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Water sorption and polymer dynamics in hybrid poly(2-hydroxyethyl-co-ethyl acrylate)/silica hydrogels

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ABSTRACT

This work probes the hydration properties and molecular dynamics of hybrid poly(hydroxyethyl-co-ethyl acrylate)/silica hydrogels. Two series of hybrid copolymers were prepared by simultaneous polymerization and silica preparation by sol–gel method, the first with hydroxyethyl acrylate/ethyl acrylate (HEA/EA) composition at 100/0, 90/10, 70/30, 50/50, 30/70, 10/90 and fixed silica content at 20 wt.%, and the second with fixed HEA/EA organic composition at 70/30 and 0, 5, 10 and 20 wt.% of silica. The hydration properties of these systems were studied at 25 °C by exposure to several controlled water vapor atmospheres (water activities 0–0.98) in sealed jars and by immersion in distilled water. Finally, the molecular dynamics of the hydrated hybrids at several levels of hydration was probed with Thermally Stimulated Depolarization Currents (TSDC) in the temperature interval between –150 and 20 °C. The results indicate that a critical region of silica content between 10 and 20 wt.% exists, above which silica is able to form an inorganic network. This silica network prevents the expansion of water clusters inside the hydrogels and subsequently the total stretching of the polymer network without obstructing the water sorption at the first stages of hydration from the dry state. As concerns the copolymer composition, the presence of EA reduces water sorption and formation of water clusters affecting directly to the hydrophilic regions. The TSDC thermograms reveal the presence of a single primary main broad peak denoted as α_{cop} relaxation process, which is closely related to the copolymer glass transition, and of a secondary relaxation process denoted as β_{sw} relaxation, which originates from the rotational motions of the lateral hydroxyl groups with attached water molecules. The single α_{cop} implies structural homogeneity at the nanoscale in HEA-rich samples ($x_{\text{HEA}} > 0.5$), while for high EA content ($x_{\text{EA}} \geq 0.5$) phase separation is detected. Both relaxation processes show strong dependence on water content and organic phase composition.

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1. Introduction

Hydrogels are crosslinked polymers which are able to absorb substantial amounts of water without dissolution [1]. This property, in combination with the fact that the majority of them are biocompatible, signifies their

importance for medical applications as tissue scaffolds, devices for controlled drug delivery, contact lenses, etc. [1–4]. Poly(2-hydroxyethyl acrylate) (PHEA) and poly(2-hydroxyethyl methacrylate) (PHEMA) are representative hydrophilic acrylic polymers for these applications. Their hydration properties are attributed to the hydroxyl groups in the side chain rendering them interesting object for research [5–8]. The present work focuses on PHEA which presents high hydrophilicity, but poor mechanical properties when it is soaked [9].

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A lot of attention has been paid in combining the attractive high hydrophilicity of PHEA with the simultaneous improvement of its mechanical endurance. Thus, one important attempt was to introduce a second hydrophobic component in the form of copolymers or interpenetrating polymer networks (IPNs). IPNs are composed by two independent networks (one from the hydrophilic and the other one from the hydrophobic component), spatially interpenetrated. These systems reveal the presence of phase separation between the two components (for IPNs with low crosslinking density) at the mesoscopic level of a few nm and subsequently two glass transitions [10–12]. Such a structure favors the hydrophilic phase to behave like in the bulk phase maintaining its sorption ability [13,14]. On the other hand, a lot of effort was attempted to combine hydrophilic and hydrophobic phase in the form of random copolymers [5,15,16]. Their molecular structure and homogeneity are guided from the chemical reactivity and the composition of the reacting monomers during radical polymerization. When the monomers exhibit a great difference in their reactivity ratio, the one monomer is able to produce exclusive domains with the same monomer unit, giving rise to phase separation, though that depends on the weight fraction of the components (i.e. when the fraction of the component with the high reactivity ratio is higher, the system becomes homogeneous, otherwise is phase separated). Such a phase separation is detected by the presence of two separated glass transition temperatures [5]. In copolymers, the hydrophilic phase behaves in a rather more complex manner, as compared to IPNs, because the presence of hydrophobic moieties among the hydrophilic phase reduces its sorption ability [13,14]. However, each system is useful for specific applications either as a material with phase continuity or as a phase-separated system. For instance, the phase separation comprises an important benefit for biomedical applications, because it imposes better adhesion, viability and proliferation of human chondrocytes in an in vitro monolayer cell culture, compared to that of the pure hydrophilic, the hydrophobic or a homogeneous phase of them [17].

Alternatively, the reinforcement of the mechanical properties is achieved by the introduction of an inorganic phase inside the polymer matrix in the form of nanoparticles. Their formation yields significant improvement of mechanical properties in nanocomposites, when a very good dispersion of nanoparticles is succeeded at the nanoscale [18]. This is achieved via the simultaneous sol–gel reaction of the organic monomers and the inorganic precursor [19]. Sol–gel technique ensures the presence of nanoparticle aggregates with a size below 400 nm rendering the samples as transparent. The silica nanoparticles are able to form an inorganic network, the continuity of which depends mainly on the initial amount of the inorganic phase, in the present work by means of acid catalyzed hydrolysis and condensation reactions of the silica precursor tetraethyl orthosilicate (TEOS). In the case of neat PHEA the percolation threshold for the formation of the silica network is close to 15 wt.% of silica [20–24]. The formation of two networks, one from the polymer and the other from the silica nanoparticles, provokes the

presence of a kind of interpenetrating network. The silica network provides significant mechanical reinforcement, which is reflected in the increase in the storage modulus (E') in the rubbery state at the expenses of preventing further volume expansion with adding water to the hydrogel [20,23].

The present work focuses on the study of the hydration properties and molecular dynamics of reinforced PHEA with the simultaneous introduction of the inorganic silica nanophase and the hydrophobic ethyl acrylate (EA). The components hydroxyethyl acrylate (HEA), ethyl acrylate (EA) and tetraethyl orthosilicate (TEOS) were mixed via sol–gel method under controlled conditions, resulting in a hybrid random copolymer with very good dispersion of silica nanoparticles inside the organic volume [25]. Thus, hybrids were prepared with fixed silica content at 20 wt.% and variant organic HEA/EA composition at 100/0, 90/10, 70/30, 50/50, 30/70, 10/90, as well as hybrids with fixed organic composition HEA/EA at 70/30 and 0, 5, 10 and 20 wt.% of silica. The hydration properties of these systems are studied at 25 °C by their exposure to several controlled water vapor atmospheres into sealed jars with a range of water activities from 0 to 0.98 and by immersion in distilled water, in both cases until equilibrium to constant weight. The Guggenheim–Anderson–de Boer (GAB) model function is fitted to the experimental data for vapor sorption and the results are discussed in terms of the effect of the composition of the polymer matrix and of the silica content on the hydration properties. Interesting correlations are observed and discussed between results obtained by sorption from the vapor phase and by immersion. Comparison is made with results obtained recently with PHEA/silica hybrids [20,23–25]. The overall work is accomplished with the investigation of molecular dynamics of the hydrated hybrids. Thermally Stimulated Depolarization Currents (TSDC) measurements were employed to that aim in a temperature interval between –150 and 20 °C. TSDC is a special dielectric technique in the temperature domain with high sensitivity and high resolving power [26,27]. The broad temperature range of measurements enables to follow both local, secondary relaxations at low temperatures and cooperative, segmental relaxations at higher temperatures. The TSDC thermograms reveal the presence of a single α_{cop} relaxation closely associated with the segmental motions of regions rich in HEA with sparse EA monomers, for the samples rich in PHEA ($x_{\text{HEA}} > 50$ wt.%), in contrast to the hybrids with high EA fraction ($x_{\text{EA}} \geq 50$ wt.%), where a second main relaxation arises, associated with EA segmental motions, indicating phase separation in the polymer phase. The evolution of the temperature position of the α_{cop} relaxation with water content, silica content and the organic composition is studied in detail. The secondary β_{sw} relaxation process, which originates from local motions of lateral hydroxyl groups with attached water molecules [28], manifests strong dependence on both water content and EA content, remains however unaffected by the presence of the silica nanophase. Finally, evidence is provided for the presence of a new obscured secondary relaxation process, denoted as β' relaxation process, which possibly originates from the local rotational motion of methacrylic groups on the crosslinking bridges [29].

2. Experimental

2.1. Materials

The hybrid PHEA-co-PEA/silica nanocomposites were obtained by the simultaneous polymerization of 2-hydroxyethyl acrylate (HEA, 96% pure, Aldrich) and ethyl acrylate (EA, 99% pure, Aldrich) at different amounts of each constituent. The HEA/EA monomer ratios were 10/90, 30/70, 50/50, 70/30 and 90/10 wt.%. Benzoyl peroxide (BPO, 97% pure, Fluka) was used as thermal initiator (2 wt.% organic phase). HEA and EA were mixed with BPO and mechanically stirred for 30 min. Tetraethylorthosilicate (TEOS, 98% pure, Aldrich) was mixed with a hydrochloric acid solution (HCl, 37% pure, Aldrich) and distilled water keeping the molar ratios HCl/TEOS equal to 1.85×10^{-2} and $H_2O/TEOS$ equal to 2, and stirred mechanically for 30 min as well. The two solutions were mixed together and stirred for 30 min more. The quotient between organic and inorganic phase was also changed in order to obtain hybrid systems with silica contents of 5, 10, 20 wt.%, as well as pure copolymers denoted as reference samples (*rs*). The thermal polymerization process was carried out in two steps, first at 60 °C for 21 h, and then heating up to 90 °C for 18 h to post-polymerize. Finally, the samples were rinsed in ethanol and distilled water for 24 h and were dried in vacuum oven at 60 °C for 24 h. Then the hybrids were kept in sealed jars with phosphorus pentoxide for 6 days in order to determine the dry masses.

The samples were rectangular plate sheets with a thickness between 0.5 and 1 mm and a surface area between 2 and 3 cm². A representative code that describes the samples is for instance 9010s20, which corresponds to a hybrid copolymer with 90 wt.% HEA, 10 wt.% EA in the organic phase and 20 wt.% silica and so on (Table 1).

2.2. Sorption from the water vapor phase

The isothermal sorption curves were determined at room temperature by exposing the samples to various water vapor atmospheres in sealed jars. The water activities a_w were achieved with appropriate saturated salt solutions in distilled water [30]. The samples were exposed to water activities of 0.11, 0.33, 0.39, 0.54, 0.69, 0.75, 0.85, 0.95 and 0.98. The attainment of equilibrium

was determined via continuous monitoring of sample weight. A Bosch SAE 200 balance with 10^{-4} g sensitivity was employed for these measurements and for immersion experiments that are described in Section 2.3. Once the equilibrium was attained, the hydration (h) was calculated on the dry basis through the expression:

$$h = \frac{m - m_{\text{dry}}}{m_{\text{dry}}} = \frac{m_{\text{water}}}{m_{\text{dry}}} \quad (1)$$

where m corresponds to the mass of the hydrogel, m_{dry} is the mass of the xerogel and m_{water} is the water mass inside the sample.

2.3. Immersion

The immersion experiments were performed by placing all the samples in distilled water. The samples were weighed at two different time intervals, 6 and 23 days, respectively. The particular time intervals were selected properly in relevance to when the weights became almost constant (i.e. first sorption stage yields a plateau region, for times ranging from 10 h to 6 days), taking also into consideration long time exposure effects (i.e. sample weight starts increasing again beyond 6 days), which had been observed in previous works with PHEA systems with different crosslinking density [9]. Before weighing, the samples were wiped in order to remove the liquid water from their surface. The water uptake in immersion is significant and leads to hydrations higher from unity, when they are calculated by Eq. (1). By dividing the mass of water by the whole polymer mass (wet basis), we can acquire a concentration which is more convenient with values lower than unity according to the expression:

$$\omega = \frac{m_{\text{water}}}{m_{\text{dry}} + m_{\text{water}}} = \frac{m_{\text{water}}}{m} \quad (2)$$

where m , m_{dry} and m_{water} have the same meaning as in Eq. (1).

2.4. Thermally Stimulated Depolarization Currents (TSDC)

TSDC measurements were performed on hydrated hybrids in the temperature interval between -150 and 20 °C under nitrogen flow, controlled by a Novocontrol Quatro Cryosystem. In TSDC experiment, the sample was inserted between the brass plates of a capacitor and polarized by the application of electric field E_p at temperature T_p (temperature of polarization) for time t_p , which was large in comparison to the relaxation time at T_p of the dielectric dispersion under investigation. With the electric field still applied, the sample was cooled to temperature T_0 (which was sufficiently low to prevent depolarization by thermal excitation), and then was short-circuited and reheated at a constant rate (b). The resulting discharge current was measured as a function of temperature by means of a KEITHLEY 617 electrometer with an accuracy of 0.01 pA. The equivalent frequency (f) of TSDC measurements spans $10^{-4} < f < 10^{-2}$ Hz; i.e. it is close to those of DSC measurements [31]. TSDC is characterized by sensitivity, which allows the detection of weak relaxations [27]. Typical conditions were $E_p = 1\text{--}5$ kV/cm for the polarizing field, $t_p = 5$ min for the polarization time, 10 grad/min for the

Table 1

Parameters extracted from the fittings of the GAB equation (3) to the isothermal sorption curves from the sealed jars.

Samples	GAB parameters (sealed jars)		
	h_m	f	c
100s20	0.029	0.92	14.7
9010s20	0.030	0.89	62.7
5050s20	0.025	0.80	19
3070s20	0.021	0.76	18.2
1090s20	0.016	0.72	93.3
7030rs	0.026	0.90	3.5
7030s5	0.022	0.92	7.1
7030s10	0.023	0.91	7.4
7030s20	0.025	0.87	10.6

cooling rate to $T_0 = -150\text{ }^\circ\text{C}$, and $b = 3\text{ grad/min}$ for the heating rate. The polarization temperature (T_p) was experimentally selected after preliminary measurements, so as to obtain an α_{cop} relaxation process well separated from ρ peak and conductivity contributions, usually present in similar systems [27,32,33]. Therefore, the range of polarization temperature spans -50 to $20\text{ }^\circ\text{C}$ depending on the composition and the hydration level.

The hybrids were exposed to ambient conditions for very short time in order to prepare the capacitor, as typically for this kind of measurements [32,33], but even for this short time a slight water absorption or desorption is inevitable. Thus, the hybrids were weighed before and after the TSDC measurement, and the average mass was used to calculate the average hydration of the measured sample.

3. Results and discussion

3.1. Equilibrium water sorption

3.1.1. Equilibrium water sorption isotherms

Fig. 1 presents the equilibrium sorption isotherms $h = h(a_w)$ which were acquired from the water vapor phase at $25\text{ }^\circ\text{C}$ for the P(HEA-co-EA) hybrids with HEA/EA composition 100/0, 90/10, 70/30, 50/50, 30/70, 10/90 and constant content of silica 20 wt.% (a) and for the fixed HEA/EA composition at 70/30 with 0, 5, 10, 20 wt.% of silica (b) using sealed jars. The isothermal curves belong to type II according to Brunauer classification [34]. Type II isotherm describes the absorption on macroporous absorbents with strong adsorbate–absorbent interactions. The increase in the water uptake for high water activities is significant for the hybrids rich in HEA and is associated with the formation of water clusters [26,34,35]. The water uptake in the case of the copolymers with different organic composition decreases significantly by increasing the EA content (Fig. 1a). This deviation is enhanced at higher water activities and is ascribed to the reduction of the hydroxyl groups per unit mass inside the polymer volume, which comprise primary sorption sites [11,13,14]. Consequently, the presence of EA weakens the compatibility between the organic phase and water molecules inhibiting the swelling process.

For the samples with specific organic composition at 70 wt.%/30 wt.% (HEA/EA) and variant contents of silica, the respective isothermal sorption curves present almost the same water uptake at water activities $a_w < 0.75$, despite the fact that the organic fraction decreases (Fig. 1b). This implies that silica contributes to the hydrophilicity of the hybrid material replacing the missing primary sorption sites of the organic phase. The hydrophilic character of bulk silica has been recently studied by equilibrium sorption isotherms measurements on pure silica obtained from TEOS [23]. The results show that silica hydration approaches a limiting value towards 12 wt.% with increasing water activity. This is attributed to the presence of the hydrophilic groups Si–OH (silanols) on silica porous surface [25]. However, the total amount of free silanols is not determined with accuracy, because it depends on the overall effective silica surface and it is different when silica

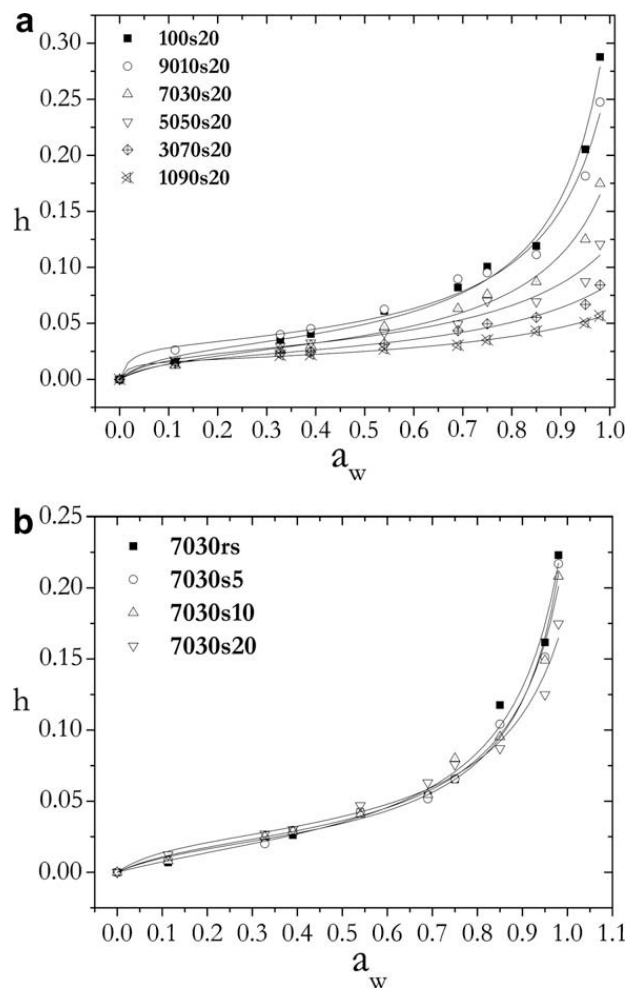


Fig. 1. Equilibrium sorption isotherms for the copolymers (a) with variant organic composition and specific silica content at 20 wt.% and (b) with the specific organic composition at 70 wt.% PHEA and 30 wt.% PEA (7030) and silica content at 0, 5, 10 and 20 wt.%, in terms of water content of the sample against water activity. The solid lines are fittings by the GAB equation (3).

is in the form of not-assembled aggregates or as a network. In the case of the inorganic network formation (above the percolation threshold), a part of silanols are converted to Si–O–Si groups reducing the number of silanol groups which constitute primary sorption sites. In addition, a significant amount of these silanols are expected to interact via hydrogen bonding with the organic phase independently of the form of silica (i.e. not-assembled aggregates or inorganic network). In any case silica maintains its hydrophilic character comprising an additional hydrophilic factor for the hybrids. Therefore it is plausible that the hydrophilic silica phase does not prevent the water sorption at the first levels of hydration, but on the contrary surrogates the missing hydrophilic organic phase.

For higher water activities ($a_w > 0.75$) there is a remarkable increase in the water uptake of the samples in Fig. 1b, which is associated with the forming of water clusters. However, the increase in water uptake is not the same for each hybrid. In particular the hybrid 7030s20 exhibits lower values of water uptake by increasing water activity ($a_w > 0.75$) with respect to 7030rs. For 7030s5 and

7030s10 this deviation is not remarkable. Similar results obtained by immersion experiments which are discussed in the following Section 3.1.2. The same behavior has been obtained also for PHEA/silica systems, where a critical content of silica was detected at approximately 15 wt.% [20,23]. Above this critical region an inorganic silica network exists, which is interpenetrated with the organic one. The presence of such an inorganic network imposes restrictions on the expansion of the organic matrix at high water activities, reducing the available space that the organic phase is able to swell though, without preventing its sorption ability at low water activities. Further discussion follows later.

The equilibrium sorption isothermal curves were quantified according to the Guggenheim–Anderson–de Boer (GAB) expression [36]:

$$\frac{h}{h_m} = \frac{cfa_w}{(1 - fa_w)[1 + (c - 1)fa_w]} \quad (3)$$

where h_m is the weight fraction measured on a dry basis of water molecules directly attached to sorption sites (bound water, first sorption layer), c is a parameter related to the energy difference between the water molecules attached to sorption sites (the first sorption layer) and that absorbed in second and higher sorption layers (loosely bound water). Finally, f measures the energy difference between water molecules absorbed in the second and higher sorption layers (loosely bound water) and pure liquid water.

The fitting parameters, which were extracted from the experimental data for the samples with different organic composition and the samples with different contents of silica, are presented in Table 1. The h_m values show a trend of decreasing with increasing EA content, invoking the decrease in the amount of the first layer sorption sites as mentioned before, while with the increase in silica content no significant changes are observed. The f values in all cases are below unity, implying that the loosely bound water is in more stable state than pure water. The third parameter (c) is accompanied with significant scattering and generally its physical meaning is less direct and usually more difficult to explain [36].

From the fitting parameter h_m it is possible to calculate the number of primary sorption sites in each polymer segment through the expression:

$$n_m = \frac{M_{HEA} h_m}{M_w w_{HEA}} \quad (4)$$

where M_{HEA} and M_w are the molecular weights of the repeating unit of the HEA monomer and of water, respectively. w_{HEA} is the weight fraction of HEA monomer units in the network, which is assumed to be equal to the initial weight ratio of monomers in the polymerization process. In Eq. (4), it is assumed that HEA moieties are the unique primary sorption sites without including the hydrophilic silica inorganic phase. Thereby, the evaluation of n_m was attempted only for 7030rs, and the value of 0.24 obtained is in agreement with previous results on similar IPNs [11]. For neat PHEA a value of 0.34 was reported recently [9,23]. In the case that every absorbed water molecule is associated with two

hydroxyl groups, an n_m value of 0.5 is expected [37,38]. In both cases, the $n_m < 0.5$ values mean that not all hydroxyl groups are available as primary sorption sites for water molecules. So the value $n_m = 0.34$ in PHEA system is explained by taking into account that a part of hydroxyl groups are self-associated via intermolecular or intramolecular hydrogen bonds. The even lower value for the copolymer 7030rs is plausibly explained bearing in mind the lower amount of hydroxyl groups per polymer unit volume because of the presence of hydrophobic moieties.

3.1.2. Immersion

In Fig. 2 the water content obtained in immersion experiment is plotted against HEA composition (a) and silica concentration (b) for all the samples. The water uptake from the water vapor phase at the highest water activity ($a_w = 0.98$) is also included for comparison. The swelling in the hybrid copolymers with variant composition of HEA and EA and silica content fixed at 20 wt.% is strongly dependent on the amount of HEA, presenting significant

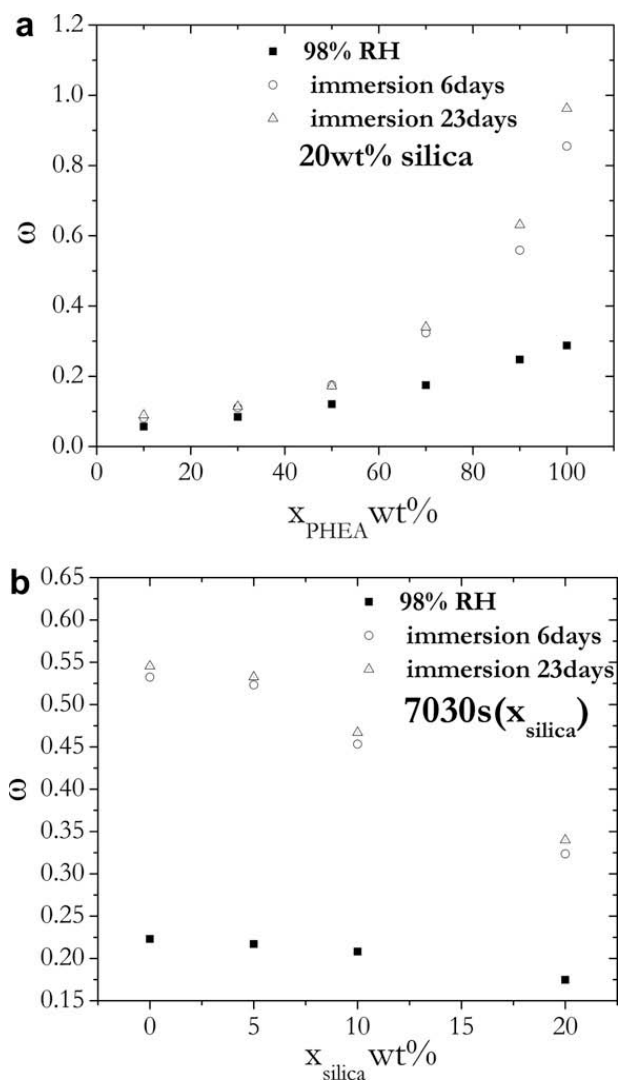


Fig. 2. Water uptake against (a) HEA content and (b) silica content by immersion in distilled water for 6 and 23 days. Experimental points of water uptake from the vapor phase at $a_w = 0.98$ water activity are also included for comparison.

water absorption with increasing HEA content (Fig. 2a). It is noteworthy that for the copolymers with HEA content $x_{\text{HEA}} \geq 0.7$ the hydration is significantly higher in immersion experiments than in sorption from the water vapor phase with water activity at $a_w = 0.98$. In addition, further water absorption beyond 6 days was observed for these samples implying long time exposure effects [9,38]. The long time exposure effects can be explained by taking into account the high hydrophilicity of HEA. The latter allows tremendous introduction of water molecules into the soaked hybrid that can gradually break down the possible hydrogen bonds between the hydroxyl groups of HEA. This process provides subsequently more available sites and space between the polymer chains facilitating the expansion of the water clusters, as a procedure which is not fulfilled in a short time. All this behavior seems to change for EA contents $x_{\text{EA}} > 50$ wt.%, where the hydration from immersion is relatively low and contiguous with the respective one from the exposure to water vapor (water activity at $a_w = 0.98$, Fig. 2a). Furthermore, the long time exposure effects are absent in these samples. The results provide evidence that the higher the hydrophobic phase the lower the compatibility between the polymer and water. On the other side, the higher the hydrophilic phase the higher the water uptake and the more intense the long time exposure effects.

Fig. 2b depicts the hydration against the silica content for the hybrids with variant concentrations of silica and specific organic composition HEA/EA at 70/30. It is evident that the hybrid 7030s20 shows a significant decrease in water uptake with respect to the hybrids 7030s5 and 7030s10, where this reduction is less remarkable. It is also noticeable that the water uptake is quite high compared to the water uptake by exposure to water vapor at $a_w = 0.98$ and that the long time exposure effects are imperceptible for all the hybrids and do not change with silica content (Fig. 2b). The results indicate that the presence of silica allows further water sorption, but finally it obstructs the expansion of the water clusters and this is pronounced in the hybrid 7030s20. These observations confirm the aforementioned results from the isotherm sorption curves (Section 3.1.1). Hence the percolation threshold, i.e. the critical content above which the silica phase forms its own network, is between 10 and 20 wt.%. These results compare well with the respective ones for PHEA/silica systems, as already mentioned [20,23]. Although the silica content was varied in relatively large steps and no composition between 10 and 20 wt.% was studied, the percolation threshold is anticipated to be around the silica content of 15 wt.% regardless of the organic phase composition. This could be rationalized by bearing in mind that the sol-gel process ensures a good dispersion of silica inside the acrylic polymer matrix for each possible organic composition. Thus, it is plausible that the percolation threshold is mainly determined by the relative distances between the silica particles inside the polymer matrix.

3.2. Thermally Stimulated Depolarization Currents (TSDC)

It is interesting to probe the dynamics of the hybrid hydrogel with respect to the xerogel [9,14], in particular

the evolution of the glass transition with hydration for each copolymer. To that aim, Thermally Stimulated Depolarization Current (TSDC) measurements were carried out for the two series of hybrids, at several levels of water activity. The global dielectric spectrum is typical for all the hybrids, where two dielectric relaxations are clearly discerned, accompanied by space charge peaks (ρ peak) and conductivity at higher temperatures (Fig. 3). A strong and very sensitive on water content secondary relaxation is present at low temperatures (-130 to -110 °C), denoted as β_{sw} process, which is attributed to the motion of the lateral groups formed by the association of one water molecule and two side chain hydroxyl groups [28]. At higher temperatures the α_{cop} relaxation process is apparent, closely connected with segmental copolymer motions and subsequently with the glass transition. Fig. 3 shows the characteristic spectra for the two hybrids 7030s20 (a) and 3070s20 (b), measured at several water activities. The current density J is divided by the applied electric field in order to normalize the experimental data, because the thickness (so the applied electric field) and the effective surface area were variant from sample to sample.

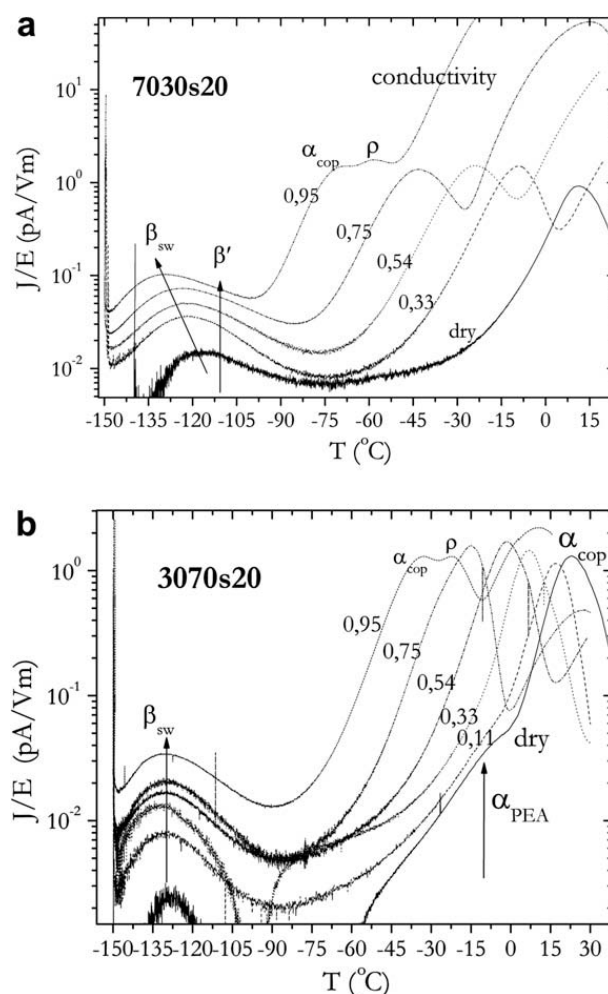


Fig. 3. Current density in TSDC thermograms divided by the applied electric field against temperature (a) for the hybrid 7030s20 and (b) for the hybrid 3070s20 and various water activities indicated on the plot.

3.2.1. Main relaxation processes

The main observation from the thermograms is the presence of a single main broad peak which corresponds to the α_{cop} process for the samples with high HEA content $x_{\text{HEA}} > 50$ wt.%. The α_{cop} process is plasticized towards lower temperatures by increasing the water content (Fig. 3). Its dielectric strength (magnitude of the peak) is quite large due to release of space charges simultaneously with the relaxation process, a phenomenon which is very common in TSDC thermograms of hydrophilic materials such as PHEA [22,32,33], and can be understood in terms of relatively high concentration of charge carriers. The presence of a single α_{cop} process manifests the high degree of structural homogeneity at nanoscale for the hybrids rich in HEA. On the other hand, for high EA content $x_{\text{EA}} \geq 50$ wt.%, the hybrids exhibit phase separation strongly pronounced in the dry state, where two peaks are observed close to each other: a strong main peak which is attributed to the copolymer's segmental motion (i.e. motion of regions rich in HEA and sparsely EA monomers) denoted as α_{cop} process at approximately 20 °C, and a second distribution which appears as a shoulder on the low temperature side of the α_{cop} relaxation process around -10 °C (Figs. 3b and 4). For higher content of EA the shoulder is well separated and in the same temperature region where the glass transition of neat PEA appears [11]. In addition, Fig. 3b shows that the water uptake plasticizes only the α_{cop} process while the α_{PEA} remains at the same position and is finally covered entirely by the α_{cop} process, in agreement with the EA component being hydrophobic. The presence of such a phase separation in polymer phase is rationalized bearing in mind the copolymerization theory. Once the free radical polymerization process is finished, the monomer molar fraction F_i in the copolymer in terms of the monomer molar fraction in the reaction mixture f_i and the reactivity ratios r_i turn out to be [39]:

$$\frac{F_1}{F_2} = \frac{f_1(f_1 r_1 + f_2)}{f_2(f_2 r_2 + f_1)} \quad (5)$$

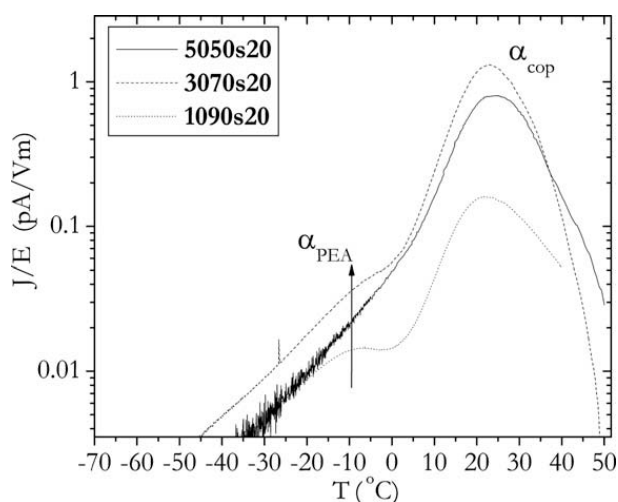


Fig. 4. Current density in TSDC thermograms divided by the applied electric field against temperature for the dry samples 5050s20, 3070s20 and 1090s20 in the temperature region of the segmental relaxations.

The reactivity ratios are 0.5 and 0.97 for EA and HEA, respectively [39]. The main consequence of this difference is that the HEA radicals have a higher tendency to react with HEA radicals, while the EA prefers HEA than itself. Once the HEA radicals are consumed during the radical polymerization, the residual EA monomers begin to react with each other leading to the formation of regions in which EA monomers dominate. The same phase separation is apparent also in P(HEMA-co-EA) systems [5], where the reactivity ratios between EA and HEMA are quite different, 0.189 and 11.2, respectively [39]. The inherent hydrophobic domains or domains rich in EA monomers contain no water molecules or less water molecules than the average [16]. As concerns the hydrophilic domains, the presence of the EA monomers is expected to reduce their sorption ability, by contrast with the HEA domains in the respective IPNs [13,14].

In Fig. 5 the temperature of the α_{cop} peak is presented as a function of the water content (h) divided by the fraction of HEA (x_{HEA}) in the hybrids. This specific normalization enhances the real effect of hydration to the hydrophilic organic regions. It is apparent that the hydrophilic domains of the copolymers are not equivalently plasticized, in agreement with results obtained with the respective copolymers P(HEA-co-MA) [13]. For the samples 100s20 and 9010s20, the α_{cop} process demonstrates contiguous plasticization, while for the 7030s20 the plasticization begins to be inhibited. For the hybrids 5050s20 and 3070s20 the plasticization is less remarkable. This behavior could be explained by taking into account the fact that when the composition of EA monomers increases, the hydrophilic regions contain a significant number of EA monomers. Their presence necessitates the reduction of hydroxyl groups per polymer unit volume, inhibiting the degree of hydrophilicity and subsequently the plasticization of the α_{cop} process with water uptake. This behavior is quite different in relevance to the respective microphase-separated IPNs, where a reduced single curve has been observed, directly indicating that the absorption ability of HEA is not affected by the presence of the hydro-

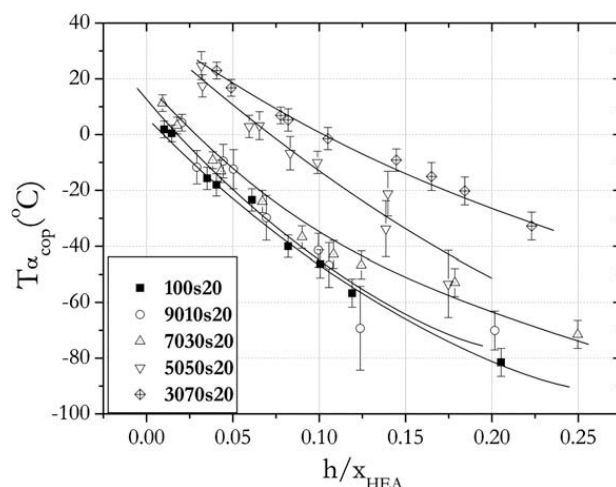


Fig. 5. Peak temperature of the α_{cop} process against water content divided by the content of HEA of the samples indicated on the plot. The silica content is fixed at 20 wt.%. The curves are guides for the eyes.

phobic component [13,14]. In the hybrid copolymers with EA content ($x_{EA} \geq 50$ wt.%), the hydrophilic regions begin to behave as isolated islands in the hydrophobic matrix, presenting lower sorption ability and slightly higher values for the glass transition in dry conditions due to restrictions by the hydrophobic phase [16]. Thus, the presence of a hydrophobic component yields the possibility to control the water uptake inside the hydrophilic regions, although in a rather complex manner. By taking into consideration the aforementioned results, it is noteworthy that the homogeneity or the phase separation in copolymers is mainly guided by the reactivity ratio of the components and the organic composition since similar effects has been observed in similar copolymers without silica content.

The next point to be examined is as to whether silica in the form of inorganic network or of not-assembled aggregates is able to affect the segmental polymer dynamics when the samples are soaked. To that aim, the hydrated hybrids with fixed composition HEA/EA at 70/30 and different amounts of silica were measured at different water activities and subsequently hydration levels.

Fig. 6 presents, as example, the global spectra for the samples 7030rs, s5, s10, s20 for two different water activities $a_w = 0.54$ (a) and 0.85 (b). The α_{cop} relaxation process peak temperature ($T_{\alpha_{cop}}$) was read from the respective thermograms at several water activities and was plotted against the hydration divided by the polymer fraction (Fig. 7), since we are interested in the evolution of glass transition with hydration for the whole polymer matrix. It is evident that α_{cop} process is plasticized towards lower temperatures with the same trend for the four samples regardless of the amount of silica. This behavior is consequence of the same amount of the water uptake in the hybrids at the first levels of hydration and is in consistency with water sorption results. The behavior of the α_{cop} relaxation is not clear at high water activities, where the formation of water clusters are restricted in size, especially when the silica content is 20 wt.%.

It is worthy mentioning that for the sample without silica content (7030rs) α_{cop} relaxation process is accompanied with a decrease in the absolute value of current density to the applied electric field and of its dielectric strength with respect to values at lower water activities and to values for the other hybrids at the same water activity ($a_w = 0.85$) (Fig. 6b). The reduction in the magnitude of α_{cop} is associated with the formation of water clusters for high water activities. Previous works on PHEA/hydrogels indicated that the magnitude of α relaxation process (segmental motions of hydrophilic portions) was enriched with space charge contributions during and after the glass transition [32]. The magnitude was enhanced with increasing water content. Furthermore, it was evident that this behavior was connected with the fact that the transport mechanism of the space charges is governed by the large-scale segmental polymer motions. However, for high hydrations, the water clusters induce restrictions to the polymer network large-scale motions due to high degree of swelling. In this case the transport mechanism of space charges is changed, controlled solely by the paths induced from the oversized water clusters [40]. The outcome is the decoupling between the α relaxation process and the

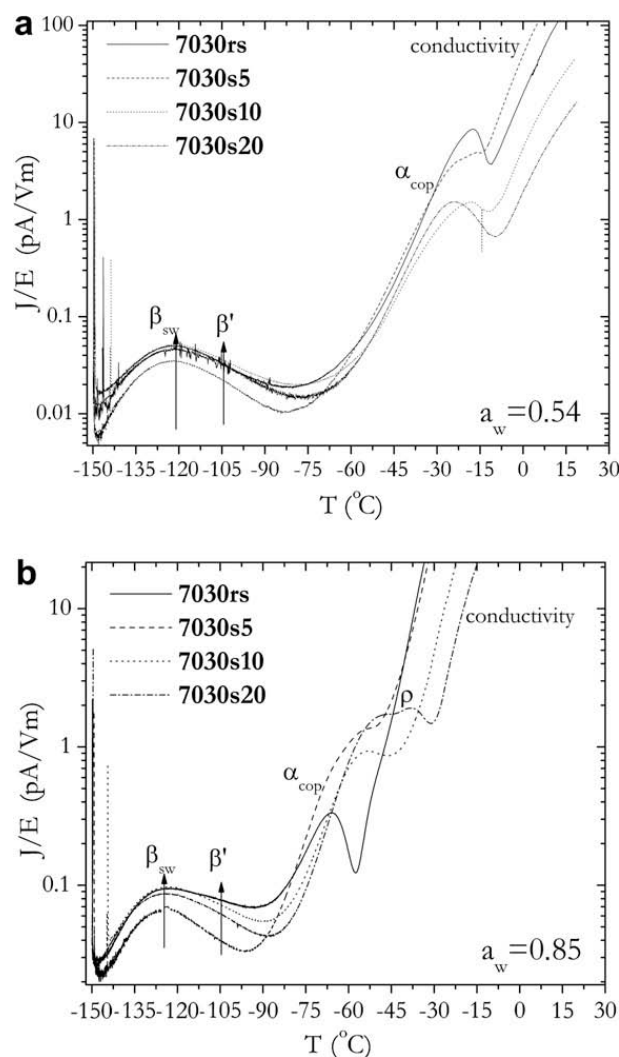


Fig. 6. Current density in TSDC thermograms divided by the applied electric field for the samples indicated on the plot at two water activities (a) $a_w = 0.54$ and (b) $a_w = 0.85$.

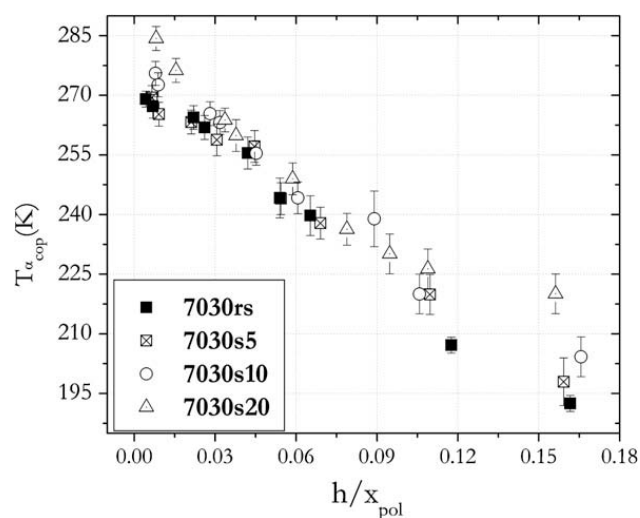


Fig. 7. Peak temperature of the α_{cop} process against hydration divided by the fraction of the organic phase for the samples indicated on the plot.

motion of the charge carriers, reducing with way the magnitude of α relaxation process, as in the sample 7030rs for high hydrations (Fig. 6b). This is not the case for the other hybrids, where silica imposes constraints to water clusters from becoming oversized, inducing complicate paths for the charge carriers to move. Thus, the decoupling between the α relaxation and space charge polarization does not occur in the hybrids with silica for high water activities (Fig. 6b).

3.2.2. Secondary relaxation processes

As mentioned earlier, the global thermograms (Figs. 3 and 6) reveal the existence of a strong secondary relaxation at low temperatures, denoted as β_{sw} . This relaxation process is strongly connected with the motion of two lateral hydroxyl groups and a water molecule which is attached to them [28]. Its dielectric strength depends on water content, showing significant increase even at low water contents, when the water molecules are mainly bound to primary sorption sites. Further water uptake swells the hydrogel and increases the distances between the chains. This is accompanied with a weakening of interactions between the lateral groups, leading to the systematic shift of the process towards lower temperatures for high water contents (Fig. 8) [13,26,32,40]. On the other hand, it was found that the presence of silica does not affect the position of the β_{sw} relaxation process, by contrast to the organic composition and the water content, since this relaxation process is local.

Fig. 8 depicts the evolution of the β_{sw} peak temperature with hydration divided by the fraction of HEA. The plasticization of the β_{sw} relaxation process for the sample 100s20 is contiguous to that for 9010s20. The total shift of the process towards low temperatures is around 20 K for these compositions. However, with increasing EA content ($x_{EA} \geq 30$ wt.%) the plasticization by water is reduced and gradually the peak temperature becomes practically independent from water content. This implies that the plasticization of the β_{sw} process does not only originate from the lodging of water molecules, but from the pres-

ence of EA as well. In any case, the β_{sw} relaxation process converges to a temperature around -130 °C. It is apparent that the β_{sw} relaxation process is facilitated with the same manner by both water and the EA radicals resulting in a common stable state. A possible explanation is that the EA monomers not only inhibit the water uptake in hydrophilic domains, but simultaneously diminish the hydrogen bonding interactions between the HEA lateral hydroxyl groups as well. This fact leads to the plasticization of the β_{sw} process even in the dry state, which is more significant with increasing fraction of EA radicals. For instance, the sample with 70 wt.% EA shows strong plasticization of the β_{sw} process in the dry state, and the peak position does not change at all with hydration. On the other side, the behavior is quite different for the respective IPNs, where the corresponding plasticization follows the same trend for all the samples independently of the content of the hydrophobic component [13,14]. The apparent consequence for the P(HEA-co-EA) copolymers under investigation is that the hydrophilic phase is strongly affected by the presence of the EA radical monomers, not only at the scale of the segmental motions, but also at a more local scale, as it was previously observed for P(HEA-co-MA) copolymer as well, though without silica content [14].

For the samples with high HEA content, $x_{HEA} > 50$ wt.%, and for high water activities, where the β_{sw} relaxation process undergoes significant plasticization, a second secondary relaxation process was detected around -105 °C, denoted as β' relaxation process (Fig. 6). Its position seems to be independent of water content, by contrast to the β_{sw} relaxation process. The origin of the β' relaxation process is not clear yet, but may be tentatively associated with the local crankshaft rotations on the crosslink-bridges between the polymer chains formed through the etherification or transesterification reactions between the HEA branches during radical polymerization. Further dielectric measurements are needed to characterize this relaxation and clarify its origin.

4. Conclusion

The poly(2-hydroxyethyl-co-ethyl acrylate)/silica hydrogels exhibit special properties regarding to the organic composition, silica and water content. Regardless of the amount of silica nanophase, the hybrids demonstrate a single main relaxation process, indicating a structural homogeneity in polymer phase for high HEA contents ($x_{HEA} > 50$ wt.%), while for EA weight fractions $x_{EA} \geq 50$ wt.% the hybrids were phase separated, with coexistence of exclusive EA hydrophobic domains and hydrophilic domains with significant amount of EA moieties. The specific amount of EA does not allow to the hydrophilic domains to behave like neat HEA, indicating a plasticization for the α_{cop} relaxation that does not follow the same trend for different EA contents. Similar changes were observed for the β_{sw} relaxation process. In any case, the water content affects mainly to the segmental dynamics of the hydrophilic domains. Measurements on the hybrids at various levels of hydration by broadband dielectric relaxation spectroscopy, similar to those

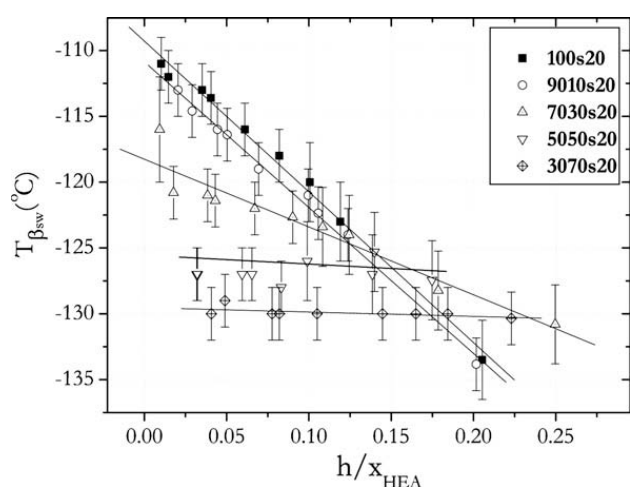


Fig. 8. Peak temperature of the β_{sw} relaxation against hydration divided by the fraction of HEA for the samples indicated on the plot. The lines are guides for the eyes.

performed in the present work by TSDC, are expected to provide additional significant information on molecular dynamics, in particular with respect to the effects of both hydration and temperature on the time scale and the strength of the segmental and the secondary relaxations. Experiments along these lines are now in progress.

As concerns the presence of the silica inorganic phase, the hybrids demonstrate special properties above a critical silica content, which was estimated between 10 and 20 wt.% according to isothermal sorption isotherms and immersion experiments, in agreement with results obtained with PHEA/silica systems. Above this critical content, the silica forms a spatial network, which restrains further volume expansion of the water clusters for high water activities, $a_w > 0.8$. On the other hand, the presence of hydrophilic silanols on the silica surface maintains the sorption ability of the hybrid, replacing by this way the missing organic hydrophilic groups. The effects of the inorganic phase on polymer molecular dynamics are not completely resolved. Thus, special techniques such Thermal Sampling are expected to provide information about the effects of silica inorganic phase to polymer molecular dynamics close to the glass transition.

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