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Porous poly(2-hydroxyethyl acrylate) hydrogels

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Abstract

Porous hydrogels were prepared by copolymerisation of 2-hydroxyethyl acrylate and ethyleneglycol dimethacrylate (as crosslinking agent) in solution using water or ethanol as solvents. Macroscopic pores are formed due to the segregation of the solvent from the polymer network during the polymerisation process. In the dry state the polymer network had nearly the same density as the poly(2-hydroxyethyl acrylate) polymerised in bulk thus showing that the pores collapse during the drying process. When the dry samples were swollen in water the pores opened and the volume fraction of pores could be determined by weighing. The pore morphology was observed by scanning electron microscopy. The dependence of the pore size on the solvent used and on the monomer/solvent ratio in the polymerisation process is shown. The elastic modulus and loss tangent were measured as a function of temperature in the region of the main (or α) dynamic-mechanical relaxation process. These spectra were correlated with the morphology of the samples.

Keywords: Porous hydrogels; Water sorption; Diffusion

1. Introduction

Synthetic polymer hydrogels have been proposed for many biomedical applications [1–5] because of their good biocompatibility and water permeation properties, and the possibility of synthesising materials with a broad spectrum of micromorphologies and specific properties.

When the hydrophilic polymer network is polymerised in bulk and then immersed in liquid water it can absorb an amount of water that can exceed the weight of polymer, depending on the crosslinking density, hydrophilicity, and elasticity of the polymer network [6]. Thus, poly(2-hydroxyethyl acrylate), PHEA, network polymerised in bulk with a 1% of ethyleneglycol dimethacrylate, EGDMA, as crosslinking agent absorbs water till a 200% of its weight measured on dry basis, as will be shown below. For small amounts of absorbed water, the hydrogel is a homogeneous material in which the water molecules are mixed with polymer segments. At least a part of the water molecules is linked to the hydrophilic groups or sorption sites of the polymer chains by hydrogen bonding. For this range of water contents of the sample, which in the case of the PHEA network mentioned above covers up to 30 wt.% measured on dry basis, there is no sign of the individual properties of polymer chains and water in the behaviour of the hydrogel at room temperature. In particular the material presents a glass transition at a temperature lower than that of dry PHEA and there is no indication of crystallisation and melting of water at a temperature close to that of pure water [7]. For higher water contents the swollen network is at room temperature a heterogeneous material, and part of the absorbed water is phase separated from the polymer in the form of bulk water domains that have the properties of pure water, in particular the bulk water domains crystallise and melt at the same temperatures as pure water does. The presence of a phase consisting in pure water plays an important role in the possibility of diffusion of low molecular weight substances across the hydrogel. The swollen material is porous but the size of the pores is small, of the order of magnitude of molecular dimensions.

A key factor which has considerably expanded the spectrum of possible applications of polymer hydrogels is the possibility of synthesising porous materials with controlled amount and morphology of pores. Small pores, with sizes below say 1 μm, what can be called micropores, are

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incapable of scattering light and thus microporous polymer hydrogels are transparent. The presence of micropores greatly increases the amount of water that the hydrogel is able to absorb, and the permeation of soluble substances is enhanced by the diffusion through the phase formed by the water filling the pores. Larger interconnected pores, macropores, could allow the cellular invasion of the material, the minimum size for that being around 10 μm [6,8]. Macroporous polymer hydrogels, also called hydrogel sponges, have been proposed to ensure a good adhesion between prosthetic implants and the biological tissue through the biocolonisation of the prosthesis [8].

One of the ways to prepare a porous hydrogel is the polymerisation in solution. Much work has been made in this area in the case of poly(2-hydroxyethyl methacrylate), PHEMA (see Refs. [9,10] and the references cited therein). Polymerisation is conducted starting from a mixture of monomers and solvent containing between 40 and 80 wt.% of solvent. Phase separation occurs as polymerisation progresses at some conversion degree which depends on the monomer/solvent ratio, the values of the solubility parameter of polymer network, solvent, and monomer/solvent mixtures, the amount of solvent, amount of crosslinking agent, of initiator, and other factors. If phase separation takes place at the initial stages of polymerisation, the resulting hydrogel consists in spherical particles loosely linked to each other, the solvent filling the spaces between polymer particles. On the contrary, when the phase separation occurs at high monomer–polymer conversions, a continuous polymer phase is formed with inclusions of the solvent, forming pores. By controlling the polymerisation conditions a broad spectrum of micromorphologies can be obtained.

In this work, a series of porous PHEA hydrogels has been obtained by solution polymerisation in water and ethanol with different monomer/solvent ratios ranging between 20 and 60 wt.% of solvent. The micromorphology and mechanical and water sorption properties are studied.

2. Experimental

2.1. Sample preparation

The PHEA networks were polymerised between glass plates to form sheets approximately 1 mm thick. The monomer (2-hydroxyethyl acrylate, HEA, from Aldrich, 96% pure) was used without further purification. Ethyleneglycol dimethacrylate, EGDMA, (Aldrich 98% pure) was used as crosslinking agent, and a 0.13 wt.% of benzoin (Scharlau 98% pure) was added as photoinitiator. Polymerisation took place at room temperature for 24 h under UV radiation. The low molecular weight substances remaining in the sample after polymerisation were extracted with boiling ethanol for 24 h and then the samples were dried at 80°C in vacuo to constant weight.

Porous samples were prepared starting from a blend of HEA/EGDMA/solvent in which the HEA/EGDMA weight ratio was 99/1 and the weight ratio monomers/solvent ranged between 80/20 and 40/60. Water or ethanol were used as solvents. Samples will be designed by the first letter of the solvent name and solvent content of the initial mixture; for instance, W40 will indicate the sample prepared with a monomer/water weight ratio 60/40 and a 99/1 weight ratio HEA/EGDMA. The sample prepared by polymerisation in bulk without solvent will be called simply B-PHEA.

2.2. Microscopy

All samples were examined in a scanning electron Jeol JSM-5410 microscope equipped with a cryounit Oxford CT 1500 using the low-temperature freeze drying technique (cryoSEM). Prior to examination the samples were swollen in liquid water for 24 h in order to open the pores of the sponges. The cryoSEM procedure is the following: the swollen sample is immersed in liquid nitrogen at low pressure (2×10^{-2} mbar) to freeze the open structure of the sponge. Afterwards it is placed in the cryostage at the same pressure and at a temperature of −150°C. At this temperature the sample is fractured and is then introduced in the sample stage at a higher vacuum (10^{-5} mbar). Under this pressure the temperature is raised and kept at −85°C over 30 min, which ensures the sublimation of water from the sample and prevents the porous structure to collapse. After the sublimation of water the temperature is lowered again until −150°C to avoid the sample structure to change and the sample is sputtered with a gold layer. The micrographs were taken at an accelerating voltage of 20 kV in order to ensure a suitable image resolution.

2.3. Water sorption and diffusion

Equilibrium water sorption isotherms were measured at 25 and 40°C. The samples were allowed to equilibrate to constant weight (weight change less than 10^{-4} g) in various desiccators where the relative humidity (rh) was maintained between 0.06 and 0.97 using different saturated salt solutions [11]. The water content h, defined as *g water/g dry sample*, was determined by weighing.

Dynamic water sorption was carried out by allowing the dry sample to equilibrate until ambient rh at 25°C on the pan of an A200 S analytic balance (Sartorius), while their weight was being recorded continuously. Dynamic desorption experiments were conducted in the same way with a sample previously equilibrated in ambients with rh = 1, 0.94 or 0.69 at room temperature. Other dynamic sorption experiments were conducted immersing the dry sample in water at 10, 25 and 55°C and measuring its weight, at selected immersion times, after superficially drying with filter paper.

Table 1
Characteristic parameters of the PHEA networks: specific volume of the dry samples v, water uptake $h_{rh0.94}$ and specific volume $v_{rh0.94}$ of a sample equilibrated in a vapour atmosphere with relative humidity 0.94, water uptake h_{lw} and volume fraction of pores $\phi_{swollen}$ in the sample after immersion in liquid water for 24 h

Sample	v ($cm^3\ g^{-1}$)	$h_{rh0.94}$	$v_{rh0.94}$ ($cm^3 g^{-1}$)	h_{lw}	ϕ_{pores}
B-PHEA	0.762	0.217	0.794	2.00	–
W20	0.764	0.214	0.794	2.34	0.11
W40	0.763	0.215	0.793	2.86	0.24
W60				3.34	0.33
E20	0.766	0.214	0.792	2.26	0.09
E40	0.765	0.211	0.791	3.30	0.32
E60				7.00	0.64

2.4. Dynamic-mechanical spectroscopy

Dynamic-mechanical spectroscopy was performed in a Seiko DMS 210 dynamic-mechanical analyser at a frequency of 1 Hz. The temperature dependence of storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) was measured from −140°C to 150°C with a heating rate of 2 K/min. Dynamic-mechanical experiments were conducted only on dry samples.

2.5. Specific volume

The specific volume of the dry networks was determined through the weight of a sample, around 0.1 g, in air and immersed in *n*-octane at 25 ± 0.5°C. A Mettler AE 240 balance with a sensitivity of 0.01 mg with a Mettler ME 33360 accessory was used in these measurements. The result obtained for a series of pieces of the same polymer sample was reproducible to within ±0.001 $cm^3\ g^{-1}$.

3. Results

3.1. Specific volume

The specific volume of the dry samples was measured in order to characterise their porosity. The results are shown in Table 1. It was found that the specific volume of the networks polymerised in presence of solvent are only slightly higher than in the bulk samples. The differences in specific volume among the different dry samples are significant but close to the experimental uncertainty, and, as we will discuss below, would yield values of the volume fraction of pores below 1%.

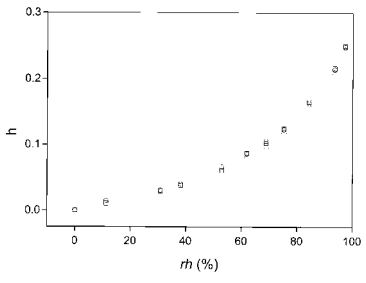

Fig. 1. Equilibrium sorption isotherms of samples: B-PHEA (○); E20 (□); and E40 (△) in terms of the water content of the sample against water activity.

3.2. Equilibrium sorption isotherms

Equilibrium sorption isotherms were determined at 25 and 45°C in samples W20, W40, E20 and E40. The influence of the presence of solvent during the polymerisation is not significant in the case of samples polymerised with water, but a decrease in the water uptake was found in the networks polymerised in ethanol. As an example, Fig. 1 shows the results obtained in samples B-PHEA, E20 and E40, and the water uptake corresponding to a water activity 0.94 is included in Table 1 for the five samples used in this study. The differences were quite small, but nevertheless this feature was confirmed by measuring the specific volume of the samples equilibrated in an ambient with rh = 0.94 (in equilibrium with a saturated solution of KNO_3 at 25°C). Assuming that the excess volume is small in the PHEA/water blend (as has been reported elsewhere [12]), the specific volume of the wet sample is directly proportional to the water content. As shown in Table 1, the differences in the specific volume among the different samples are parallel to those of the water content measured on dry basis.

3.3. Sorption kinetics from liquid water

The weight of samples immersed in liquid water at 25°C was measured as a function of the immersion time. As shown in Fig. 2, corresponding to the experiment performed at 25°C, the sorption process has a first step in which a plateau zone is attained in around 24 h. This plateau zone covers between one and two decades of time, depending on the sample, and after that the weight of the sample increases again. No equilibrium value was found in the time scale of the experiments (around 60 days). The water uptake in the plateau zone, which will be called h_{lw}, is shown in Table 1.

3.4. Water diffusion

Sorption and desorption experiments were conducted in samples B-PHEA, E20, E40, W20 and W40.

If the sorption and desorption process is assumed to obey Fick's law with a constant diffusion coefficient D, Eq. (1) holds for relatively small values of time t, corresponding to $(\Delta m)_t/(\Delta m)_\infty < 0.5$ [13]

$$\frac{\Delta m_t}{\Delta m_\infty} = \frac{4}{\sqrt{\pi}}\sqrt{\frac{tD}{l^2}} \tag{1}$$

where $(\Delta m)_t$ and $(\Delta m)_\infty$ are the weight gains (in the case of a sorption experiment) or loss (in desorption) of the sample at time t and at equilibrium, respectively, and l is the sample thickness.

Different values of D were found when Eq. (1) was used

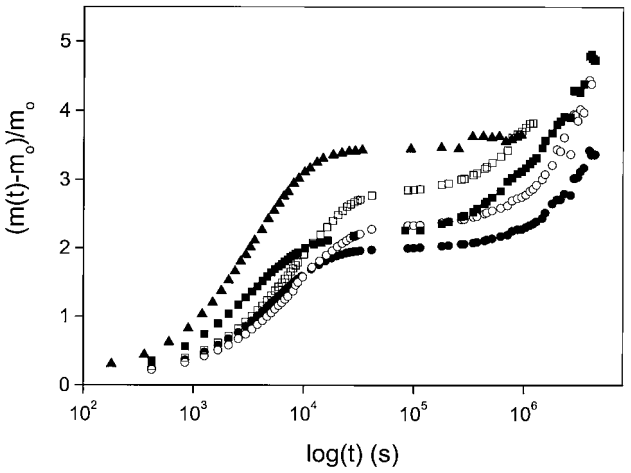

Fig. 2. Water uptake as function of time in samples: B-PHEA (●); E20 (■); E40 (▲); W20 (○); and W40 (□) immersed in liquid water at 25°C.

to analyse the results of desorption experiments, which started with the sample equilibrated in vapour atmospheres with different relative humidities, and thus, with different initial water contents. This dependence of the diffusion coefficient with the sample water contents implies that the diffusion process is not Fickian, but anyway the value of D obtained from Eq. (1) can be used as an apparent diffusion coefficient to compare the sorption and desorption kinetics of the different samples. The results are included in Table 2. Eq. (1) was also used to determine an apparent diffusion coefficient from immersion experiments in liquid water. In this case the water content after 24 h was used as $(\Delta m)_\infty$. The values found for D are also shown in Table 2.

3.5. Pore morphology

Direct observation of the pore morphology of samples immersed 24 h in liquid water can be achieved by cryoSEM. Fig. 3 shows the microphotograph obtained after sublimating water in the PHEA network polymerised in bulk. The surface of the sample shows some relief due to the sublimation of water, but no macroscopic pores. Fig. 4 shows the microstructure of the networks polymerised in water. No pores are revealed in sample W20 (Fig. 4a), although the pattern of the surface is different from that shown in Fig. 3. In samples W40 and W60 (Fig. 4b and c, respectively) a well-defined porous structure can be observed. The shape of the pores is irregular with sizes ranging between 0.1 and 0.25 μm. Clearly, the polymer phase is continuous and the pores might be interconnected only in the case of sample W60.

Ethanol is more effective in creating the porous structure in the hydrogel. Pores with sizes up to 0.2 μm can be observed in samples E20 and E40 (Fig. 5a and b, respectively). Their pattern is similar to that found in samples polymerised in water, but sample E60 shows a very special spongy structure with pores up to 5 μm (Fig. 5c). In this sample the polymer phase is still continuous, and pores are interconnected as shown in more detail in Fig. 5d.

Table 2
Apparent diffusion coefficient ($D \times 10^7$ cm^2 s^{-1}) determined in sorption experiments, and desorption experiments starting with the sample equilibrated in a vapour atmosphere with different relative humidity, and immersion experiments at three different temperatures

	B-PHEA	W20	W40	E20	E40
Sorption	0.22	0.17	0.24	0.14	0.11
Desorption rh = 0.69	0.34	0.45	0.31	0.34	0.29
Desorption rh = 0.94	1.4	1.3	1.5	1.1	0.9
Desorption rh = 1	1.6	1.4	1.6	1.1	1.1
Immersion 10°C	1.8	1.5	1.5	1.4	1.1
Immersion 25°C	2.9	2.3	2.0	2.0	1.65
Immersion 55°C	4.7	4.3	2.8	2.9	2.7

3.6. Dynamic-mechanical analysis

The dynamic-mechanical relaxation spectra of the dry B-PHEA and the networks polymerised in ethanol are shown in Fig. 6 (networks polymerised in water shows exactly the same features than those of the ones polymerised in ethanol).

At temperatures below the main relaxation, in the glassy state, a secondary relaxation, which is usually called γ in the literature (both in PHEA [7,14–16] and poly(2-hydroxyethyl methacrylate), PHEMA [17–19]), appears around −75°C. This relaxation process is associated to local motions within the side-chain group. The presence of very small amounts of water absorbed produces a new relaxation peak, β_{sw}, at temperatures higher than those of the γ relaxation, due to the link of two side-chain groups by a water molecule through hydrogen bonding producing a bulkier molecular group of reduced mobility, whose relaxation takes place at a higher temperature [17–19]. The elastic modulus in the glassy state is nearly independent of the

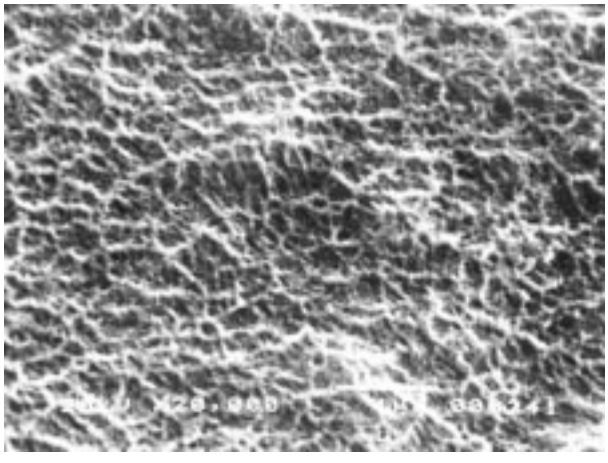

Fig. 3. SEM microphotograph obtained in a PHEA sample polymerised in bulk, immersed in liquid water for 24 h. The sample was cryogenically fractured and water was allowed to sublimate a −80°C at high vacuum for 30 min.

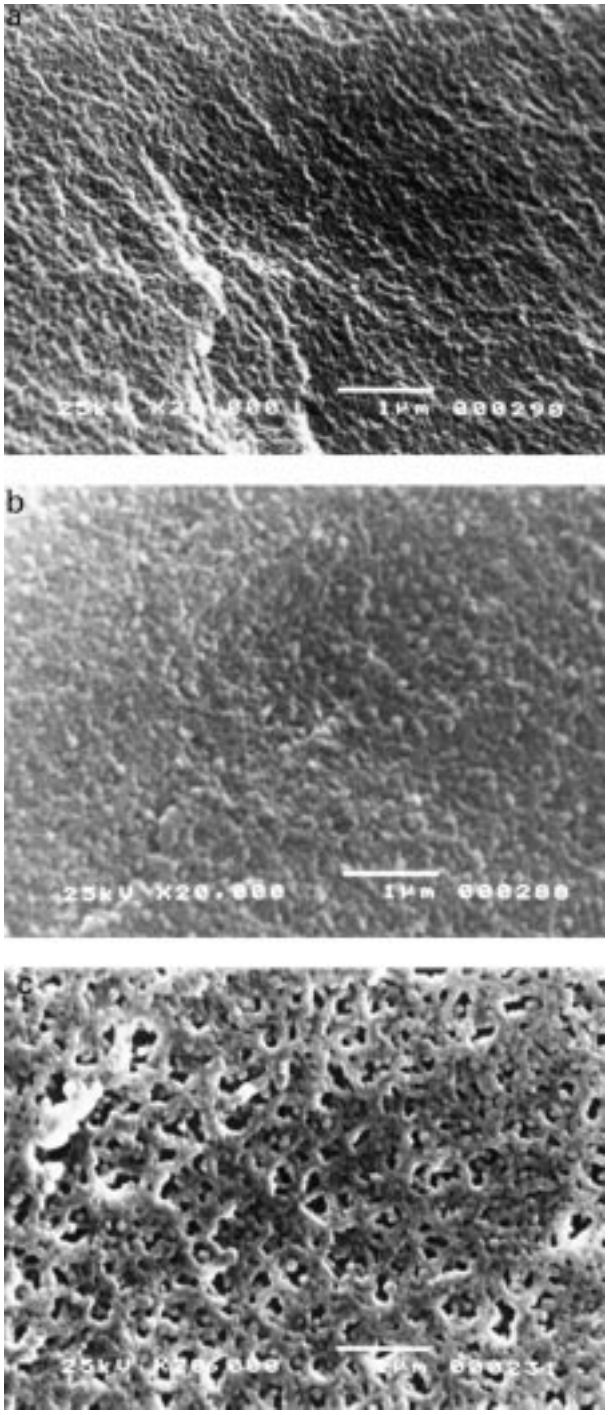

Fig. 4. SEM microphotographs, obtained as explained in the caption of Fig. 3, of PHEA networks polymerised in water: (a) sample W20; (b) sample W40; (c) sample W60.

amount of solvent used in the polymerisation, whereas the value of the elastic modulus in the rubber-like state decreases rapidly with it.

The position of the maximum of the loss tangent corresponding to the main relaxation process is independent of the amount of solvent and even the loss tangent curves measured for the three samples of the series perfectly superpose on the curve corresponding to sample B-1 in the temperature interval between 25 degrees below the maximum to 10 degrees above it. In the glassy state the shape of the spectra in the temperature interval between the γ and the α relaxation is not reproducible with accuracy, especially in the networks polymerised in water, even in samples prepared exactly with the same experimental procedure or in different pieces of the same polymer sheet. Since this is the zone in which the β_{sw} relaxation appears, this behaviour could be related to the difficulty of completely drying these samples.

4. Discussion

The porosity of the different networks can be analysed taking the bulk polymerised networks as a reference non-porous material. An increase in specific volume in the samples polymerised with water or ethanol would be attributed to the presence of pores. If one assumes that the porous sample consists of a polymer phase with the properties of the bulk polymerised sample, i.e. sample B-PHEA, and holes, then the volume fraction of pores ϕ can be determined by

$$\phi = 1 - \frac{v_B}{v} \tag{2}$$

were v_B is the specific volume of the sample polymerised in bulk and v is the specific volume of the porous sample. As shown in Table 1 the values of the specific volume of the samples polymerised with water and ethanol are very close to v_B, the differences are in the order of the uncertainty of the measurement and would yield values of ϕ always lower than 1%. This means that the pores formed during the polymerisation process, in the form of domains of segregated solvent, get closed during the drying process due to the network contraction. Thus, in the dry samples most of the volume of the sample is occupied by the polymer chains.

The water sorption process in this complex system is expected to be very different if the water comes from the vapour phase or if it comes from the liquid phase. In the former case, if the vapour phase consists of a mixture of air and water with a relative humidity lower than 100%, the thermodynamic equilibrium between the polymer–water blend and the vapour phases cannot allow the presence of liquid water condensed in the hydrogel pores, since this third phase would not be in equilibrium with the vapour phase if the air is not saturated. The amount of water absorbed in equilibrium by the polymer phase is controlled by the relationship

$$\hat{\mu}_w^{\text{hydrogel}} = \hat{\mu}_w^{v} \tag{3}$$

with $\hat{\mu}_w^{v}$ and $\hat{\mu}_w^{\text{hydrogel}}$ the chemical potential of water in the vapour phase and absorbed in the polymer network, respectively.

The absorption of water from a non-saturated vapour

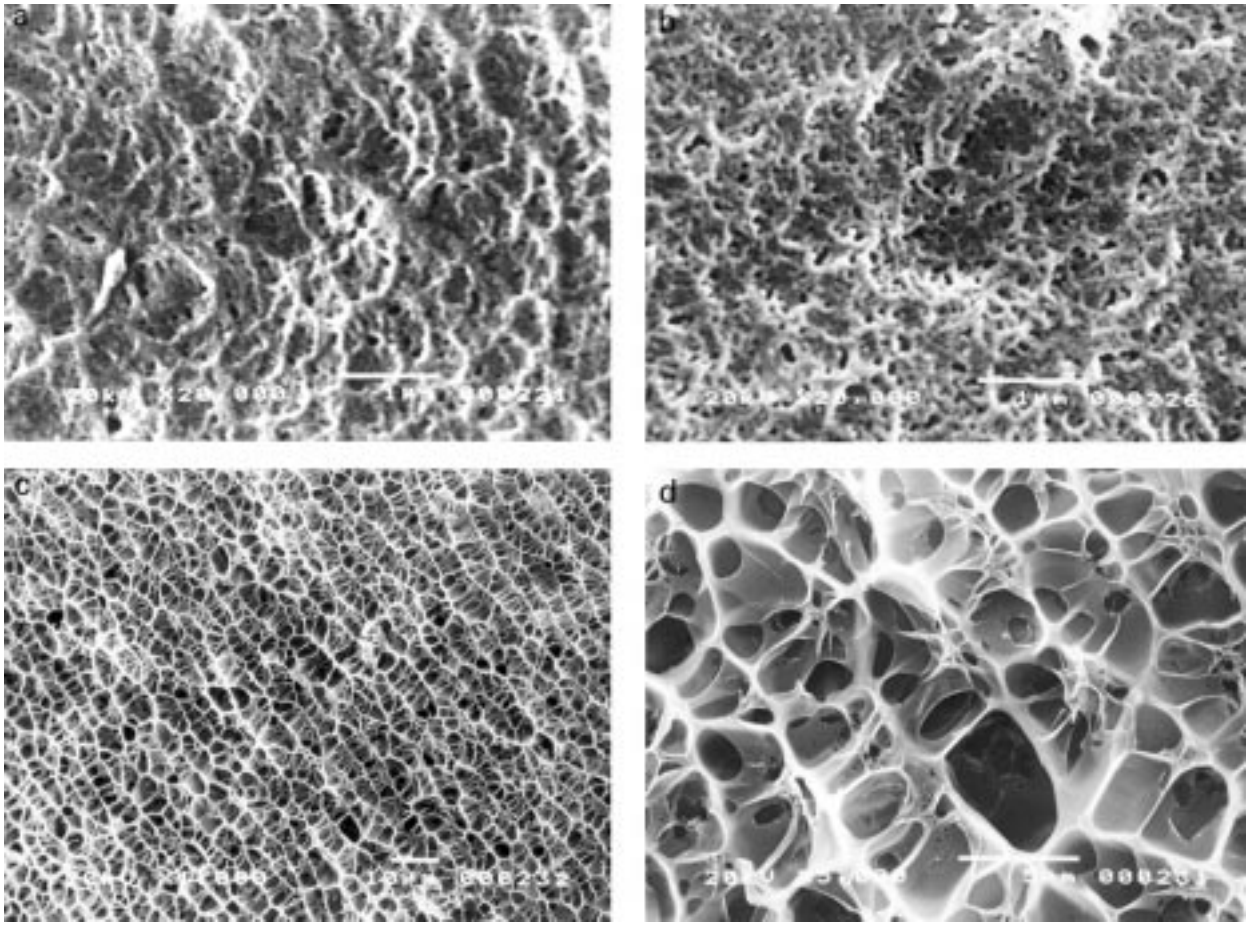

Fig. 5. SEM microphotographs, obtained as explained in the caption of Fig. 3, of PHEA networks polymerised in ethanol: (a) sample E20; (b) sample E40; (c) sample E60; (d) sample E60 at higher magnification.

phase produces a limited expansion of the polymer network, since the amount of water absorbed is not high if the relative humidity of the vapour phase (water activity) is less than one. Values of $h$below 0.30 were found in all the samples, in good agreement with previous results on PHEA networks. Contrary to what one would expect at a first sight from porous samples, the amount of water absorbed by the samples polymerised in ethanol is slightly lower than in sample B-PHEA, and the same occurs with the specific volume. Less pronounced, the same subtle difference is found for the samples polymerised in water. The kinetics of water sorption of the samples polymerised in water and in ethanol was also different as will be discussed below. These data confirm the suggestion that the water absorbed from environments with activities less than one is not able to expand the polymer network up to a point where the pores begin to open. This means, from a thermodynamical point of view, that water sorption at these values of the chemical potential of water is a process of an essentially entropic nature, i.e. a process of dissolution, or mixture, of polymer chains and water molecules, in which the elastical (energetic) contribution stemming from the network expansion is still negligible. When the hydrogel is immersed in liquid water, besides a fraction of water homogeneously mixed with the polymer chains, h_H, a fraction of water can be now present in the polymer phase in the form of water domains with properties characteristic of those of bulk

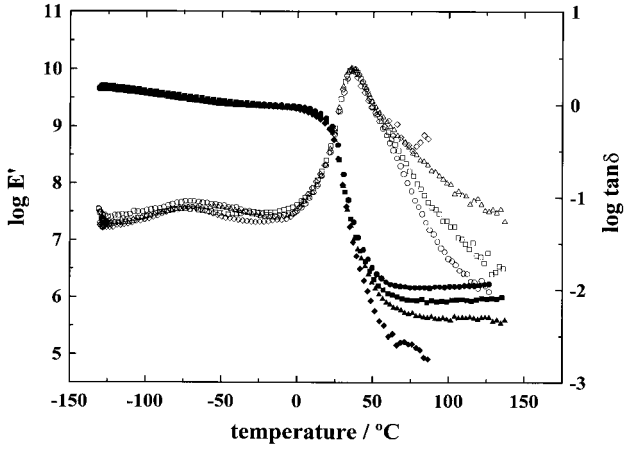

Fig. 6. Temperature dependence of the real part of the elastic modulus (full symbols) and the loss tangent (open symbols) of PHEA polymerised in bulk (●), and the series of samples polymerised in ethanol: E20 (■); E40 (▲); and E60 (◆).

water, for instance, the ability to crystallise and melt [7]. In the case of a bulk-polymerised ("non-porous") hydrogel this amount of water, h_B, would occupy the nanopores which can be formed by the expansion of the network; in the case of the porous samples, water can be absorbed additionally in the form of liquid filling the bigger, macroscopic pores, h_P. Since the water uptake of the hydrogel at water activities less than unity is small, the expansion of the network is negligible, and the thermodynamic condition for equilibrium which determines the value of h_H for each activity, Eq. (3), depends solely on the chemical nature of the interacting groups through the Flory–Huggins parameter [20]. On the contrary, the values of h_B and h_P depend additionally on the capability of the network to expand when swollen: the polymer network expands when immersed in liquid water, each chain tending to the dimension of the solved random coil, and the elastic contribution to the free energy of the network stops the expansion process at an equilibrium value which depends on the cross-link density and the topology of the network [20].

The amount of water absorbed in the first stage of the sorption process from liquid water, h_{lw}, is strongly dependent on the amount of solvent present during the polymerisation. Sample B-PHEA can absorb a weight of water which is twice the weight of dry polymer ($h = 2$). The comparison of this quantity with the maximum amount of water absorbed from unsaturated vapour phase shows that much of the water contained in the network in equilibrium with liquid water is in the form of bulk or free water; this is further verified by its ability to crystallise and melt at the temperatures of pure water [7]. The thermodynamic phase formed by the bulk water in this hydrogel should occupy nanopores formed by the expansion of the network during the sorption process.

In the case of a porous sample, in addition to the nanopores present in the bulk sample B-PHEA, the expansion of the network entails the increase in size of the bigger pores formed during polymerisation. An estimation can be given for the volume fraction of such pores filled with water in the swollen state. In this state the hydrogel consists of a phase formed by the polymer network which contains the water fractions h_H and h_B occupying a volume $V_{\text{swollen polymer}}$ (we can assume as a first approximation for this calculation that the sorption behaviour of this phase would be not very different from that of sample B-1), and a phase formed by pure liquid water occupying the volume of the pores V_{pores}. The volume fraction of pores in the swollen hydrogel is then

$$\phi_{\text{pores}} = \frac{V_{\text{pores}}}{V_{\text{swollen polymer}}} = \frac{v_{\text{water}}(h - h_B)}{v_{\text{swollenB}}(1 + h_B) + v_{\text{water}}(h - h_B)} \quad (4)$$

where v_{water} is the specific volume of pure water, and v_{swollenB} and h_B are the specific volume and the water uptake of the swollen sample B-PHEA. $v_{swollenB}$ was estimated, as a first approximation, assuming null excess volume in the PHEA/water blend

$$v_{\text{swollenB}} = v_{\text{water}}\omega_B + v_{\text{dryB}}(1 - \omega_B) = 0.918\ \text{cm}^3\ \text{g}^{-1} \quad (5)$$

with v_{dryB} the specific volume of the dry sample B-PHEA and ω_B the mass fraction of water in the swollen sample B-PHEA, $\omega_B = h_B(1 + h_B)$.

The volume fraction of pores in the swollen samples is included in Table 1. The expansion of the network opens the pores formed during polymerisation in presence of a solvent mixed with the monomers. The volume fraction of such pores is greater the greater the amount of solvent present in the polymerisation, reaching a 64% in sample E60.

These results agree with the observation based on microscopy described in the preceding section that ethanol is more effective in the formation of pores: these are bigger and their volume fraction is larger too than in samples polymerised in water as solvent.

As expected, the presence of solvent during the polymerisation has almost no influence on the sorption isotherm of the hydrogel. Table 1 shows nevertheless that there is a very small decrease of water uptake at $\text{rh} = 0.94$ of the porous samples with respect to bulk PHEA. This can be attributed to the fact that the samples with collapsed pores have a volume distribution of microsurfaces, the inner surfaces of the collapsed pores which self-adhere by hydrogen bonding and electrostatic interactions of the surface monomer units facing each other. As long as these collapsed pores remain as closed and folded blisters they represent discontinuity surfaces inside the volume of the sample along which the deformation tensor is zero, and thus act as constraints to the expansion of the network, constraints which do not exist in the bulk polymerised sample.

The apparent diffusion coefficients determined from sorption and desorption experiments in samples polymerised in water are very similar to those of PHEA polymerised in bulk. The values found for the networks polymerised in ethanol are slightly smaller. In any case, the value of D is lower in sorption experiments than in desorption ones, and in the latter it decreases as the initial water content does. This means that the diffusion of water molecules is hindered by the interaction with the hydrophilic groups of the polymer chains. As these sorption sites are occupied by water molecules diffusion becomes easier. In this kind of experiments the amount of water absorbed is small and, as a consequence, the pores should be nearly closed. Even in this situation, the formation of pores during polymerisation produces in the material internal surfaces of discontinuity corresponding to collapsed pores which interrupt and increase the winding of the trajectories of the diffusing water molecules through the network. This could explain the tendency of porous samples to have smaller values of D. In immersion experiments this tendency is more clear in all the samples studied and at any temperature, but now an additional effect to take into account is the great expansion of the network when it absorbs large amounts of

water, which can explain the slowing down of the diffusion process as the final amount of water absorbed increases.

The main feature found in dynamic-mechanical spectroscopy is the decrease of the elastic modulus in the rubber-like region as the porosity of the sample increases. Again, it is noteworthy that the experiments were conducted on dry samples, and thus the pores are expected to be closed. At least this is so at room temperature, as confirmed by density measurements. To confirm that this situation persists when temperature increases the expansion coefficients were measured both in the glassy and the rubber-like states, in the same temperature intervals as the dynamic-mechanical measurements. No significant differences were found between porous samples and bulk PHEA: the linear expansion coefficients in the glassy and rubbery states were, respectively, 0.8×10^{-4} and 2.04×10^{-4} in the case of B-PHEA, 0.80×10^{-4} and 2.34×10^{-4} in the case of the samples polymerised in water, and 1.16×10^{-4} and 2.06×10^{-4} in the case of the samples polymerised in ethanol. The decrease of the elastic modulus with sample porosity can be ascribed to the additional deformation mechanisms associated to motions (relative sliding, partial opening) of the defects represented by the internal surfaces of discontinuity mentioned above in the discussion of the sorption and desorption experiments, motions which can be excited by the forces of the dynamic-mechanical experiment.

5. Conclusions

Porous PHEA hydrogels can be prepared by polymerisation in solution with ethanol or water as solvents. After polymerisation, if the solvent is eliminated and the sample dried the pores collapse and the density of the sample is the same as that of the network polymerised in bulk. Nevertheless, the presence of discontinuity surfaces represented by the closed pores decreases the elastic modulus of the sample in the rubber-like state. Also, the amount of water absorbed by the porous samples from a vapour atmosphere is slightly smaller than that of the bulk network for the same reason. When the porous network is immersed in liquid water, the pores open and the amount of water absorbed can reach up to seven times the weight of the dry sample. The amount of water absorbed allows to determine the volume fraction of pores in the swollen sample.

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References

[1] Hoffman AS. Hydrogels — a broad class of biomaterials. In: Kronenthal, Oser, Martin, editors. Polymers in medicine and surgery. New York: Plenum Press, 1975. p. 33–43.
[2] Tanzawa H, Nagaoka S, Suzuki J, Kobayashi S, Masubuchi Y, Kikuchi T. Cell adhesion and growth on the surface of synthetic hydrogels. In: Goldberg E, Nakajima A, editors. Biomedical polymers. Academic Press, 1980. p. 189–211.
[3] Peppas NA, editor. Hydrogels in medicine and pharmacy, vol. 3. Boca Raton, FL: CRC Press, 1987.
[4] Peppas NA, Langer R. Science 1994;263:1715.
[5] Bell CL, Peppas NA. Adv Polym Sci 1995;122:125.
[6] Erman B, Mark JE. Structure and properties of rubberlike networks. New York: Oxford University Press, 1997.
[7] Kyritsis A, Pissis P, Gómez Ribelles JL, Monleón Pradas M. J Non-Cryst Solids 1994;172–174:1041.
[8] Chirila TV, Constable IJ, Crawford GJ, Vijayasekaran S, Thompson DE, Chen YC, Fletcher WA, Griffin BJ. Biomaterials 1993;14:26.
[9] Chirila TV, Chen YC, Griffin BJ, Constable IJ. Polym Int 1993;32:221.
[10] Okay O, Gürün C. J Appl Polym Sci 1992;46:401–10.
[11] Greenspan L. J Res Natl Bur Stand (US) 1977;81:89.
[12] Pissis P, Kyritsis A, MartÍnez Romero T, AzorÍn Tortosa S, Gallego Ferrer G, Monleón Pradas M, Gómez Ribelles JL. In: Konsta AA, Vassilikou-Dova A, Vartzeli-Nikaki K, editors. Proceedings of 10th International Symposium on Electrets. ISE10. IEEE Service Center, Piscataway, USA.
[13] Crank J, Park GS, editors. Diffusion in polymers. London: Academic Press, 1968.
[14] Gómez Ribelles JL, Meseguer Dueñas JM, Monleón Pradas M. Polymer 1988;29:1124.
[15] Kyritsis A, Pissis P, Gómez Ribelles JL, Monleón Pradas M. J Polym Sci, Polym Phys Ed 1994;32:1001.
[16] Kyritsis A, Pissis P, Gómez Ribelles JL, Monleón Pradas M. Polym Gels Networks 1995;3:445.
[17] Janáček J, Kolařik J. Collect Czech Chem Commun 1965;30:1597.
[18] Janáček J, Kolařik J. J Polym Sci (C) 1967;16:279.
[19] Ledničký F, Janáček J. J Macromol Sci (B) 1971;5:335.
[20] Monleón Pradas M, Gómez Ribelles JL, Serrano Aroca A, Gallego Ferrer G, Suay Antón JJ, Pissis P. Submitted for publication.