

DIELECTRIC PROPERTIES OF POLY(VINYL ALCOHOL) HYDROGELS PREPARED BY FREEZING/THAWING TECHNIQUE

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ABSTRACT

The dielectric behavior of poly(vinyl alcohol) –PVA– crosslinked hydrogels obtained by the repeated freezing/thawing (F/T) technique have been investigated by dielectric relaxation spectroscopy (DRS) and differential scanning calorimetry (DSC). The crosslinked polymer is produced by the clustering of chains caused by the association of a polar group of the dissolved polymer followed by polymer crystallization. The dielectric spectra obtained from -50 °C to -10 °C show a broad secondary relaxation process associated to local mobility, β relaxation, which is related to the terminal polar groups (OH). This process is strongly affected by the freezing/thawing cycles applied. The values of $\tan \delta$ are below 1 indicating the dielectric phenomenon is predominant in all samples. The effect of crosslinking PVA on the dynamics of the secondary relaxation process was further analyzed.

KEY WORDS: dielectric properties; hydrogels; freezing/thawing; dielectric spectroscopy.

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PROPIEDADES DIELECTRICAS DE HIDROGELES DE ALCOHOL POLIVINILICO OBTENIDOS POR LA TÉCNICA DE CONGELAMIENTO/DESCONGELAMIENTO

RESUMEN

Por medio de espectroscopia dieléctrica (DRS) y calorimetría diferencial de barrido (DSC) se investigaron las propiedades dieléctricas de los hidrogeles de alcohol polivinílico –PVA– entrecruzados por ciclos repetidos de la técnica congelamiento/descongelamiento. La asociación de los grupos polares del polímero disuelto seguida de su cristalización produce la reticulación del polímero. La espectroscopia dieléctrica obtenida entre $-50\text{ }^{\circ}\text{C}$ y $-10\text{ }^{\circ}\text{C}$ demostró la existencia de un proceso de relajación secundario asociado con la movilidad de grupos laterales polares OH de la cadena principal, la relajación β . Los ciclos de congelamiento/descongelamiento afectan fuertemente este proceso. El fenómeno dieléctrico predomina en todas las muestras como lo evidencia el valor menor de 1 de $\tan \delta$. Además, se analizó el efecto del entrecruzamiento en la dinámica de la relajación secundaria.

PALABRAS CLAVE: propiedades dieléctricas; hidrogeles; congelamiento/descongelamiento; espectroscopia dieléctrica.

PROPIEDADES DIELECTRICAS DE HIDROGEIS DE ÁLCOOL POLIVINILICO OBTIDOS PELA TÉCNICA DE CONGELAMENTO/DESCONGELAMENTO

RESUMO

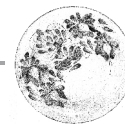
Por médio de espectroscopia dieléctrica (DRS) e calorimetria diferencial de varredura (DSC) pesquisaram-se as propriedades dieléctricas dos hidrogeis de álcool polivinílico –PVA– entrecruzados por ciclos repetidos da técnica congelamento/descongelamento. A associação dos grupos polares do polímero dissolvido seguida de sua cristalização produz a reticulação do polímero. A espectroscopia dieléctrica obtida entre $-50\text{ }^{\circ}\text{C}$ e $-10\text{ }^{\circ}\text{C}$ demonstrou a existência de um processo de relaxação secundário associado com a mobilidade de grupos laterais polares OH da corrente principal, a relaxação β . Os ciclos de congelamento/descongelamento afetam fortemente este processo. O fenômeno dieléctrico predomina em todas as mostras como o evidência o valor menor de 1 de $\tan \delta$. Ademais, analisou-se o efeito do entrecruzamento na dinâmica da relaxação secundária.

PALAVRAS-CHAVE: propriedades dieléctricas; hidrogeis; congelamento/descongelamento; espectroscopia dieléctrica.

1. INTRODUCTION

Hydrogels are defined as a physically or chemically crosslinked polymer network able to absorb large amounts of water without being dissolved. Physically cross-linked PVA hydrogels prepared by repeated freezing and controlled thawing show excellent properties, when a PVA solution is subjected to freezing, the pure solvent crystallizes initially, while the solute stays in the liquid part of the specimen.

Such state leads to stronger polymer-polymer interaction, which results in a stable three-dimensional cryogel network (Lozinsky, 1998). Such a technique produces stable hydrogels that are physically cross-linked because of the presence of crystalline regions arising upon the interaction between neighbor polymer chains due to the hydrogen bonding of pendant hydroxyls of PVA groups (Hassan and Peppas, 2000; Hatakeyema *et al.*, 2005; Lozinsky *et al.*, 2008). PVA



hydrogels offer several beneficial properties: biocompatibility, biodegradability, high water content, bio-inertness, and sterilizability, also they can be molded into desired shapes (Fergg y Keil, 2001; Ricciardi *et al.*, 2003; Cascone *et al.*, 2004). On the other hand, they have been examined in separation processes (Pissis and Kyritsis, 1997; Konsta *et al.*, 1999) and for their application as polymer electrolyte membranes in fuel cells due to the fact they enhance ionic conductivity (Awadhia, Patel and Agrawal, 2006).

Different characterization techniques, such as cryo-transmission electron microscopy (cryo-TEM), chromatographic or scattering techniques, mechanical measurements, DSC, X ray diffraction (Wilcox *et al.*, 1999, McGann *et al.*, 2009), carbon nuclear magnetic resonance (CNMR), proton and high resolution solid-state (Ricciardi, Auriemma and De Rosa, 2005) have been used to study the structure of PVA hydrogels. It is a complicated network structure, based on different phenomena: crystallization, hydrogen bonding, liquid-liquid phase separation, and covalent bonds. However, most of the characterizations require the manipulation of the hydrogel sample, driving changes in the original structure. For example, by NMR Valentín *et al.* (2009) showed that PVA hydrogels obtained by F/T cycles exhibit a complex heterogeneous network structure. The crystallites are quantitatively detected as a rigid-like fraction of quickly relaxing magnetization and the mesh size constraints on the motion of the mobile chains (i.e., cross-links) that render the segmental motion locally anisotropic (Valentín *et al.*, 2009). Dielectric measurements were carried out in PVA films of different crystallinities (not hydrogels) and a single broad relaxation region was observed at a low temperature. These investigations show that the dielectric relaxation process is associated with the motions of dipole in the amorphous regions of the polymer (McCrum, Read and Williams, 1991; Schartel, Wendling and Wendorff, 1996; De La Rosa, Heux and Cavaillé, 2001). Although numerous pa-

pers have been devoted to PVA hydrogels obtained by freezing/thawing, their dielectric behavior has not yet been studied.

Dielectric spectroscopy is sensitive to the heterogeneous system and can provide insights into the structures and electrical properties of the materials at molecular and macroscopic levels (Ni and Zhao, 2007). The dielectric constant and dissipation factor are crucial quantities required in the design of devices and furthermore, as a function of temperature or frequency, they reveal much information on the chemical or physical state of polymer (Abd El-kader *et al.*, 2008). The dielectric behavior of polymers is determined by the charge distribution and also the statistical thermal motion of its polar groups. Electrical properties of pure and doped PVA films (Kulanthaisami, Mangalaraj and Narayandass, 1995; Singh and Gupta, 1998; Abd El-kader *et al.*, 2008), complex electrolytes of PVA and PVA blends (Mishra and Rao, 1998), solution grown PVA films (Chandar *et al.*, 1999), polyaniline-polyvinyl alcohol composites (Dutta, Biswas and Kumar, 2002), PVA gel electrolytes (Awadhia, Patel and Agrawal, 2006), solution poly(vinyl alcohol) + poly(vinyl pyrrolidone) (Sengwa and Sankhla, 2007) have been studied using different models. To our best knowledge there is no work about the dielectric behavior studies of PVA hydrogels obtained by a F/T technique and how this process and the number of cycles affect the relaxation processes.

The main aim of this work is to investigate the dielectric behavior of polyvinyl alcohol hydrogels with different crosslinking degree obtained by an F/T technique, between $-50\text{ }^{\circ}\text{C}$ and $-10\text{ }^{\circ}\text{C}$, and 1^{-1} Hz to 10^6 Hz using dielectric spectroscopy. The regimes of cryogenic treatment processes have a pronounced effect on the properties of PVA hydrogels, and temperatures lower than $-10\text{ }^{\circ}\text{C}$ are usually employed in the F/T technique, so our interest is in this temperature range.

2. EXPERIMENTAL

2.1 Materials and preparation of PVA hydrogels

PVA with molecular weight of approximately 89,000 to 98,000 and a degree of hydrolysis 99+ % (Sigma-Aldrich) was used to prepare an aqueous solution of 15 % wt PVA by heating the solution at 80 °C and stirring the solution until it was completely homogeneous. The solution was then cast onto a glass mold and the samples (dimensions 7,0 x 7,0 x 0,1 cm) were exposed to four, six and twelve cycles of freezing for 12 hours at -20 °C and thawing 20 °C at a rate of 1.8 °C/min to obtain physical crosslinked hydrogels; the degree of crosslinking varies with the number of F/T cycles. After that, the samples were dried in a vacuum oven (at 25 °C) until constant weight.

2.2 Characterization

2.2.1 Differential scanning calorimetry

Differential scanning calorimetry (DSC Jade, Perkin Elmer) was used to analyze the crystalline nature, melting point and glass transition temperature of PVA hydrogels prepared by F/T processes. In a typical experiment, 6-8 mg of a dried sample were placed in an aluminum pan and cooled until -40 °C to freeze the sample and then heated at a scanning rate of 5 °C/min from -50 °C to 250 °C.

2.2.2 Dielectric relaxation spectroscopy

The dielectric measurements were performed using an impedance analyzer Alpha-S from Novocontrol Technologies, covering a frequency range from 1×10^{-1} Hz to 1×10^6 Hz. The samples of the

PVA system were placed between two electrodes (10 mm of diameter) of a parallel plate capacitor. The sample cell with active head dielectric converter was mounted on a controlled temperature cryostat (BDS 1100) and exposed to a heated gas stream being evaporated from a liquid nitrogen dewar. The temperature control was assured by the Novocontrol Quatro cryosystem and performed within ± 0.5 °C. The isothermal experiments were performed from -50 °C to -10 °C every 5 °C and the dielectric response (complex permittivity ϵ^* and conductivity σ) were determined as a function of frequency.

3. RESULTS AND DISCUSSION

The crosslinked nature of the hydrogels obtained in this study can be proved putting the samples in polar and apolar solvents and noting the insoluble character of samples (Hickey and Peppas, 1995). Figure 1 shows the DSC curves of PVA hydrogel samples. The peaks around 217, 216 and 220 °C correspond to the apparent melting point of the PVA hydrogel crystallites, where the temperature became lower with 4 and 6 cycles F/T. The degree of crystallinity rises with increasing the number of cycles of cryogenic treatment (Hickey and Peppas, 1995; Lozinsky *et al.*, 2008), the increases in the crystallinity for the samples with 6 and 12 cycles F/T are probably due to the oriented crystallization (Nakano *et al.*, 2007). This is evident with the corresponding heat of fusion value. The samples that were exposed to four, six and twelve cycles of F/T had a similar glass transition temperature from 66 to 70 °C. The small changes in the glass transition temperature can be due to a decrease in the number of hydroxyl groups available for hydrogen bonding caused by an increase of the entanglement which hinders other hydrogen bonding formation from weakening of physical network and decreasing T_g (Shafee and Naguib, 2003).

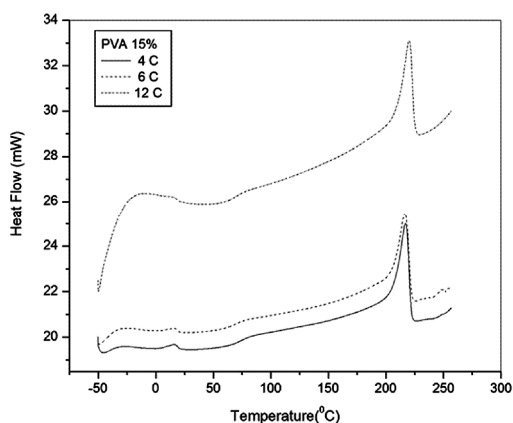
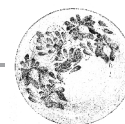


Figure 1. DSC curves of PVA hydrogels at 4, 6 and 12 cycles

The dielectric behaviors of PVA hydrogels obtained by different cycles of F/T have been studied and results are analyzed below in terms of different parameters. Figures 2a, 2b and 2c show the variation of the dielectric constant ϵ' with frequency of temperatures between -50 and -10 °C for xerogels of PVA with different crosslinking degrees (4, 6 and 12 F/T cycles respectively). It is observed from the figures that the dielectric constant ϵ' continuously decreases with increasing frequency. The rapid decreases in the dielectric constant noticed over the frequency range 10^{-1} to 10^4 Hz may be attributed to the tendency of dipoles in macromolecules to orient themselves in the direction of the applied field in the low frequency range. However, in the high frequency range the dipoles will hardly be able to orient themselves in the direction of the applied field, and hence the value of the dielectric constant decreases (Blythe and Bloor, 2005). The sample with fewer cycles, 4, shows high ϵ' values. This can be understood in terms of the degree of crosslinking and changes in crystallinity. Crystallization prevents the movement in the chains; the crystalline phase is rigid and shows no dielectric relaxation processes and, as a consequence, the dielectric response is lower (Blythe and Bloor, 2005). The increase in the number of dipoles is due to less crosslinking in the sample. It was also observed that temperature affects the dielectric properties of PVA hydrogels. In fact, the rise in the temperature and

the resulting drop in relaxation time of the sample increase the degree of the dipole orientation and consequently enhance the value of the dielectric constant (Singh and Gupta, 1998).

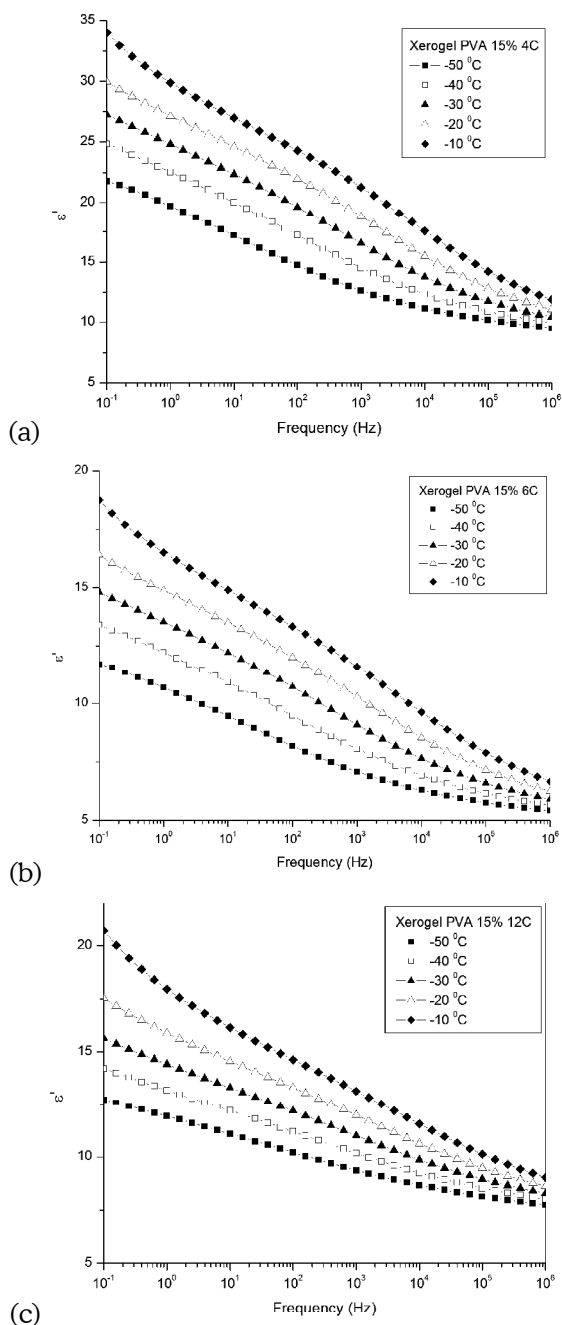


Figure 2. The real part of dielectric permittivity vs frequency of PVA xerogels for different freezing/thawing cycles: a) 4 cycles, b) 6 cycles, c) 12 cycles

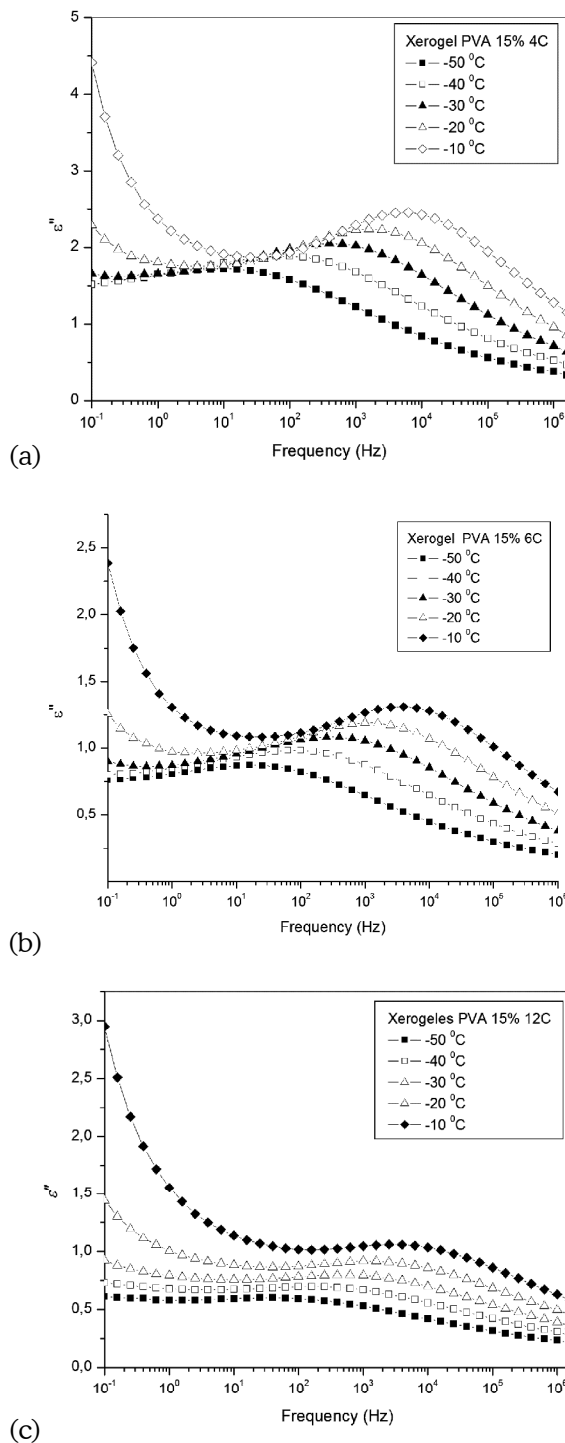


Figure 3. The dielectric spectra ϵ'' of PVA xerogels for different freezing/thawing cycles: a) 4 cycles, b) 6 cycles, c) 12 cycles

Figures 3a, 3b and 3c show the variation of dielectric loss, ϵ'' , with frequency of temperatures between -50 and -10 °C for PVA hydrogels with 4, 6 and 12 F/T cycles. All samples exhibit relaxation processes, β relaxation; this relaxation is caused by some local movement of side dipole groups, in this case by motions of hydroxyl groups (Hickey and Peppas, 1995). High dielectric loss values are observed for the samples with fewer F/T cycles, which may be due to the lower degree of crosslinking present in the sample with 4 cycles which in turn makes the neighboring network chain more flexible; hence the conductivity increases. From figure 3 it can also be observed that the temperature largely influences the dielectric loss of the samples and the intensity of this relaxation rises with the increases of temperature (De La Rosa, Heux and Cavaillé, 2001).

It is worth notice that the sample with 12 F/T cycles has a different behavior both in ϵ' and ϵ'' due a greater crowding caused by the increase of the mass density due to the entanglement and crosslinking in the sample.

3.1 Dielectric loss $\tan \delta$ (f)

Figures 4 a, 4b and 4c present the frequency dependence of $\tan \delta$, equal ϵ'' / ϵ' , for PVA hydrogels with different F/T cycles at temperatures between -50 and -10 °C. The $\tan \delta$ spectrum shows relaxation process for all samples, and as the degree of crosslinking increases, the magnitude of the relaxation peak decreases (Kao, 2004) and the breadth increases (Casalini and Roland, 2010). The values of $\tan \delta$ are below 1 indicating the dielectric phenomenon is predominant in all samples.

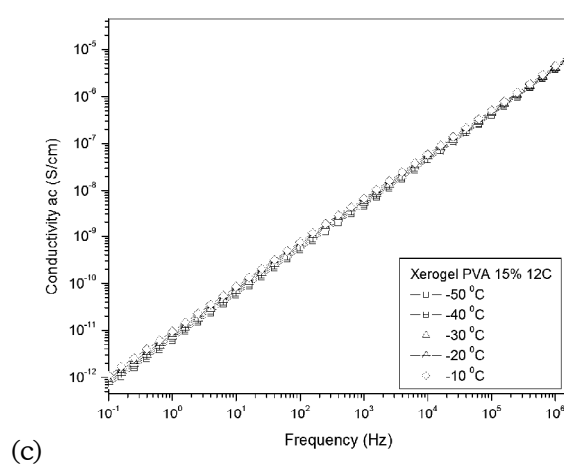
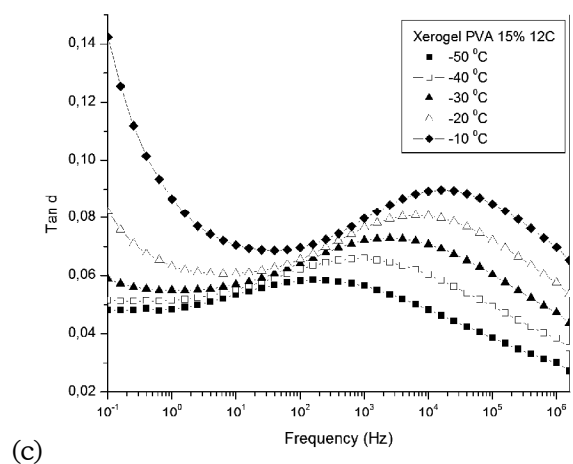
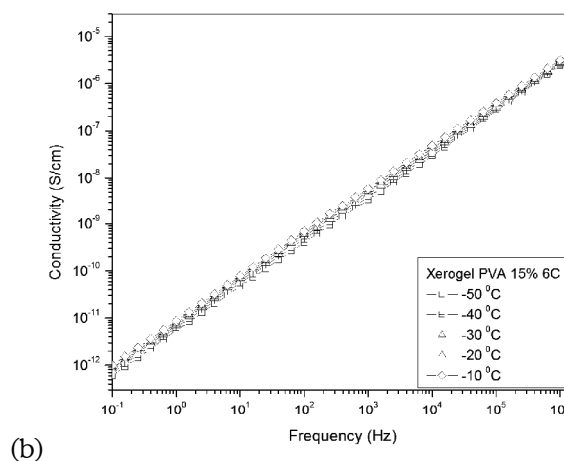
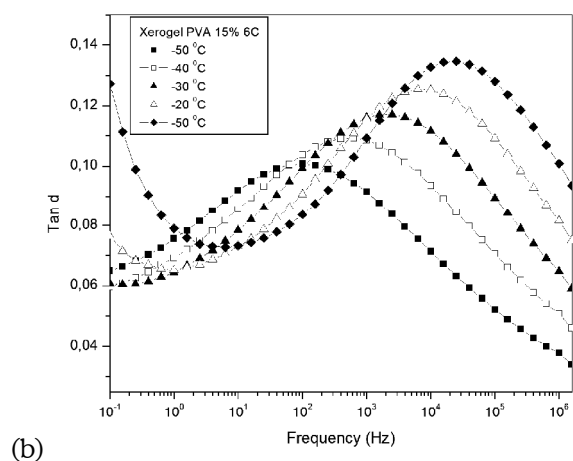
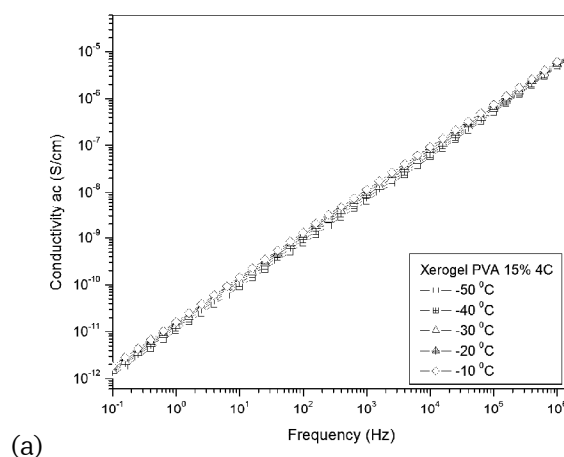
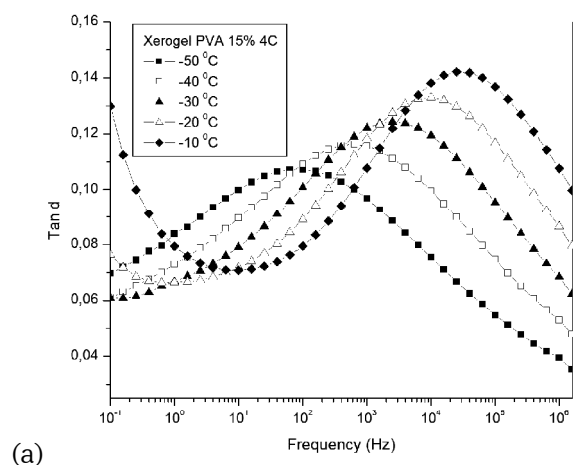
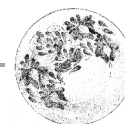


Figure 4. The $\tan \delta$ spectra of PVA xerogels for different freezing/thawing cycles: a) 4 cycles, b) 6 cycles, c) 12 cycles

Figure 5. Variation of log conductivity with log frequency of PVA xerogels for different freezing/thawing cycles: a) 4 cycles, b) 6 cycles, c) 12 cycles

3.2 Conductivity (AC)

The plots of A.C. conductivity vs frequency for hydrogels with different cycles of F/T are shown in figures 5a, 5b and 5c. The conductivity increases linearly with the frequency at temperatures below zero (-50 to -10 °C). This linear variation is described by $\sigma_{ac} = a\omega^n$; where a is a constant, ω is the angular frequency and n is a value close to 1. This conduction takes place via localized hopping of carriers between randomly distributed trapping centers (Kulanthaisami, Mangalaraj and Narayandass, 1995). The low values of conductivity may suggest the electrode polarization is not significant in these samples (Pietrucha and Marzec, 2005).

Figure 6 represents the plot $\tau_{\max}(\frac{1}{2\pi f})$ as a function of reciprocal temperature (as calculated experimentally from the maximum of ϵ'') and fitted to a straight line. The relaxation process can be modeled by Arrhenius temperature dependence equation:

$$\tau(T) = \tau_0 e^{\frac{E_a}{kT}} \quad (1)$$

where τ_{\max} is the relaxation frequency at which $\tan \delta$ is maximum, E_a is the energy barrier for dipole relaxation (activation energy) and τ_0 is the constant parameter characteristic for a particular relaxation process. The activation energies, taken from slopes on the straight line, for the PVA xerogels at 4, 6, 12 F/T cycles were 68.027, 68.917 and 55.537 kJ/mol respectively. These results suggest that the samples submitted to 4 and 6 cycles had the lowest binding forces which oppose dipolar reorientation (Abd Elkader *et al.*, 2008). The difference in the apparent activation energy between the samples with less F/T cycles and the sample with 12 F/T cycles is around 13 kJ/mol indicating the influence of the crosslinking existence in the hydrogels (Ghilarducci, Salva and Marzocca, 2009) and how the number of F/T cycles affects the activation energy. The lack of dependence of the activation energy on the degree of crosslinking is caused by the counterbalance exerted between the concentration of hydrogen bonds and the density of chemical branch points in local mobility (Shteinberg *et al.*, 1980), but chemical branch points do not ex-

ist in PVA hydrogels and therefore no balance exists and this could cause the change in the energy of activation with crosslinking. The increases in the value of activation energy may be related with the increases of crosslinking degree which depends on the number of F/T cycles; high degree of crosslinking severely reduces molecular mobility (Kaiser, 1989) due to increases of the mass density (Casalini and Roland, 2010). Likewise, relaxation times become larger for the sample with 12 cycles, $3,0 \times 10^{-16}$ s, shorter for 6 and 4 cycles, $8,0 \times 10^{-19}$ s and $7,0 \times 10^{-19}$ s respectively. The increase in the relaxation time for the sample with 12 cycles is evidence of the effect of greater crowding caused by the increase of the mass density due to the entanglement and crosslinking in the sample (De La Rosa, Heux and Cavaillé, 2001). However, this effect is less visible between samples with 4 and 6 F/T cycles.

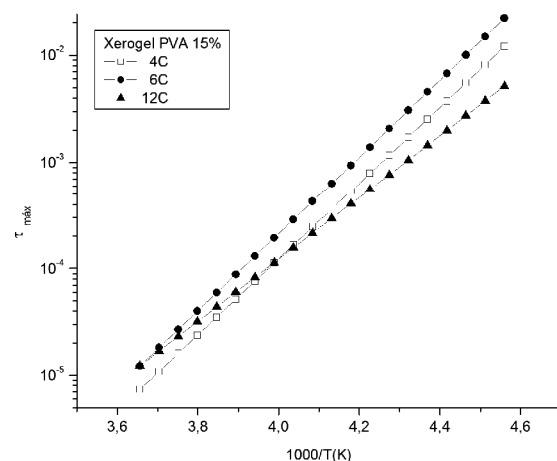
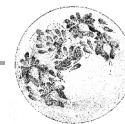


Figure 6. Arrhenius plot (τ_{\max} versus reciprocal temperature) for PVA at xerogels at 4, 6 and 12 F/T cycles

4. CONCLUSIONS

Study of dielectric behavior of PVA hydrogels obtained by F/T technique with different crosslinking degrees showed that dielectric constant and dielectric loss diminish due to the increase of crosslinking degree. Only one relaxation was observed in all samples, the β dielectric relaxation which increases with the increase of temperature and corresponds to



some local movement of OH groups. In the samples studied, the values of $\tan \delta$ below 1 suggest that the dielectric phenomena are predominant, whereas the conduction takes place via localized hopping of carriers. Energy of activation and relaxation time have a complex dependence on number of F/T cycles due to different structures obtained by this process. The greater crowding caused by the increase of the mass density due to the entanglement and crosslinking in the polymer disturb the dielectric properties of the hydrogels. The PVA hydrogels show a complex dielectric behavior, unlike other polymers, and more effort will be necessary to understand the influence of the structure in the dielectric behavior.

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