fast-fast coincidence circuit with 280 ps of time resolution, from the  $^{60}\text{Co}$  prompt curve.  $^{22}\text{NaCl}$ , of approximately  $4 \times 10^5 \text{ Bq}$  activity, sandwiched between two 7- $\mu\text{m}$ -thick foils of Kapton, was used as the positron source. Two samples of PVA/PES in the form of pellets with approximately  $8 \times 8 \text{ mm}^2$  of area and 1.5 mm thickness were sandwiched between the positron source. The measurements were carried out at  $(21.0 \pm 0.5)^\circ\text{C}$ .

The lifetime spectra were satisfactorily resolved into three components using the POSITRONFIT-EXTENDED program,<sup>13</sup> leading to the intensities ( $I_i$ ) and lifetimes ( $\tau_i$ ) of the various positron states: subscripts 1, 2, and 3 refer to *para*-positronium (*p*-Ps), free positron, and *ortho*-positronium (*o*-Ps), respectively. The *o*-Ps lifetimes ( $\tau_3$ ) and intensities ( $I_3$ ) were determined from the spectral analysis with all  $\tau_i$  free and with  $\tau_1$  fixed at 120 ps.

The samples were measured in triplicate, with the mean value taken for each experiment. The lifetimes, obtained in the experimental spectrum analysis, are average values of the positronic species lifetimes distribution. The free volume size, determined by the eqs. (1) and (2), also represents average values.

## RESULTS AND DISCUSSIONS

The PALS and DSC results are shown in Tables I and II, respectively. The results summarized in

**TABLE I**  
PALS Parameters Obtained for the PES/PVA Systems, at  $(21.0 \pm 0.5)^\circ\text{C}^a$

PES (wt %)	$\tau_3$ (ns)	$I_3$ (%)	$R$ (Å)	$V_f$ (Å <sup>3</sup> )
0	1.88	29.8	2.74	86.2
2.7	1.53	23.0	2.37	55.8
5.3	1.50	27.5	2.34	53.6
7.7	1.55	21.3	2.40	57.9
10.0	1.52	27.8	2.36	55.1
14.3	1.59	20.6	2.44	60.5
20.0	1.58	20.4	2.42	59.5
25.0	1.45	24.7	2.28	49.7
33.3	1.61	18.5	2.47	62.8
50.0	1.66	23.9	2.51	66.5

<sup>a</sup> The mean deviations associated with the positron annihilation parameters are  $\pm 0.03$  ns,  $\pm 0.6\%$ ,  $\pm 0.03$  Å, and  $\pm 5.0$  Å<sup>3</sup> for  $\tau_3$ ,  $I_3$ ,  $R$ , and  $V_f$ , respectively (the  $\tau_2$  values were nearly constant at  $(0.400 \pm 0.003)$  ns and  $I_2$  values were in the range 51%–57%).

Tables I and II show that the values of  $\tau_3$ ,  $I_3$  (positron annihilation parameters), related to free volume hole size and Ps formation probability, respectively, as well  $\chi$  (degree of crystallinity, from DSC measurements) are lower than those values for pure PVA. In amorphous polymers, the *o*-Ps is preferentially formed and localized within the free volume holes, while in the crystalline phase of semicrystalline polymers *o*-Ps may be formed within interstitial free volume, at vacancy-type defects, or at the crystalline-amorphous interfaces regions.<sup>14–19</sup> Therefore, the PALS parameters are average values taking into account the different dimensions of holes related to

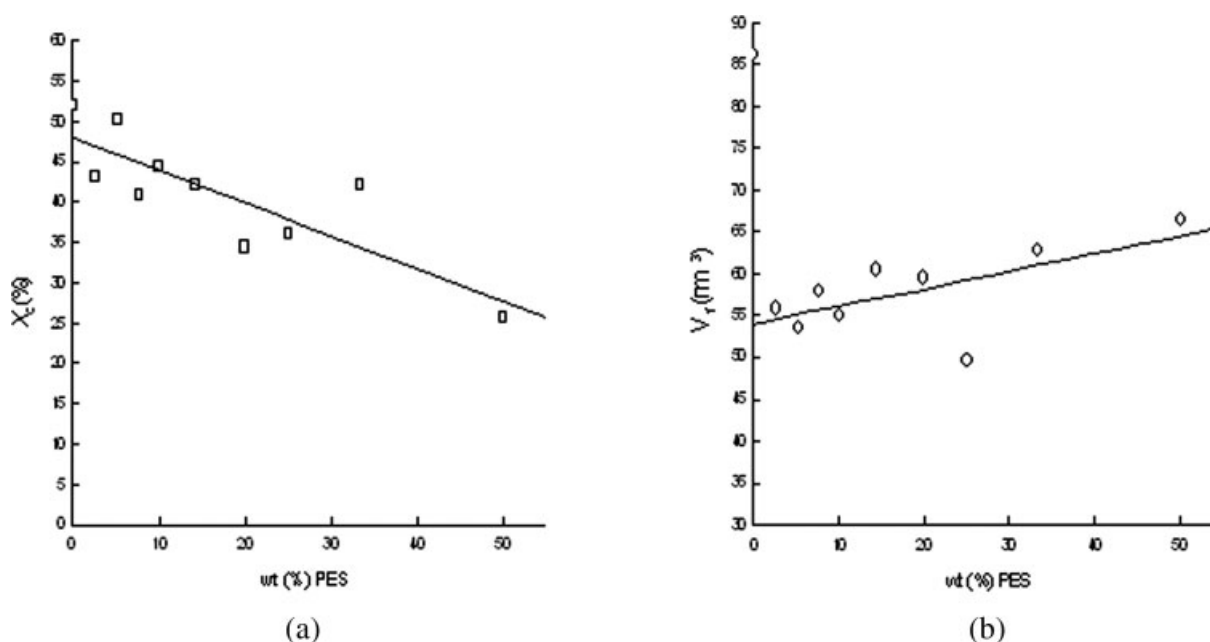
**TABLE II**  
Melting Temperature,  $T_m$ ; Enthalpy of Melting,  $\Delta H_m$ ; and Degree of Crystallinity,  $\chi$ ; for the PES/PVA Systems, As Obtained Using DSC Measurements<sup>a</sup>

PES (wt %)	$T_m$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$\chi$ (%)
0	229	71	52
2.7	229	59	43
5.3	232	69	50
7.7	228	56	41
10.0	229	61	44
14.3	231	58	42
20.0	225	47	34
25.0	227	49	36
33.3	231	58	42
50.0	229	35	26

<sup>a</sup> The experimental errors associated with the thermal analysis experiments are  $\pm 1^\circ\text{C}$ ,  $\pm 1$  J g<sup>-1</sup>, and  $\pm 1.5\%$  for  $T_m$ ,  $\Delta H_m$ , and  $\chi$ , respectively.

the phases and interphases present in these materials. The results shown in Table II and Figure 1(a) reveal a strong dependence of the degree of crystallinity,  $\chi$ , with wt % PES. The degree of crystallinity (and indeed  $\Delta H_m$ ) decreases almost linearly from 52% for the PVA (wt % PES = 0) to 25.8% when wt % of PES is 50.0.

Cowie et al.<sup>20</sup> have shown the effect of hydrogen bonding on the free volume in polymer blends based in poly(*N*-vinylpyrrolidone) and poly(vinyl acetate-co-vinyl alcohol), revealing an increase of the free volume with the increase of hydrogen bonding, specially caused due to hydroxyl and carbonyl groups. Muramatsu et al.<sup>21</sup> have founded that for fully



**Figure 1** Variation of degree of crystallinity,  $\chi\%$  (a) and free volume hole size,  $V_f$  (b), as a function of the content of PES, in the PVA/PES systems.

saponificated PVA samples, regardless of degree of polymerization,  $\tau_3$  was found to be independent on the degree of crystallinity. We suggest that the hydrogen bonding is the driving force for the crystalline disorder in PVA/PES hydrogels, mainly caused due carbonyl and sulfonated groups of PES and the hydroxyl groups of PVA. Therefore, an increase in  $V_f$  of the PVA/PES hydrogels is expected, once an increase of the amorphous fraction contributes to an increase number of available free volume. In fact, as can be seen in Table II, the melting point,  $T_m$ , of PVA/PES hydrogels differs slightly from the PVA hydrogels.  $T_m$  is directly related to the lamellar thickness of crystalline fraction: thick spherulites tend to melt at higher temperatures than thin spherulites. Once formed, the crystalline domain of PVA is not affected by the presence of PES, as a result of strong intramolecular interactions.

As shown in Table I and Figure 1(b), the free volume hole sizes, as calculated using eqs. (1) and (2),  $V_f$ , increase with the increasing PES content, in the PES/PVA systems. This behavior—decrease of  $V_f$  with increasing  $\chi\%$  in the system—is not surprising and was observed recently by different authors.<sup>22,23</sup> In fact, the free-volume hole sizes in the amorphous phase are normally higher than the dimensions of the free spaces present in the crystalline phase, or at the crystalline-amorphous interfaces regions.

As shown in Table I, the  $I_3$  values are highly scattered not allowing a physical interpretation, in despite to indicate a tendency of decreasing with the wt % PES.

## CONCLUSIONS

The microstructure of PVA/PES hydrogels obtained by freezing and thawing cycles was analyzed by positron annihilation lifetime spectroscopy (PALS) and differential scanning calorimetry (DSC). Hydrogels were characterized in terms of the lifetimes and the intensities of the *ortho*-positronium (*o*-Ps) and the degree of crystallinity. The presence of PES leads to disorder the crystalline domains of PVA, resulting in a decrease of the degree of crystallinity as well as a decrease in the average radius and the concentration

of the free volume holes. The results indicate the presence of inter- and intramolecular interactions between PVA and PES, resulting in an “opened” structure, that reflects the increase of  $\tau_3$  as a function of the PES content.

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