Dielectric studies of molecular dynamics and hydration properties of poly (hydroxyl ethyl acrylate) – co – poly (ethyl acrylate) copolymers

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ABSTRACT

The hydration properties and polymer dynamics of hydrogels based on random copolymers of poly (hydroxyl ethyl acrylate) (PHEA) and poly (ethyl acrylate) (PEA), at the ratios of 100/0, 90/10, 70/30, 10/90 PHEA/PEA components, were investigated by means of equilibrium sorption isotherms (ESI), thermally stimulated depolarization currents (TSDC) and broadband dielectric relaxation spectroscopy (DRS) measurements. The copolymers are homogeneous at nm scale, except at very high PEA content. Correlations were observed between results on the organization of water in the hydrogels, provided by ESI measurements, and on water effects on polymer dynamics, provided by the dielectric techniques.

1 INTRODUCTION

Hydrogels based on hydrophilic cross-linked polymers may absorb large amounts of water preserving their integrity. They find many applications in medicine, pharmacy, agriculture, and other fields [1],[2]. Good biocompatibility and water permeation properties, in addition to several other good properties arising from their polymeric nature, form the basis for these applications. Of particular interest are issues related with the organization (state) of water and the influence of water on the final properties and the performance of the hydrogel. Such issues are of fundamental interest for other hydrated biomaterials too, including proteins [3] and saccharides [4]. In fact, there are many similarities between these apparently different systems, as well as hydrated inorganic materials, with respect to structure, thermal transitions and dynamics of water and effects of water on the thermal transitions and dynamics of the matrix material, this point being worth to be systematically followed in future work [5].

Two different approaches may be followed, and have in fact been followed in the past, to investigate water effects in hydrogels. The first is based on the classification of water in hydrogels into different classes, depending on the experimental technique employed, such as freezable and non-freezable water, mobile, immobile and clustered water, and free and bound water [6],[7]. The properties of water, which are determined to a large extent by specific polymer-water interactions [6] and by geometrical confinement of water in the pores of the hydrogel [7], and the influence of water on the properties of the polymer matrix are different for the different classes of water. Within the second approach, results obtained with hydrogels are discussed and explained in terms of phase diagrams [8] and chemical exchange processes between water protons and hydroxyl protons of polymer chains [9] and no resource is made to the concept of different classes of water.

In previous work we employed broadband dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization currents (TSDC) techniques, in combination with several other partly
complementary techniques, to study water effects in biocompatible hydrogels based on poly(hydroxyethyl acrylate), PHEA [10]-[15]. In order to improve mechanical stability, PHEA was often combined with a second, hydrophobic polymer in the form of blends, copolymers and interpenetrating polymer networks (IPNs) [13],[14]. This work was later extended to include porous hydrogels, either homopolymers or IPNs, aiming to improve water capacity [16], and organic/inorganic polymer nanocomposites as matrices, aiming to further improve mechanical stability [17].

In this work we focus on the hydration properties and polymer dynamics in random copolymers of PHEA and poly (ethyl acrylate) (PEA). PEA is a hydrophobic polymer, added to improve mechanical stability [14]. The investigation was carried out by means of equilibrium sorption isotherm (ESI) measurements and, mainly, dielectric DRS and TSDC techniques. ESI measurements allow us to study the organization of the adsorbed water molecules within the copolymers, while TSDC and DRS techniques provide information with respect to the effects of adsorbed water molecules on the molecular dynamics of the PHEA–co–PEA copolymers. Information is extracted by the study of water effects on the dynamics of secondary (γ and β_{SW} processes) and segmental relaxation (α relaxation) and on the conduction mechanism. The results are discussed in terms of confinement of water in small volume and specific polymer-water interactions.

2 EXPERIMENTAL

2.1 Materials

The PHEA-co-PEA copolymers were obtained by simultaneous polymerization of 2-hydroxyethyl acrylate (HEA, 96% pure, Aldrich) and ethyl acrylate (EA, 99% pure, Aldrich) at the ratios of 100/0, 90/10, 70/30, and 10/90 PHEA/PEA components. Benzoyl peroxide (BPO, 97% pure, Fluka) was used as thermal initiator. Details of preparation have been described in [18]. Samples for ESI, DRS and TSDC measurements were in the form of free-standing films with a thickness in the range of 1 – 1.5 mm. They are coded by XX/YY PHEA-co-PEA, where XX and YY are the weight fractions of PHEA, respectively PEA components.

2.2 Experimental techniques

For ESI measurements samples were allowed to equilibrate to constant weight over saturated salt solutions in sealed jars at controlled relative humidities (RH) at room temperature. The water content h, defined as the ratio of the weight of water in the hydrogel to the weight of the dry sample (dry basis), was determined by weighing [12]. Dry weights were determined by drying to constant weight in vacuum (5x10^{-2} Torr) for at least 24 h at 80 °C. DRS (10^{-2}-10^{6} Hz) and TSDC techniques (-180 to 30 °C) have been described elsewhere [10],[11]. The TSDC technique corresponds to measuring dielectric losses against temperature at low frequencies of 10^{-2}-10^{-4} Hz, i.e. in a range not easily accessible by DRS measurements. Moreover, the technique is characterized by high sensitivity and high peak resolving power [10]. DRS measurements were performed isothermally at several temperatures in the range -150 to 60 °C. Dielectric measurements were performed at several water contents, adjusted as in ESI measurements. In the following the water content h or the relative humidity RH of equilibrating the sample will be given as parameter at each measurement. It was checked in separate experiments that the water content of a sample remained practically constant during dielectric measurements, obviously because of the relatively low temperatures of measurements.

3 RESULTS AND DISCUSSION

3.1 ESI measurements
Fig. 1(left) shows the results of ESI measurements for pure PHEA and two copolymers. At each relative humidity \( h \) decreases with increasing PEA content, reflecting the decreasing hydrophilicity of the sample. For pure PHEA and 70/30 PHEA-co-PEA a steep increase of \( h \) is observed at RH larger than 0.5-0.6, reflecting the formation of water clusters around primary hydration sites [12]. The experimental data were fitted by the Guggenheim-Anderson-DeBoer (GAB) model, which describes water sorption by considering different “states” of water (compare section 1), i.e. water directly fixed to primary hydration sites (water in the first layer, tightly bound water), water absorbed in the second and successive layers (water absorbed in clusters, loosely bound water) and free (bulk) water [12],[14]

\[
\frac{h(RH)}{h_m} = \frac{c f RH}{(1 - f RH)(1 + (c - 1)f \alpha)}
\]  

(1)

In this equation \( h_m \) is the first monolayer sorption capacity, \( c \) is the ratio of the chemical potential of water molecules in the first monolayer to that of water in the second and successive layers and \( f \) is the ratio of the chemical potential of water molecules in the second and successive layers to that of liquid water at the same temperature and pressure. The results show that \( h_m \), the most significant parameter in (1), decreases with increasing PEA content, from 0.07 in pure PHEA to 0.035 in 70/30 PHEA-co-PEA and to 0.007 in 10/90 PHEA-co-PEA. From the value for pure PHEA and the molar masses of HEA and water a value of 0.44 is calculated for the number of primary hydration (sorption) sites in each polymer segment, which is relatively high with respect to values of 0.25 for PHEA and 0.31 for PHEMA obtained in previous work [12]. Bearing in mind that hydration of PHEA involves association of one water molecule and two hydroxyl groups of neighbor side chains [14], this result suggests that only approximately 10% of the hydroxyl groups are not accessible as sorption sites. Finally, the results show that \( f \) in (1) is smaller than 1 (0.82 in PHEA, 0.85 in 70/30 PHEA-co-PEA and 0.70 in 10/90 PHEA-co-PEA), indicating that indirectly bound water molecules (in the second and successive layers) are in a more stable state than bulk (free) water molecules.

### 3.2 TSDC measurements

TSDC thermograms in the temperature region from -180 to 30 °C for pure PHEA and the copolymers recorded at different water contents (RH of equilibration) show, in general, three dipolar peaks, which correspond, in the order of increasing temperature, to the secondary \( \gamma \) and \( \beta_{SW} \) processes and the segmental \( \alpha \) relaxation associated with the glass transition. The peak temperatures provide
information on the time scale of the corresponding relaxations and will be considered later in the construction of the Arrhenius plots together with the DRS data. Here we focus on the α peak. Previous work with various polymeric systems has shown that the temperature position of this peak, $T_\alpha$, is a good measure of the calorimetric glass transition temperature $T_g$ [12]-[15]. The dependence of $T_\alpha$ on RH can be followed in Fig. 1(right) for pure PHEA and 70/30 PHEA-co-PEA. A single α peak was observed for that copolymer, indicating phase homogeneity at the scale of a few nm, the characteristic length (cooperativity length) of the glass transition [18]. For the copolymer with the highest amount of PEA, 10/90 PHEA-co-PEA, on the contrary, a double peak was observed, in agreement with the results of DRS measurements, indicating microphase separation. This point will be further followed in future work. Here we focus on the behaviour of pure PHEA and 70/30 PHEA-co-PEA in Fig. 1(right). For dry samples $T_\alpha$ decreases in the copolymers with increasing PEA content (by considering also the data for the 90/10 PHEA-co-PEA copolymer not shown here), implying plasticization by the PEA component. A strong plasticization by water is observed for both samples in Fig. 1(right). The steeper decrease at higher values of RH reflects simply the steeper increase of water content h in this RH range, compare Fig. 1(left). It is interesting, with respect to the behaviour of PHEA/PEA IPNs [13], to plot $T_\alpha$ against water content divided by PHEA content. In such a plot the data corresponding to the different IPN compositions fall on a single curve, which coincides with the prediction of the Couchman-Karasz equation for compatible blends, indicating that those IPNs were microphase-separated systems with hydrophilic domains behaving essentially as the pure hydrophilic component polymer [13]. A different behaviour is observed here for the copolymers. In the corresponding plot, not shown here, the data do not fall on a single curve, indicating that, for the same value of water content divided by PHEA content, $T_\alpha$ (and, thus, $T_g$) depends on matrix composition.

### 3.3 DRS measurements

Fig. 2 shows, as an example of DRS measurements, the imaginary part of dielectric function (dielectric loss), $\varepsilon''$, for the 90/10 PHEA-co-PEA copolymer at two temperatures to follow the evolution of the secondary relaxations (-80 °C, left) and of the segmental relaxation (50 °C, right) with RH. We observe that the $\beta_{sw}$ process emerges with the first traces of adsorbed water molecules and that this process is accelerated with increasing water content. The γ process is less sensitive to water content. At high hydrations the two processes merge and we observe only the $\beta_{sw}$ process, because of its higher strength.

![Fig. 2: Imaginary part of dielectric function, $\varepsilon''$, vs frequency for the 90/10 PHEA-co-PEA copolymer at the temperature ranges of secondary γ and $\beta_{sw}$ relaxations (left) and of the main (α) relaxation (right) at various values of relative humidity for the conditioning of the sample prior to each measurement indicated on the plot](image-url)
Analysis will provide more information on the two processes. The \( \gamma \) process is attributed to the motion of the polar group \(-\text{CH}_2\text{-CH}_2\text{-OH}\) in the side chain of the HEA monomer and the \( \beta_{\text{sw}} \) process is then assigned to the association of one water molecule with the polar groups of two adjacent side chains \[11\]. Comparative results for the dry samples, not shown here, indicate that the \( \gamma \) process is sensitive to the plasticization action of PEA, in the sense that the process becomes faster with increasing PEA content. Also the segmental \( \alpha \) relaxation is accelerated with increasing water content (Fig. 2, right). For higher water contents the relaxation is masked by conductivity, indicated by the steep increase of \( \varepsilon'' \) with decreasing frequency and only by analysis we can follow the relaxation.

The experimental results, similar to those shown in Fig. 2, were further analyzed by fitting the Havriliak-Negami (HN) model function \[19\]

\[
\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\Delta \varepsilon}{1 + (i\omega \tau)^{\alpha}}
\]

(2)

to the experimental data. In this expression \( \Delta \varepsilon \) is the dielectric strength, \( \Delta \varepsilon = \varepsilon_s - \varepsilon_\infty \), where \( \varepsilon_s \) and \( \varepsilon_\infty \) are the low- and high-frequency limits of \( \varepsilon' \), respectively, \( \tau \) is the relaxation time, \( \tau = 1/2\pi f_{\text{HN}} \), where \( f_{\text{HN}} \) is a characteristic frequency closely related to the loss peak frequency \( f_{\text{max}} \), and \( \alpha, \beta \) are the shape parameters describing the shape of the \( \varepsilon''(\omega) \) curve below and above the frequency of the peak, respectively, \( 0 < \alpha \leq 1 \) and \( 0 < \beta \leq 1 \). This expression becomes the single Debye form for \( \alpha = 0, \beta = 1 \), the symmetric Cole-Cole form for \( \alpha \neq 0, \beta = 1 \), and the asymmetric Cole-Davidson form for \( \alpha = 0, \beta \neq 1 \). Depending on the shape of the data a more complex expression, e.g. consisting of a sum of two HN terms (analysis of \( \gamma-\beta_{\text{sw}} \) processes) or one HN term plus a term for conductivity (analysis of \( \alpha \) process), was used. Details of analysis will be given elsewhere. Analysis provides information on the time scale, the strength and the shape of each relaxation process. Here we focus on the time scale of the three processes.

Time scale is best discussed in terms of the Arrhenius plot (activation diagram) shown in Fig. 3 for the 90/10 PHEA-co-PEA copolymer. Included in the plot are also TSDC data for the \( \beta_{\text{sw}} \) and the \( \alpha \) processes, peak temperatures at the equivalent frequency of 1.6 mHz, corresponding to a relaxation time of 100 s \[10\], generally in good agreement with the DRS data.

**Fig. 3:** Arrhenius plot for the \( \alpha \) and \( \beta_{\text{sw}} \) (left) and the \( \gamma \) (right) relaxation processes observed in 90/10 PHEA-co-PEA copolymer at various values of relative humidity for the conditioning of the sample prior to each measurement indicated on the plot. The lines are fittings of the Arrhenius equation (3) to the data for the \( \beta_{\text{sw}} \) and the \( \gamma \) relaxations.
For most of the hydrations the $\gamma$ process was out of the temperature range of TSDC measurements, which becomes now clear in Fig. 3(right). The temperature dependence of the three relaxations was further studied by fitting the Vogel-Tammann-Fulcher (VTF) equation \[18\], characteristic for cooperative processes, to the data for the $\alpha$ relaxation; and the Arrhenius equation, characteristic for local, secondary relaxations (one-barrier activated processes), to the data for the $\gamma$ and the $\beta_{sw}$ processes.

We focus here on the secondary relaxations. The lines in Fig. 3 are fits of the Arrhenius equation \[11\],\[18\],

$$f_{\max}(T) = f_o \exp \left( -\frac{w}{kT} \right)$$  \hfill (3)

where $w$ is the activation energy of the process and $f_o$ a pre-exponential factor, to the $\gamma$ and the $\beta_{sw}$ data. The activation energy takes values in the range 0.25-0.45 eV for the $\gamma$ process and 0.55-0.85 eV for the $\beta_{sw}$ process, which show systematic changes with composition and water content (RH). Of particular interest is the fact that significant changes are observed at the RH (water content) where the first monolayer is completed, as predicted by the GAB equation. Also the behavior of the relaxation strength of the $\beta_{sw}$ process, obtained by the HN analysis, changes at this value of RH. These results, to be presented and discussed in more detail elsewhere, provide strong evidence that microscopic changes in the structure and dynamics of the hydrogel induced by water can be detected and analyzed dielectrically. Interestingly, these results show distinct similarities with DRS results reported for other water systems, namely fructose-water mixtures \[4\] and water mixtures with various glass-forming liquids \[20\], which should be further followed in future work.

DRS may provide significant information also on electrical conductivity (charge carrier motion) in a hydrogel \[11\],\[21\]. For the dry copolymers under investigation here conductivity is reduced with increasing PEA content, indicating the dominant role of PHEA component in the conduction mechanism of the copolymers. Conductivity in hydrogels is protonic and takes high values at high water contents, which are promising for various applications \[21\]. Fig. 4 shows, as an example, the Arrhenius plot of dc conductivity at various values of RH in pure PHEA. Similar plots were obtained also with the copolymers.

![Fig. 4: Arrhenius plot of dc conductivity (left) and normalized plot of dc conductivity (right) for PHEA at various values of relative humidity for the conditioning of the sample prior to each measurement indicated on the plot.](image-url)
Conductivity increases significantly with water content at temperatures higher than $T_g$ and its VTF-type temperature dependence suggests that it is governed by the motion of the polymeric chains. However, increase of charge carrier concentration on addition of water may be also at the origin of the increase of conductivity with RH in Fig. 4 [21]. To further follow this point we show in Fig. 4 (right) the corresponding $T_g$-normalized plots (conductivity against $T_g/T$), where $T_g$ has been obtained from the TSDC thermograms ($T_g = T_α$). The points for the different values of RH come now very close to each other, indicating that the main factor for the increase of conductivity with RH is the concomitant drop of $T_g$ (Fig. 1) rather than the increase of charge carrier concentration.

4 CONCLUSIONS

Hydrogels based on random copolymers of the hydrophilic poly (hydroxyl ethyl acrylate) (PHEA) and the hydrophobic poly (ethyl acrylate) (PEA) polymers were prepared and investigated. Equilibrium sorption isotherm (ESI) measurements provided information on the organization of water in the hydrogels at different levels of relative humidity (RH). Effects of water on polymer dynamics were studied by following the evolution of the local, secondary $γ$ and $β_{SW}$ relaxations and of the segmental $α$ relaxation, associated with the glass transition, with RH. Dielectric techniques, thermally stimulated depolarization currents (TSDC) and broadband dielectric relaxation spectroscopy (DRS), were employed to that aim.

The results show that the dry copolymers rich in PHEA are homogeneous at nm scale, the cooperativity length of the glass transition, whereas for the 10/90 PHEA-co-PEA copolymer two dynamic glass transitions were observed indicating microphase separation, a point which should be further followed in future work. Water uptake by the copolymers increases with increasing PHEA content and is well described by the GAB model. TSDC and DRS measurements show, in good agreement with each other, that the segmental $α$ relaxation is strongly plasticized by water, leading to a remarkable decrease of the glass transition temperature $T_g$. Analysis of the DRS data for the secondary $γ$ and $β_{SW}$ processes indicates significant changes of the dynamics (activation energies) and the relaxation strength at the RH of completion of the first monolayer, as indicated by the GAB analysis. The results provide strong evidence that microscopic changes in the structure and dynamics of the hydrogel induced by water can be detected and analyzed dielectrically, a point which will be further followed in future work. It is interesting to note distinct similarities of these results with DRS results reported for other water systems. Electrical (protonic) conductivity increases significantly in the hydrogels with increasing water content. Analysis shows that the main factor for the increase of conductivity with RH is the concomitant drop of $T_g$ rather than the increase of charge carrier concentration.

5 REFERENCES


