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Synthesis and properties of hydrogels from poly (vinyl alcohol) and ethylenediaminetetraacetic dianhydride

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Abstract

Crosslinked poly(vinyl alcohol) with different amounts of ethylenediaminetetraacetic dianhydride was synthesized and characterized by elemental analysis, ^{13}C-NMR and IR spectroscopy. The average molecular weight between crosslinks ($\bar{M}_c$), the mesh size (ξ) and the crosslinking density (ρ_x) were calculated from swelling studies and related to OH/anhydride ratios. The polymer-solvent interaction parameter (χ) was calculated by mechanical measurements. The swelling behaviour of hydrogels was studied as a function of the crosslinking degree. A kinetic study of the absorption determined the transport mechanism. The diffusion coefficient was calculated for the Fickian mechanism, and the swelling behaviours were analyzed in buffer solutions at various pH and temperature ranges. Swelling ratios were relatively high and sensitive to pH and ionic strength, but not to temperature. © 2001 Published by Elsevier Science Ltd.

Keywords: Hydrogels; Poly(vinyl alcohol); Ethylenediaminetetraacetic dianhydride

1. Introduction

Poly(vinyl alcohol) (PVA) hydrogels are widely used in cooling media, contact lenses and material for drug delivery systems [1]. The hydrophilicity of such hydrogels can be enhanced by incorporating ionizable functional groups such as the carboxylic groups. Polyelectrolytes are polymers that contain relatively ionizable groups at levels ranging from a few mol% to 100% of the repeating units.

Much attention has been directed in recent years to polyelectrolyte-type hydrogels that undergo controllable volume changes in response to small variations in solution conditions [2]. Temperature and pH are the normal solution variables in physiological, biological and chemical systems [1,3]. Temperature- and pH-sensitive gels have been suggested for a variety of novel applications, including controlled drug delivery [4,5].

In this study we prepared hydrogels of PVA crosslinked with ethylenediaminetetraacetic dianhydride (EDTAD) and as a result of crosslinking, ionizable carboxylic acid groups were introduced to the network. In a previous study we investigated the crosslinking of PVA with several carboxylic acid dianhydrides [6], a type of crosslinker that is not frequently used with PVA, to obtain tridimensional polymers. These polymers had a high degree of crosslinking and a moderate ability to absorb water [7]. In this study, we used small amounts of crosslinker to achieve low degrees of crosslinking and a high water uptake in order to obtain superabsorbent polymers whose swelling behaviour and mechanical properties were then studied. From the data obtained and by applying several equations, we were able to calculate various parameters of the crosslinked structure, including average molecular weight between crosslinks ($\bar{M}_c$), mesh size (ξ), crosslinking density (ρ_x), effective crosslinking degree (ν_e/V_0) and polymer–solvent interaction (χ). A more complete study of the swelling behaviour of these hydrogels as a function of the crosslinking degree, ionic strength, pH and temperature was also carried out. A kinetic study of the absorption determined the transport mechanism and the water diffusion coefficient was calculated for the Fickian mechanism.

2. Experimental part

2.1. Materials

PVA (Fluka) had a degree of hydrolysis of 86–89% and a degree of polymerization of 300. EDTAD (Aldrich) and dimethylsulphoxide (DMSO) (Panreac) were used as received.

Hydrochloric acid (Prolabo), potassium chloride (Probus), citric acid (Probus), sodium chloride (Panreac), sodium

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hydroxide (Prolabo), di-sodium hydrogen phosphate (Probus), potassium dihydrogen phosphate (Probus) and sodium tetraborate (Probus) were used to prepare buffer solutions (pH = 1,3,5,7 or 8).

2.1.1. Preparation of gel films. Crosslinking with EDTAD

PVA (18 mmol of OH group) was dissolved in 5 ml of DMSO at room temperature. The dianhydride compound was dissolved in 2 ml of DMSO at room temperature and added at a OH/anhydride group ratio of 1/0.250, 1/0.100, 1/0.050, 1/0.033 and 1/0.025. The reaction mixture was then stirred for 2 min and introduced between two 170 × 120 × 3 mm glasses separated by microscope slides to adjust the thickness (ca. 1 mm). Gels were obtained after a few minutes, but the reaction was considered complete after 24 h. To remove DMSO the gels were immersed in deionized water to equilibrium, and the water was changed 3 or 4 times.

2.1.2. Water absorption measurements

The dynamic absorption water measurements of the samples were determined by the gravimetric method. The samples were weighed at different times until the hydrated weight remained constant. Absorbency was calculated as the weight or volume swelling ratio (SR): weight or volume of swollen gel/weight or volume of dried polymer. An accurately weighed polymer sample was immersed in deionized water or buffer solution (pH = 1,3,5,7 or 8) at different temperatures ($T = 10,20,30$ or 40°C) and left until equilibrium was reached. When the polymer sample had stopped swelling, the surface was dried and weight gain measured. The equilibrium was reached after an immersion time of about 4–8 h.

To determine the equilibrium swelling ratio and calculate the polymer volume fractions in the relaxed and in the swollen state, five samples of each hydrogel were cut immediately after crosslinking. These samples were weighed in air and *n*-heptane and then placed in deionized water or buffer solution (pH = 1,3,5,7 or 8) at different temperatures ($T = 10,20,30$ or 40°C). Once they had swelled to equilibrium they were weighed in air and *n*-heptane. Finally, the samples were dried at room temperature and re-weighed in air and *n*-heptane. To calculate volumes of relaxed, swollen and dried polymers, we used $V_{\mathrm{pol}} = (W_{\mathrm{air}} - W_{n\text{-heptane}})/\rho_{n\text{-heptane}}$, where W_{air} is the weight of the corresponding polymer in air, $W_{n\text{-heptane}}$ is the weight of the corresponding polymer in *n*-heptane and $\rho_{n\text{-heptane}}$ is 0.684 g/ml.

2.2. Instrumentation

^{13}C-NMR spectra were obtained using a Gemini 300 spectrometer. Dried polymers were swollen using D_2O as solvent and acetonitrile (ACN) was added as internal standard. IR spectra were recorded on a MIDAC GRAMS/386 FTIR spectrometer. Elemental analyses were carried out using a Carlo Erba 1106 device. T_g data were evaluated on a Mettler DSC-30 thermal analyzer, using modified PVA samples of known weight (ca. 5 mg) in covered aluminium pans under nitrogen atmosphere at a heating rate of 20°C/min.

The equilibrium absorption of water was measured for all the samples using an electronic microbalance (Mettler AB204) and a Sartorius GMBH microbalance, both of which had an accuracy of $\pm 10^{-4}$ g. The reported equilibrium water uptakes are averaged over 9 measurements and, for each type of sample, water absorption was replicated three times.

Network mechanical properties were measured using a dynamic mechanical thermal analyzer (DMTA) (TA 2980) with a parallel plate accessory. Cylinder samples of the swollen networks, between 10 and 40 mm of diameter, were slightly compressed to assume small deformations (less of 5%) at 37°C.

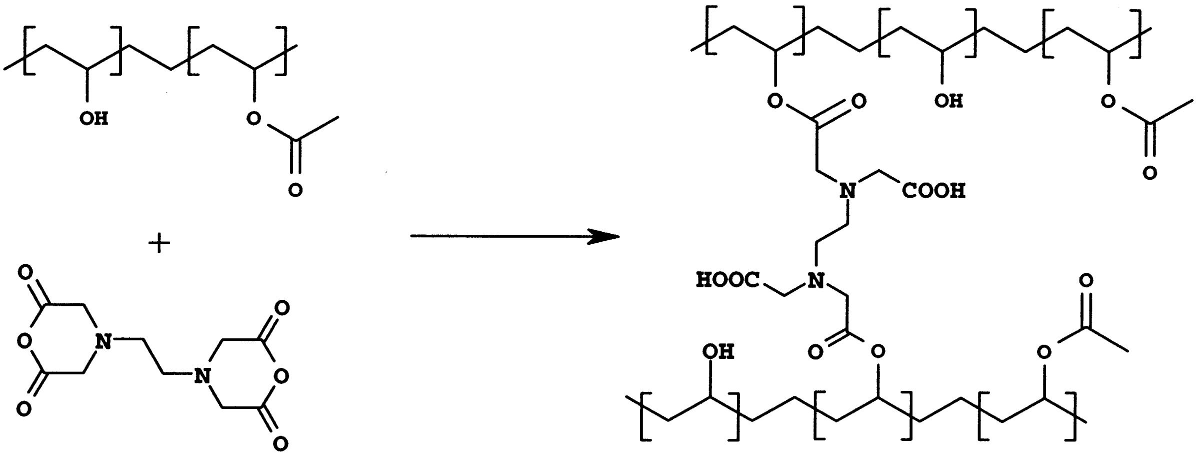
3. Results and discussion

PVA can be readily crosslinked to improve its water resistance and mechanical properties in hydrogel applications. All multifunctional compounds that react with the hydroxyl group can be used as crosslinking agents, but in this study we chose EDTAD because the dianhydride reacts readily with the hydroxyl group and the reaction gives a network with ionizable carboxylic acid. The crosslinking mechanism uses a nucleophilic agent without a catalyst to open the anhydride ring. Although reactions of alcohols with anhydrides usually require a catalyst (dimethylamine-pyridine or pyridine), in this case the catalyst had to be eliminated in order to prevent an instantaneous reaction that would not allow the gel to homogenize. The presence of an amine group in the crosslinker, which may have acted as a catalyst, may explain the fast crosslinking. The large number of hydroxylic groups in the PVA seem, in theory, to favour this reaction. When the hydroxylic group reacts with the anhydride, an ester forms and a free carboxyl acid is left in the network (Scheme 1).

3.1. Hydrogel characterization

PVA (86–89% hydrolyzed) was crosslinked at room temperature in a solution of DMSO using different ratios of dianhydrides (OH/anhydride group 1/0.250, 1/0.100, 1/0.050, 1/0.033 and 1/0.025) between two glasses separated by microscope slides to obtain gels in a few minutes. Table 1 shows the results of the elemental analyses of nitrogen. The modification is almost quantitative and the percentages of nitrogen coincide with the theoretical values calculated from the feed. It can be seen, that the T_g increase slightly as the amount of crosslinker increases, which is consistent with a higher degree of crosslinking.

The PVA modification can be seen in the ^{13}C-NMR spectra. Fig. 1 shows ^{13}C-NMR spectra of PVA (bottom)



Scheme 1.

and modified PVA (top). In both spectra, the methylene and methine carbons of the main chain are split. This is due to the esterified units, and while the former is shifted upfield, the latter goes downfield, which is the expected result of esterification. In the spectrum of PVA crosslinked with the anhydride, the intensity of these signals increases and new signals, corresponding to the methylene carbons of the crosslinker appear between 52 and 60 ppm. The lines at 172–174 ppm can be assigned to the carbonyl groups of the new ester linkage and the free carboxylic acid. The signal at around 176 ppm corresponds to the acetate carbonyl group.

The IR spectra of these compounds allowed us to confirm the introduced modification. OH stretching and a significant absorption due to the carboxylic acid at about 3500–2500 cm^{-1} are observed in all cases. The carbonyl region shows two absorptions due to ester and carboxylic acid groups. The former at 1720 cm^{-1}, higher than starting PVA (with only acetate group), and the latter at 1640 cm^{-1}, probably being due to the intramolecular hydrogen-bonded carboxylic groups. As an example, Fig. 2 shows the IR spectrum of PVA–EDTA 25.

3.2. Analysis of crosslinked structure

One of the basic parameters that describe the structure of an electrolyte and nonelectrolyte-type hydrogel is the molecular weight between crosslinks ($\bar{M}_\mathrm{c}$). This describes the average molecular weight of polymer chains between two consecutive junctions. These junctions may be chemical crosslinks, physical entanglements, crystalline regions, or even polymer complexes [8]. Several theories of calculating the molecular weight between crosslinks in polymer networks have been proposed.

Table 1
Characterization results: % N (elemental analysis) and glass transition temperature (differential scanning calorimetry)

Sample	OH/anhydride (molar ratio)	Theoretical (wt% N)	EA (wt% N)	DSC T_g (°C)
PVA–EDTA 25	1/0.250	4.0	3.5	53
PVA–EDTA 10	1/0.100	2.1	2.0	46
PVA–EDTA 5	1/0.050	1.1	1.1	43
PVA–EDTA 3.3	1/0.033	0.8	0.7	41
PVA–EDTA 2.5	1/0.025	0.6	0.6	40
PVA	–	–	–	41

The molecular weight between crosslinks, $\bar{M}_\mathrm{c}$, was calculated from the swelling data by Eq. (1), as suggested by Peppas and Merrill [9]. This equation can be applied to systems such as ours that have solvent present during the crosslinking process of the macromolecular chains. It also introduces an additional term to represent the polymer volume fraction in the relaxed state. This equation has also been used in PVA/poly(acrylic acid) interpenetrating networks [10], but modified swelling equations have been developed more recently by Brannon-Peppas and Peppas [11] in an attempt to predict the swelling behaviour of hydrogels with monoprotic acid moieties. A way of determinining $\bar{M}_\mathrm{c}$ from swelling behaviours of diprotic acid-containing hydrogels has just been developed by Sen et al. [12] and applied to copolymeric hydrogels that contain *N*-vinyl 2-pyrrolidone/itaconic acid and acrylamide/maleic acid [13]. However, these methods lead to contradictory results when applied to our hydrogels. This is because when each equation is used for the same polymer, $\bar{M}_\mathrm{c}$ values at different pH and ionic strength are very different. These equations therefore seem to be unsuitable and Peppas and Merrill's equation is sufficient for relating $\bar{M}_\mathrm{c}$ values to degrees of crosslinking

$$\frac{1}{\bar{M}_\mathrm{c}} = \frac{2}{\bar{M}_\mathrm{n}} - \frac{\dfrac{\bar{\nu}}{V_1}[\ln(1-\nu_{2m}) + \nu_{2m} + \chi\nu_{2m}^2]}{\nu_{2r}\left[\left(\dfrac{\nu_{2m}}{\nu_{2r}}\right)^{1/3} - \dfrac{2}{\phi}\left(\dfrac{\nu_{2m}}{\nu_{2r}}\right)\right]} \qquad (1)$$

Here, $\bar{M}_\mathrm{n}$ is the number-average molecular weight of the

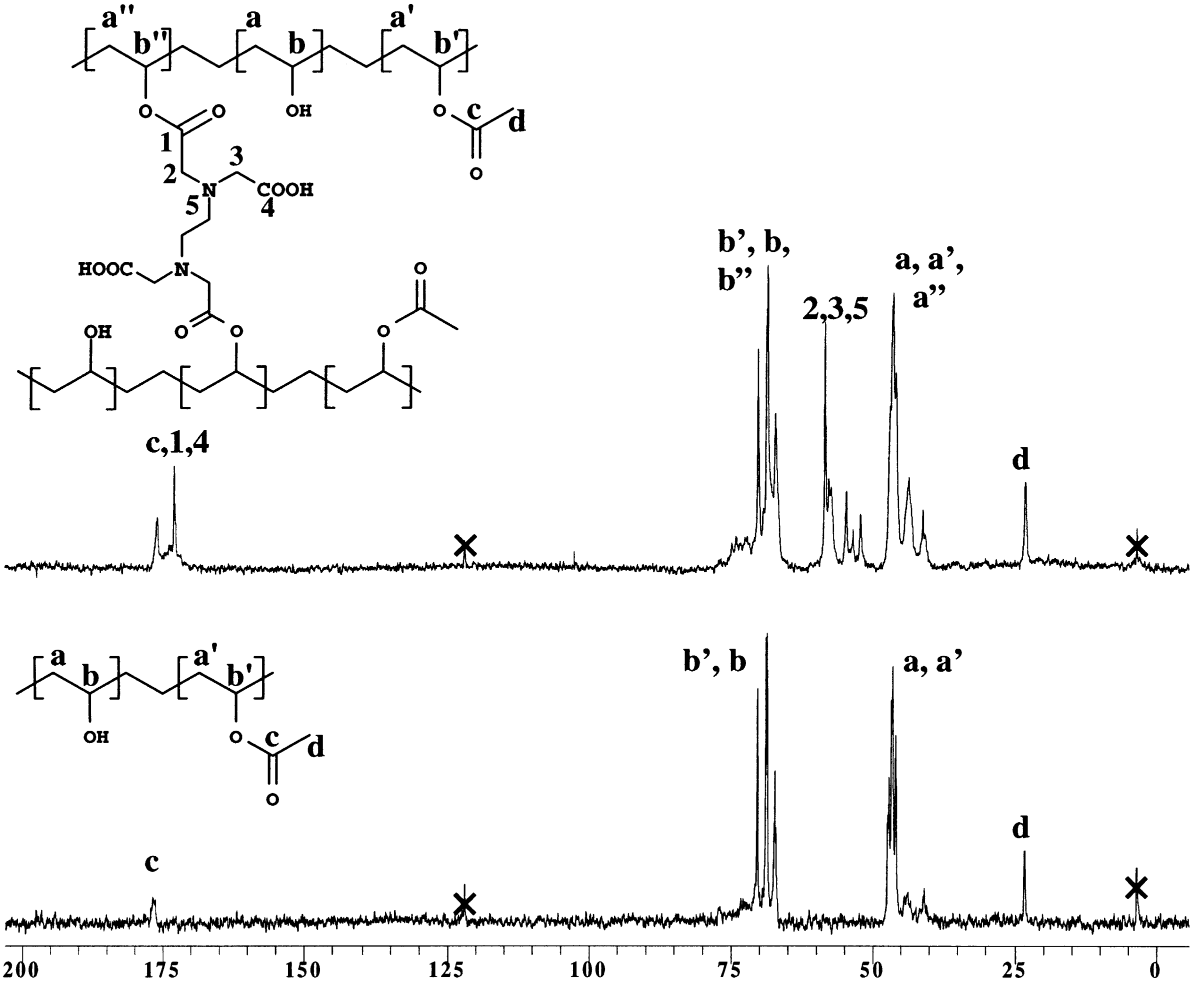


Fig. 1. ^{13}C-NMR spectra of PVA and hydrogel PVA–EDTA 25 (OH/anhydride 1/0.250) recorded in D_2O with ACN as reference.

polymer before crosslinking (ca. 15 000), $\bar{v}$ is the specific volume of PVA (0.788 cm^3/g) [14], V_1 is the molar volume water (18.1 cm^3/mol), ν_{2m} is the polymer volume fraction in the swollen state, χ is the interaction parameter of PVA–water ($=0.494$) [10], and ν_{2r} is the polymer volume fraction in the gel in the relaxed state. $\nu_{2m} = V_{\mathrm{pol}}(\mathrm{dried})/V_{\mathrm{pol}}(\mathrm{swollen})$, $\nu_{2r} = V_{\mathrm{pol}}(\mathrm{dried})/V_{\mathrm{pol}}(\mathrm{relaxed})$ and ϕ is the junction functionality $= 3$. From swelling data, specific volumes of PVA–EDTAs were similar to that of pure PVA (0.784–0.802 cm^3/g). Crosslinked PVA–water interaction parameters χ were calculated from mechanical measurement (0.504–0.527) and used instead of the PVA–water interaction parameter, which is normally used when only water absorption data are available. Because the mechanical properties of hydrogels with very low degrees of crosslinking (PVA–EDTA 2.5 and PVA–EDTA 3.3) are poor, we did not calculate their χ parameters. We used the PVA–water interaction parameter because we considered that the actual values could not be very different. Table 2 shows all of these values.

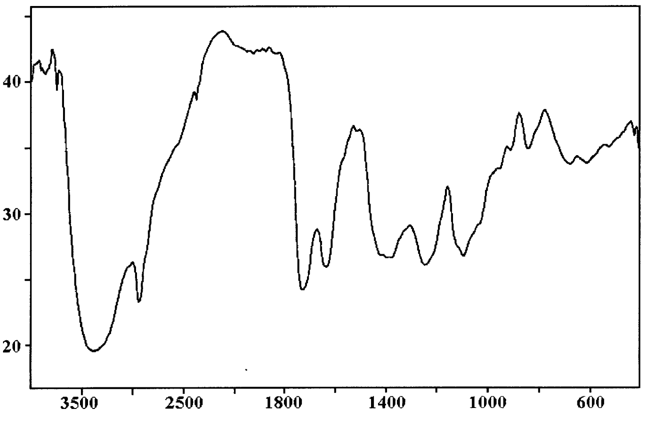


Fig. 2. FTIR spectrum of hydrogel PVA–EDTA 25 (OH/anhydride 1/0.250), recorded as a film.

The number-average molecular weight of a chain between crosslinks can also be calculated from mechanical measurements. From the various equations for calculating $\bar{M}_c$ we chose the following [15]. This is because like the Peppas and Merrill equation, it takes into account the $\bar{M}_n$, so

Table 2
Swelling and mechanical characterization results: PVA–EDTA–water interaction parameter (χ), average molecular weight between crosslinks ($\bar{M}_c$), effective crosslinking degree (ν_e/V_0) and Young modulus (E)

Sample	OH/anhydride (molar ratio)	χ	$\bar{M}_c$ (g/mol) (swelling eq.)	$\bar{M}_c$ (g/mol) (mechanical eq.)	$\nu_e/V_0 \times 10^3$ (mol/l)	E (KPa)
PVA–EDTA 25	1/0.250	0.527	2720[a]	3400	202	199
PVA–EDTA 10	1/0.100	0.519	5380[a]	5700	55	33
PVA–EDTA 5	1/0.050	0.504	7180[a]	7260	5.5	3
PVA–EDTA 3.3	1/0.033	–	7300[b]	–	–	–
PVA–EDTA 2.5	1/0.025	–	7490[b]	–	–	–

[a] $\bar{M}_c$ (Peppas–Merrill equation), χ from mechanical data.
[b] $\bar{M}_c$ (Peppas–Merrill equation), $\chi = 0.494$ pure PVA–water.

the comparison of the experimental values of $\bar{M}_c$ calculated from elastic modulus or swelling data is more accurate (Table 2).

$$\bar{M}_c = \frac{\rho_2}{\dfrac{\nu_e}{V_0} + \dfrac{2\rho_2}{\bar{M}_n}} \tag{2}$$

Here, ρ_2 is the density of dry hydrogel and (ν_e/V_0) is the effective crosslinking degree.

This effective network chain concentration (ν_e/V_0) can be calculated from the stress compression-strain modulus for small deformations using the following equation [16]:

$$\tau_s = \left(\frac{\nu_e}{V_0}\right) RT \nu_{2m}^{1/3} \nu_{2r}^{2/3} (\alpha - \alpha^{-2}) \tag{3}$$

Here, τ_s is the applied force per unit area of swollen hydrogel, R is the gas constant, T is absolute temperature, and α is the deformation ratio ($\alpha = L/L_0 \geq 0.95$). Fig. 3 shows the plot of the stress of the swollen hydrogel against the strain expressed as $(\alpha - 1)100$. From the slopes we can calculate elastic moduli (E) and from a plot of τ_s against $(\alpha - \alpha^{-2})$, which is linear at low deformations, we can also calculate (ν_e/V_0). All these values are given in Table 2, where, as expected, each series of the $\bar{M}_c$ values decreases when the crosslinking degree increase. For less crosslinked hydrogels very similar values of $\bar{M}_c$ are obtained from elastic moduli and swelling data. However, for more crosslinked hydrogels the $\bar{M}_c$ from compression tests are slightly higher than those from swelling studies. Here, the differences are not as significant as for tensile stress testing [17,18], probably because there is no disentanglement process. The other parameters (χ, ν_e/V_0 and E) increase when the degree of crosslinking increases. The uncertainty is similar in all cases because they include swelling (±5%) and mechanical (±10%) measurements.

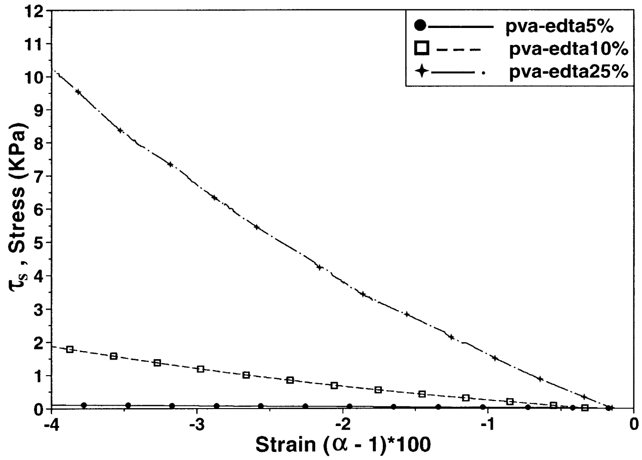


Fig. 3. Stress–strain plot, PVA–EDTA 25 (OH/anhydride 1/0.250), PVA–EDTA 10 (OH/anhydride 1/0.100) and PVA–EDTA 5 (OH/anhydride 1/0.050).

We can also calculate other parameters of the network, e.g. mesh size and crosslinking density. Both calculations require previous knowledge of $\bar{M}_c$. As $\bar{M}_c$ values from elastic moduli and swelling data are similar we used only the latter.

The mesh size, ξ, was calculated from Eq. (4) [19]

$$\xi = \nu_{2m}^{-1/3} \left[C_n \left(\frac{2\bar{M}_c}{M_r} \right) \right]^{1/2} l \tag{4}$$

Here, C_n is the Flory characteristic ratio (= 8.3) for PVA [20], M_r is the average of the molecular weights on the repeating units of VOH (= 44) and VAc (= 86), and l is the carbon–carbon bond length (= 1.54 Å).

The crosslinking density, ρ_x, was calculated from Eq. (5) [21].

$$\rho_x = \frac{1}{\bar{\nu}\bar{M}_c} \tag{5}$$

Table 3
Swelling characterization results: average molecular weight between crosslinks ($\bar{M}_c$), mesh size (ξ) and crosslinking density (ρ_x)

Sample	OH/anhydride (molar ratio)	$\bar{M}_c$ (g/mol)	Mesh size ξ (Å)	$\rho_x \times 10^4$ (mol/cm^3)
PVA–EDTA 25	1/0.250	2720	88	4.82
PVA–EDTA 10	1/0.100	5380	143	2.53
PVA–EDTA 5	1/0.050	7180	227	1.78
PVA–EDTA 3.3	1/0.033	7300	286	1.72
PVA–EDTA 2.5	1/0.025	7490	517	1.69

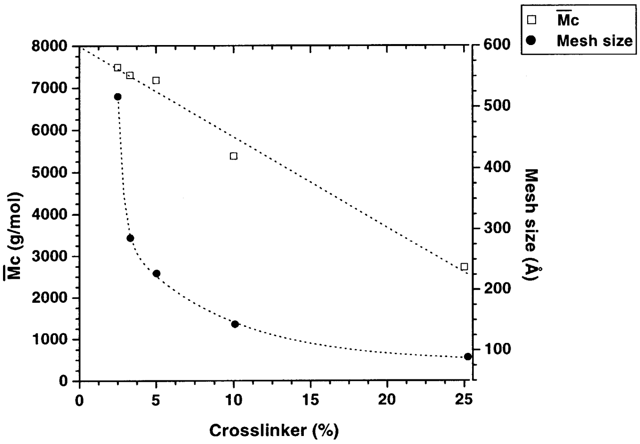


Fig. 4. Swelling characterization results: average molecular weight between crosslinks ($\bar{M}_c$) and mesh size (ξ) vs. crosslinker ratio (%).

Table 3 shows molecular weights between crosslinks (from swelling data), and the mesh size and crosslinking density for each hydrogel. As the amount of crosslinker decreases, the space between the crosslinks and the mesh size increases and the crosslinking density decreases. Fig. 4 shows the plot of $\bar{M}_c$ and ξ against OH/anhydride. As can be seen, the former shows an almost lineal dependence, while the latter shows an exponential decay fit similar to that of water absorption (Fig. 5).

3.3. Swelling behaviour

The hydrogel equilibrium swelling ratio is an important parameter that describes the amount of water within the hydrogel at equilibrium. It is a function of network structure, crosslinking ratio, hydrophilicity, and degree of ionization of the functional groups. Hydrogels may contain functional groups that interact with the external environment (temperature, ionic strength and pH of the swelling agent). Their response to environmental conditions may increase or decrease the mesh size of the hydrogel [6,22].

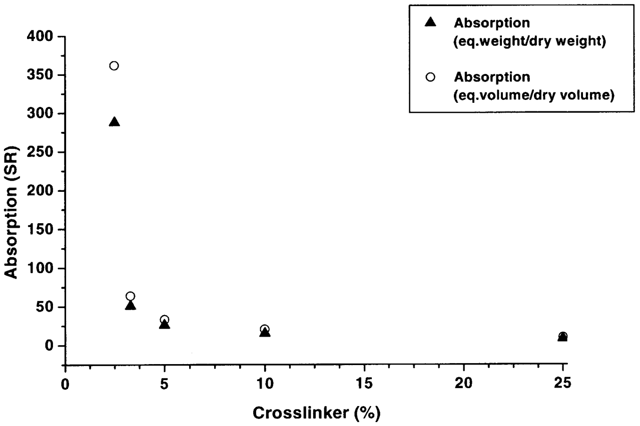


Fig. 5. Equilibrium swelling ratio (volume and weight ratio) of PVA–EDTA hydrogels as function of crosslinker ratio (OH/anhydride 1/0.025 to 1/0.250), deionized water, $T = 20°C$.

The water absorption of the hydrogel was determined gravimetrically as a function of time. When immersed in water, the films readily swelled up to a size that depended on the degree of crosslinking. Fig. 5 shows the equilibrium swelling ratios of hydrogels as a function of the amount of crosslinker. We can see that absorption significantly increases when there is less than 5% of crosslinker. When there is more, the swelling ratio slowly decreases for the degrees of crosslinking we studied. Clearly, the absorption of water depends noticeably on mesh size but polar groups (OH and COOH) must also contribute. However, it is difficult to calculate the relative influence of each group, since the more the OH groups there are, the fewer the COOH groups, and both of them can interact with water.

The solvent sorption rate indicates the solvent uptake per unit of time. It is directly related to the hydrogel's equilibrium degree of swelling. Fig. 6 shows sorption–time curves for the PVA–EDTA hydrogels obtained with 2.5, 10 and 25% of crosslinker. To find out the transport mechanism, the initial swelling data were fitted to the following exponential equation [23]:

$$\mathrm{Mt}/\mathrm{M}_\infty = \mathrm{kt}^\mathrm{n} \qquad (6)$$

where M_t is the mass of water absorbed at time t, M_∞ is the mass of water absorbed at equilibrium, k is a characteristic constant of the hydrogel, and n is a characteristic exponent of the mode of transport of the penetrant. The constants n and k were calculated from the slopes and intercepts of the graph of $\log(M_t/M_\infty)$ against $\log(t)$. For a film, a value of $n = 0.5$ indicates Fickian diffusion, a value $0.5 < n < 1$ indicates non-Fickian or anomalous transport and $n = 1$ implies case II (relaxation-controlled transport). For the Fickian mechanism the sorption curve as a function of the square root of time is linear in the initial stage, and above the linear portion the absorption curve is concave to the abscissa [24]. From data shown in Fig. 6 values of n were 0.50, 0.54 and 0.74 for the PVA–EDTA hydrogels with 2.5,

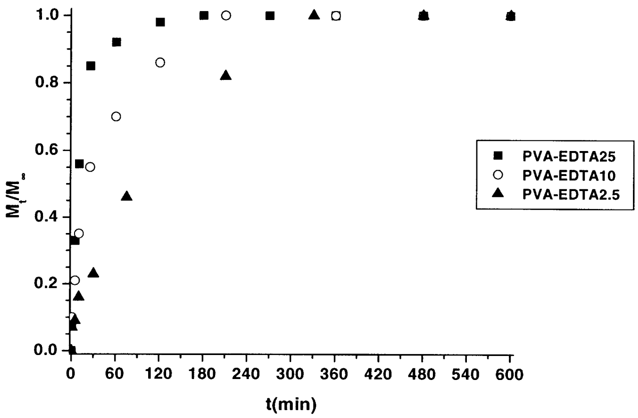


Fig. 6. Sorption–time curves for PVA–EDTA 25 (OH/anhydride 1/0.250), PVA–EDTA 10 (OH/anhydride 1/0.100) and EDTA 2.5 (OH/anhydride 1/0.025).

10 and 25% of crosslinker, respectively. These results indicate that the swelling transport mechanism will change from Fickian to non-Fickian as the degree of crosslinking increases.

For the Fickian transport mechanism, the rate of approach to equilibrium can be characterized by a diffusion coefficient. In this case, $k = 4D^{1/2}/\pi^{1/2}L$, (k in Eq. (6)), where D is the diffusion coefficient and L is the initial thickness of the dry sample. It must be pointed out that D can vary in the same sense as the swelling ratio with variables such as temperature, pH, crosslinking ratio or content of ionizable groups. Thus, a decrease in D together with an increase in crosslinking degree [25] or a decrease in the content of ionizable groups [26] have been reported for polymers with a low content of ionizable groups.

PVA–EDTA hydrogel with 2.5% of crosslinker in which $n = 0.50$ shows a Fickian mechanism ($D = 1.05 \times 10^{-7}$ cm^2/s). This value is within the range of the results mentioned above. D is not calculated for the highly crosslinked polymer because it has a non-Fickian behaviour ($n = 0.74$), but as Fig. 6 shows, it reaches equilibrium faster probably due to a higher content of carboxylic acid groups. One possible explanation for this behaviour is that the crosslinker contains the ionizable group and both variables increase together. Therefore, although an increase in the crosslinking ratio should imply a decrease in D, the opposite is observed because the ionizable groups affect the value of D more significantly.

The fact that hydrogels are extensively used in the biomedical field where the swelling does not take place in deionized water but in a saline aqueous medium makes knowledge of swelling behaviour as a function of ionic strength very important. Fig. 7 shows this equilibrium swelling ratio. As can be seen, a higher concentration of ions (ionic strength) in the swelling medium leads to a decrease in the equilibrium swelling ratio. This is a general trend in ionizable hydrogels. A greater ionic strength decreases the swelling because the ions in the solution surrounding the network counteract the mutual repulsion of the fixed ions on the network itself.

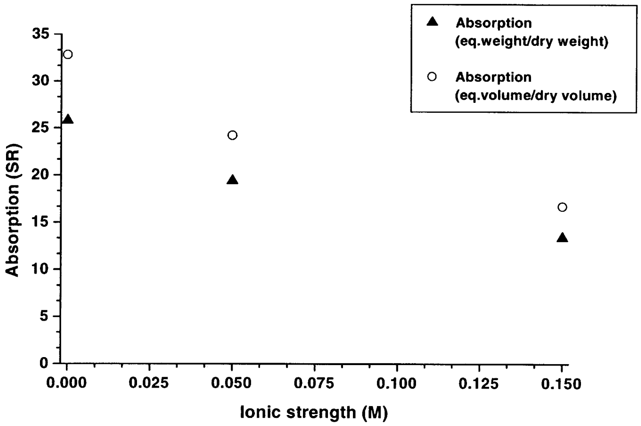


Fig. 7. Equilibrium swelling ratio (volume and weight ratio) of PVA–EDTA 5 hydrogel (OH/anhydride 1/0.050) as function of ionic strength, $T = 20°C$, pH = 7.

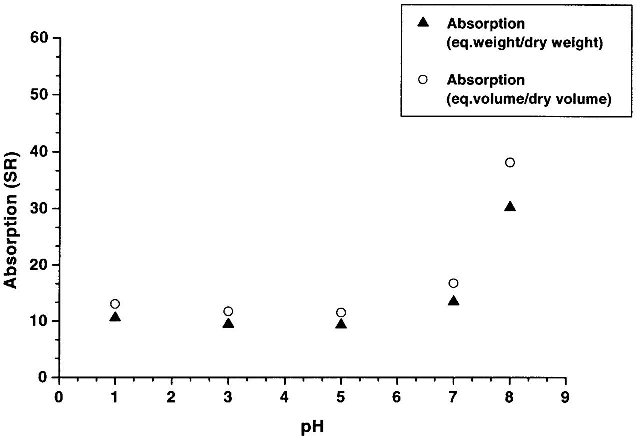


Fig. 8. Equilibrium swelling ratio (volume and weight ratio) of PVA–EDTA 5 hydrogel (OH/anhydride 1/0.050) as function of pH, $T = 20°C$.

Fig. 8 shows the equilibrium swelling ratio as a function of the pH. As we can see, swelling increases as the pH increases which is consistent with the presence of negatively charged groups. It must be noted that because buffers are used to obtain the different pHs, the ionic strength of the medium is greater than that of deionized water, and absorption at pH = 7 is therefore slightly lower than in a deionized water medium.

Another variable that can influence swelling is temperature. In an aqueous system, the temperature dependence of the swelling of a polymeric gel is closely related to the temperature dependence of polymer–water and polymer–polymer interaction. When the gel is cold, the swollen state is thermodynamically stable, but as the gel warms, interaction of the molecular chains stabilizes the shrunken state instead. Much of the fundamental swelling behaviour of hydrogels has been investigated by Tanaka [27] for poly(isopropylacrylamide) derivatives.

Some studies have shown that the degree of swelling of PVA hydrogels decreases slightly as the temperature decreases. This is because there is more interaction between

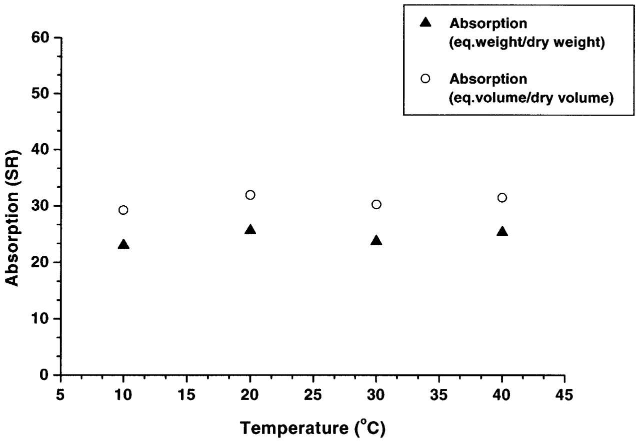


Fig. 9. Equilibrium swelling ratio (volume and weight ratio) of PVA–EDTA 5 hydrogel (OH/anhydride 1/0.050) as function of temperature, deionized water.

polymeric chains and because the chemical affinity with water weakens as temperature increases [28,29]. However, when we studied how temperature affects swelling behaviour in PVA–EDTA hydrogels we found no significant effect on water absorption (see Fig. 9). Therefore, these hydrogels do not seem to be thermosensitive polymers.

Acknowledgements

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