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Water sorption in cross-linked poly(vinyl alcohol) networks

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Abstract

Poly(vinyl alcohol) (PVA) networks of different cross-linking densities were prepared by reaction with hexamethylene diisocyanate in solution and casting. The dynamic-mechanical properties of PVA films have been investigated in the temperature range of − 150 to + 150 °C. Two relaxations processes labeled α and β in order of decreasing temperature were observed. The α-relaxation shifts to lower temperature and the average molecular weight between cross-links decreases with increasing cross-linking density. Isothermal sorption from vapor and liquid water allowed determination of the Flory–Huggins interaction parameter between water and the polymer chain segments, which decreased with the water activity in the hydrogel and increased with the cross-linking density as a consequence of the hydrophobic character of the cross-linking agent. The water diffusion coefficients, *D*, in the networks obtained by means of dynamic sorption experiments increased with increasing water activity. This behavior is interpreted in terms of plasticization of the polymer by water molecules.

Keywords: Poly(vinyl alcohol); Hydrogel; Dynamic-mechanical properties

1. Introduction

Polymer hydrogels find many applications in medicine, pharmacy [1], agriculture, and other fields. Their good biocompatibility and water permeation properties are the basis of these applications.

Poly(vinyl alcohol) (PVA) is water-soluble polymer that readily reacts with different cross-linking agents to form gel [2]. PVA is also biocompatible and biodegradable and is widely used in medical, cosmetic, and packaging materials [2–4]. For PVA, several cross-linking methods have been published for different uses. For example, chemically cross-linked PVA are prepared by glutaraldehyde [5], whereas physically cross-linked PVA are obtained by repeated freezing–thawing process [6–8]. Since as a rule, all multi-functional compounds are capable of reacting with the hydroxyl groups of PVA, these compounds can be used to obtain three-dimensional PVA networks [9–11]. The reaction of alcohols with isocyanates to form carbamates is well known and analogous reactions with PVA could be realized. Thus, cross-linking of the PVA may be achieved by reacting the hydroxyl groups along the polymer chain with diisocyanates to give urethane cross-linker. The cross-linking reaction of PVA with hexamethylene diisocyanate has been investigated recently [12]. The presence of urethane cross-links in the polymer has been proven by IR measurements [13].

In this work, the interaction of water molecules and a hydrophilic urethane cross-linked PVA network is investigated as a function of the cross-linking density of the network and as a function of the water content in the hydrogel. Dynamic-mechanical thermal analysis was also used to characterize the polymer chain mobility and the average molecular weight between cross-links.

2. Experimental

2.1. Materials

Atactic PVA with a weight-average molecular weight of 160,000 and a degree of hydrolysis greater than 99.3% was purchased from Air Product and Chemicals, Inc. The polymer was kept in a dry environment to prevent moisture absorption prior to use. All other chemicals: hexamethylene diisocyanate, dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), and tetrahydrofuran (THF) were obtained from Aldrich and were used as received.

2.2. Cross-linking reactions

PVA was first dissolved in DMSO/DMF (1:1, by volume) mixture by heating 8 wt% PVA solution at 80 °C.

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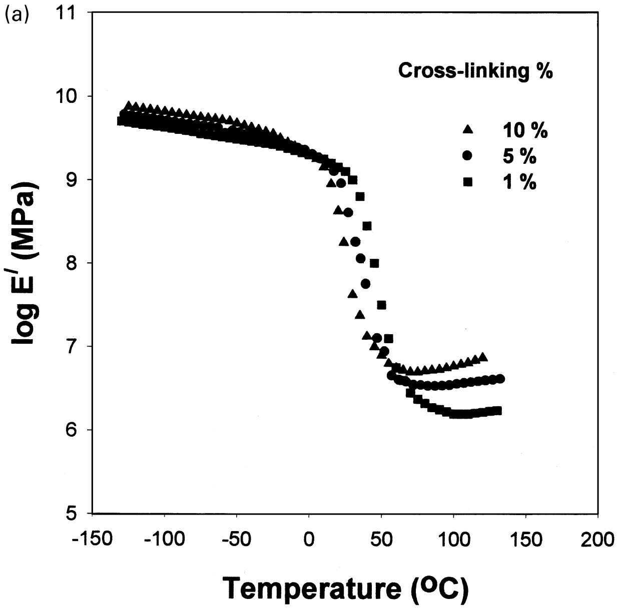
When the polymer was completely dissolved, the solution cooled down to 0 °C. A solution of hexamethylene diisocyanate of appropriate concentration was prepared at 0 °C using the same mixture of solvents. The cross-linker solution was then added to the PVA solution under vigorous stirring according to the desired cross-linking ratio (1, 5, and 10 mol% of diisocyanate per vinyl alcohol repeating unit). The homogeneous reaction mixtures were then cast into glass Petri dishes and the reaction was carried out at room temperature for 24 h. The films of cross-linked PVA were purified by extraction with THF in a Sohxlet apparatus for 12 h and then dried at 40 °C under vacuum for 24 h.

2.3. Measurements

Dynamic-mechanical spectroscopy of the cross-linked polymers was performed using a Seiko DMS 210 apparatus working in tensile mode at a constant stress. The complex modulus, $E^* = E' + iE''$, of each sample was determined at 1 Hz over a temperature range from − 150 to + 150 °C at a heating rate of 2 °C/min. The dimension of the specimen was around 200–300 μm, 2 mm in width, and 1–2 cm in length. The densities of the three networks were determined through the weight of a sample, around 0.1 g, in air and immersed in *n*-octane.

Equilibrium water sorption isotherms were measured at 25 °C by allowing the samples to equilibrate to constant weight (until the sample weight change was less than 10^{-4} g) in various desiccators where the relative humidity (RH) was kept constant between 0.06 and 0.97 using different saturated salt solutions [14]. The water contents, *h*, defined as the ratio of the weight of water to the weight of the dry sample was determined by weighing. Dynamic water sorption experiments were carried out by allowing the dry sample to equilibrate at different water activity (identical with RH) at 25 °C on the pan of an analytical balance while its weight was being recorded continuously. Other dynamic sorption experiments were conducted by immersing the dry sample in distilled water at 25 °C and measuring its weight, at selected immersion times, after gently drying the surface of the sample with filter paper.



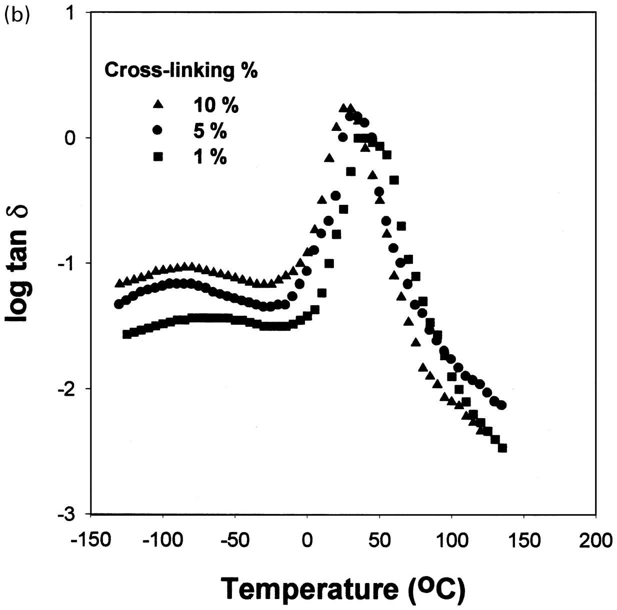


Fig. 1. Temperature dependence of the storage modulus, E' (a) and loss tangent, tan δ (b) of the PVA networks with different degrees of cross-linking.

3. Results and discussions

3.1. Dynamic-mechanical thermal analysis

The temperature dependence of the storage modulus, E', and loss tangent, tan δ, measured at 1 Hz for the PVA networks of different degrees of cross-linking is shown in Fig. 1. In the experimental range of temperatures investigated, two relaxation peaks labeled as α and β in order of increasing temperature, were observed. The β-relaxation is seen as a broad peak of relatively low intensity. This broadening is indicative of a complex relaxation process produced by local twisting motions of hydroxyl groups connected to water molecules around main-chain bond [15]. This probably results from the presence of small amounts of absorbed moisture in the sample investigated here. The temperature location of the maximum of the β-relaxation slightly shifted to lower temperature with increasing the degree of cross-linking. This observation can be explained with the slight increase of the side-chain movements due to the introduction of cross-linker.

The assignment for the β-relaxation presented here is in agreement with those proposed previously from a study of added water content in the relaxation processes in PVA [16].

The intense peak in tan δ versus temperature plot is accompanied by a sharp decrease in E' and corresponds to the segmental relaxation associated to the glass transition (T_g). This peak broadens as the cross-linking density increases, which can be interpreted in the sense that there is a broader distribution of the mobilities or the relaxation times of the chain segments that contribute to conformational rearrangements. This could also imply a broader distribution of the lengths of the elastic chains between cross-links.

However, contrary to one would expect the glass transition decreases with increasing cross-linking density. This is an interesting behavior that can be explained by considering the factors affecting the T_g values of cross-linking polymers. These factors are main-chain rigidity, cross-linking density, and the chemical structure of the cross-linker. In case of PVA the hydroxyl groups contribute to the stiffness of the polymer via hydrogen bonding. When the hydrophobic cross-linker is introduced, the number of hydroxyl groups available for hydrogen bonding decreases thereby decreasing the stiffness. An important property derived from the chemical structure of the cross-linker itself is its flexibility. In our case, the cross-linker consists of a sequence of six methylene groups. This has the effect of increasing the flexibility in the individual polymer chains and leads to a lower glass transition. This means that the expected increase in T_g due to the formation of the chemical network is insignificant when compared to the decrease in T_g ought to the weakening of the physical network and to the plasticizing effect of the introduced flexible moieties.

It's worth mentioning that the T_g value for the low cross-linked sample is lower than the literature value PVA [2]. This is again due to the adsorbed moisture in the sample.

The value of the elastic modulus at temperature higher than the main relaxation, in the plateau region corresponding to the rubber-like behavior is slightly increasing function of temperature. According to the theory of rubber elasticity, this value permits the calculations of the mean molecular weight between cross-links of the elastically active chains, $\bar{M}_e$, as:

$$\bar{M}_e = \frac{\rho RT}{G_e} \tag{1}$$

where G_e is the modulus in the elastomeric region, which can be estimated as $G_e = E'/3$, ρ the density and R the gas constant. Using the value of the density measured at 25 °C for the three networks, and the value of the elastic modulus at the same temperature obtained by linear extrapolation to 25 °C of the experimental data of the rubber-like region, one can calculate the values of $\bar{M}_e$ for the three networks studied; these are cited in Table 1. The mean number of monomeric units between cross-links of the elasticity active strands, $\bar{n}_e$, decreases as the amount of cross-linker in the initial mixtures increases.

Table 1

Characteristic parameters of the PVA network as a function of cross-linking percent. ρ: density at 25 °C; $\bar{M}_e$: average molecular weight between cross-links; and $\bar{n}_e$: average number of PVA units between cross-links in elastically active chains

	Cross-linking percent		
	1%	5%	10%
ρ (g/cm^3)	1.313	1.312	1.311
$\bar{M}_e$	12283	4890	2750
$\bar{n}_e$	286	114	64

3.2. Sorption isotherm

Equilibrium water sorption isotherms were measured for the three PVA networks at 25 °C and are represented in Fig. 2 in terms of the weight of water sorbed by the film at a given water activity divided by the dry weight of the polymer. The isotherms show a small but significant decrease in the equilibrium water uptake of the network with increasing cross-linking density. This is not an unexpected fact since the number of hydroxyl groups per unit mass of the sample decreases as the amount of cross-linking agent increases. All isotherms are almost linear at low water activities, but significant upturn at high activities, as expected from the Flory–Huggins theory. Two possible interpretation of equilibrium isotherms that show a large degree of upturn at high activities are: (1) the plasticization of the polymer by the penetrant, or (2) the clustering of water molecules. These two phenomena can be distinguished from the behavior of the diffusion coefficient. Plasticization results in an increase in the diffusion coefficient with activity or concentration due to increased segmental polymer mobility caused by penetrant molecules. When water molecule cluster, on the other hand, the effective diameter of the diffusing species increases, which

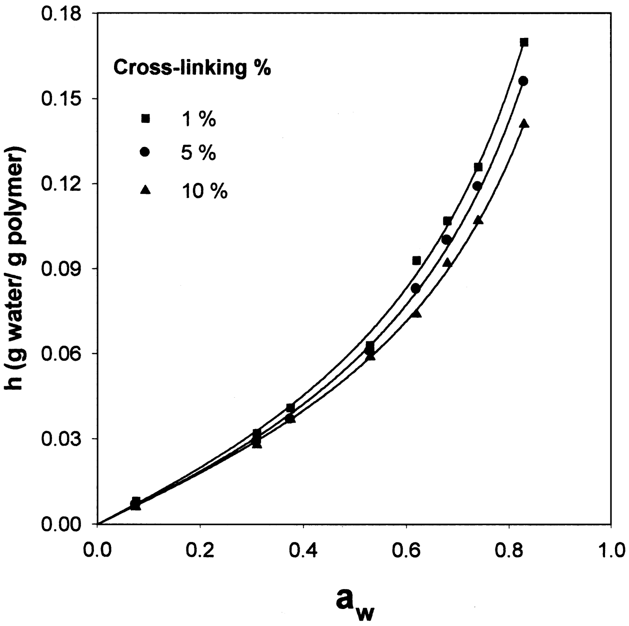


Fig. 2. Sorption isotherms of PVA networks at 25 °C. The full lines represent the prediction of the GAB equation.

decreases penetrant mobility or diffusion coefficient. Assignment to either of these possibilities will be done in the next sections.

Generally, the isothermal equilibrium sorption curves of polymeric networks deviate from Henry's law. The experimental data of water content versus RH yield parabolic or sigmoidal curves, which are better, described by power law function [17]. Moy and Karasz report that low temperature sorption of water by epoxy resins is a multiplayer process [18], usually represented by sigmoidal isothermal curves of type II in the Brunauer–Emmet–Teller (BET) classification [19]. This indicates that, initially, sorbed water molecules are able to interact with the binding sites of the polymer, while subsequent molecules associate with the primary layer in liquid water-like structures. At more elevated temperatures, isotherms approach linearity, revealing simple solution sorption, which is asymptotically approximated by Henry's law [18].

The negative and positive deviations of the experimental results from Henry's law of isothermal equilibrium water absorption have been described by Galin and Galin [20,21], in other polymeric systems by the use of the Guggenheim–Anderson–de Boer (GAB) model [22]. This model is an amended form of the classical Brunauer–Emmet–Teller (BET) model [23] and allows us to take into account the experimental data over a broad range of water activity.

The equilibrium water isotherms of aforementioned shapes (Fig. 2) were analyzed according to GAB model. This model describes a relationship between the equilibrium water content of the hydrogel, h, and the activity of water, a_w, inside it, in the form of an equation with three adjustable parameter

$$\frac{h(a_w)}{h_m} = \frac{cfa_w}{(1 - fa_w)[1 + (c - 1)fa_w]} \tag{2}$$

where h_m is the weight fraction measured on a dry basis of the water molecules directly attached to sorption sites, c a parameter related to the energy difference between the water molecules attached to sorption sites (the first sorption layer) and that absorbed in successive sorption layers, and f measures the energy difference between water molecule absorbed in the second and successive sorption layers and pure liquid water. When $f = 0$, the GAB equation reduces to the well-known BET equation [23]; f values smaller than unity reflect that indirectly bound water molecules are still in a more stable state than the water molecules in the bulk liquid state. The parameters of Eq. (2) for the three PVA networks studied in this work were determined by the two-step methods recommended by Timmermann [22] and are given in Table 2. The full lines in Fig. 2 shows prediction of the GAB equation with these parameter values. The decrease in h with increasing cross-linking density is correlated to the decrease in the number of water molecules absorbed in the first absorption layer, h_m. Since the cross-linker has a hydrophobic character, it is safe to assume that the primary sorption sites are in the hydrophilic PVA monomeric units, and thus the increase in the degree of cross-linking is reflected in a slight decrease in h_m. The value of f is less than unity in all cases and is not significantly dependent on the degree of cross-linking. This means that the adsorbed water molecules have a lower free energy than the water molecules of the surrounding environment, and thus their adsorbed state is more stable. As regards parameter c, its values are normal for hydrogels [22], but their physical significance is less direct and usually more difficult to explain [20,21]. In our case, it shows a slightly higher value for the 10 mol% sample. This may indicate a loosening of the interaction between the sorbed water molecules and substrate [22], but we cannot attempt a more thorough explanation of it.

Table 2
Parameters of the GAB equation and equilibrium water uptake in immersion, h_{imm}

	Cross-linking percent		
	1%	5%	10%
h_m	0.066	0.062	0.056
f	0.83	0.83	0.82
c	1.70	1.70	1.90
n_m	0.16	0.15	0.13
h_{imm}	2.11	1.20	0.65

From the value of the parameter h_m, it is also possible to calculate the number of primary sorption sites in each PVA segments:

$$n_m = \frac{M_{PVA} h_m}{M_w} \tag{3}$$

where M_{PVA} and M_w are the molecular weights of PVA repeating unit and water, respectively. The values of n_m are listed in Table 2. Assuming that only one water molecule is linked to two-hydroxyl group in the first layer, so 0.5 water molecule per polymer segment is absorbed in the first layer. The values of n_m listed in Table 2 is much less than 0.5. This means that not every hydroxyl group of the PVA monomer is available as a primary sorption site for the water molecule, probably because a number of them are mutually linked in inter- or intramolecular hydrogen bonds and are thus not accessible to water molecules, and that this effect increases slightly with cross-linking density.

3.3. The Flory–Huggins interaction parameter χ

The ability of a polymer network to absorb water depends for small network expansions mainly on the specific interaction between water molecules and polymer chains. According to the Flory–Huggins theory [24], the free energy of mixing polymer chains and water molecules is

$$\Delta G_m = kT[n_w \ln \phi_w + \ln(1 - \phi_w) + \chi n_w(1 - \phi_w)] \tag{4}$$

where χ is water–polymer interaction parameter and n_w and ϕ_w are the number of water molecules and the volume fraction of water in the hydrogel, respectively. Unfortunately, χ takes higher values with increasing hydrophobicity of the polymer network. From Eq. (4), an expression for the chemical potential of water mixed with the polymer network, μ_w^{hydrogel}, can be deduced. When a hydrogel is kept in an environment consisting of a vapor phase containing water, the thermodynamic equilibrium requires that

$$\mu_w^{\text{hydrogel}} = \mu_w^{\text{vapor}} \qquad (5)$$

with μ_w^{vapor} is the chemical potential of water in the vapor phase. From Eq. (5), it can be deduced that the activity of water in the swollen network, a_w, equals approximately the RH of the vapor phase, which thus becomes a controllable parameter, and from Eq. (4) it follows that

$$\ln a_w = \ln \phi_w + (1 - \phi_w) + \bar{\chi}(1 - \phi_w)^2 \qquad (6)$$

where $\bar{\chi}$, which is closely related to χ and coincides with it when χ is independent of composition [25], can be called an apparent interaction parameter. This apparent interaction parameter can thus be calculated from experimental data of equilibrium uptake of the network in the presence of a vapor phase containing water. ϕ_w is the volume fraction of water in the hydrogel which can be calculated from the known weight fraction, h, as:

$$\phi_w = \frac{\gamma h}{1 + \gamma h_w} \qquad (7)$$

where γ is the ratio of the density of the polymer to the density of water.

Its worth mentioning that Flory–Huggins theory (lattice model) assumes random mixing in polymer–solvent mixtures and obviously it cannot hold at small water contents owing to the hydrogen bonding between water molecules and polymer polar groups. It remains, however, of a definite interest to point out any concentration dependence of the apparent interaction parameter χ: such dependence is precisely ascribed in most cases to an inhomogeneous distribution of the solvent molecules and polymer segments throughout the solution. At low water contents, an increase in the interaction parameter with water content has been reported [21,22,26]; for higher water contents decreasing values of $\bar{\chi}$ with water contents have been found [22,26]. The concentration dependence of the interaction parameter is shown in Fig. 3. One can see that $\bar{\chi}$ decreases with increasing the volume fraction of water in the hydrogel and increases slightly with increasing cross-linking density. This type of behavior is generally found in hydrogels cross-linked with hydrophobic cross-linkers [27, 28] and is explained by the decreasing hydrophilicity of the network with increasing content of the hydrophobic cross-linking agent.

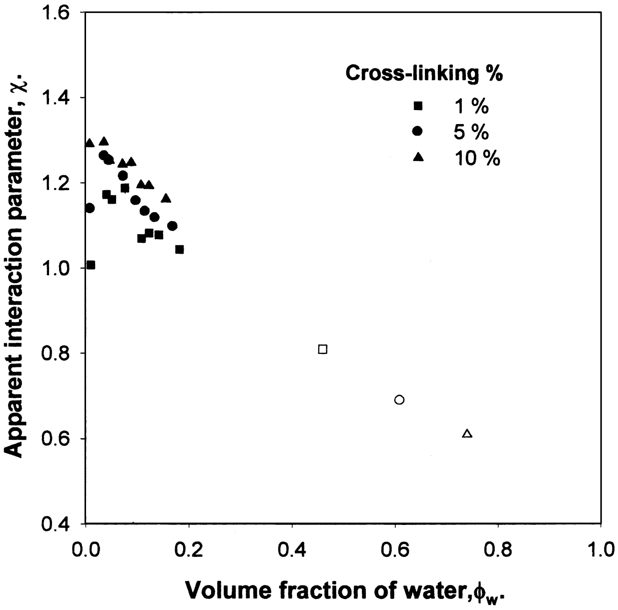


Fig. 3. Apparent Flory–Huggins interaction parameter at 25 °C as a function of water activity. Open symbols are the values calculated from immersion experiment using Eq. (8) (see the text).

3.4. Sorption from liquid water

The amount of water absorbed by the samples immersed in water as a function of time is shown in Fig. 4. The results follow the expected trends; PVA hydrogel cross-linked from 1% mixture swelled faster and to higher swelling ratios than those formed from 5 or 10% mixture. The equilibrium values of the water uptake in immersion (see Table 2) greatly exceed those reached during sorption from a vapor phase.

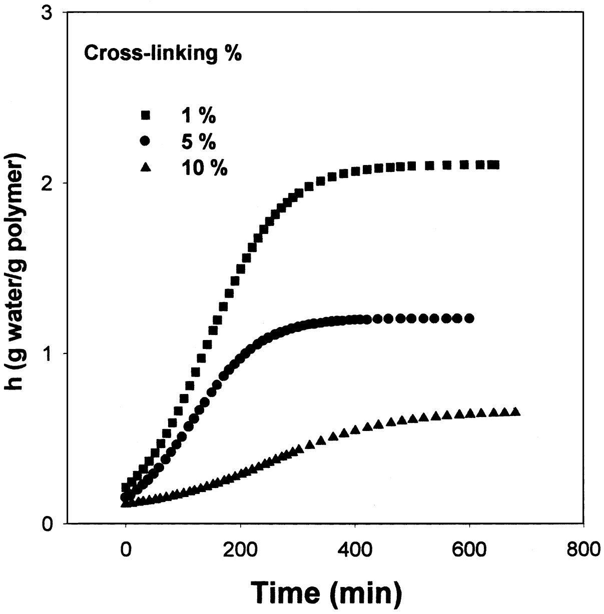


Fig. 4. Water uptake as a function of time in PVA networks immersed in liquid water at 25 °C.

For these high water uptakes of the hydrogel, a significant elastic expansion of the polymer network takes place, and the contribution to the chemical potential of this elastic force has to be taken into account in the free energy equation of the system. In such case, the apparent interaction parameter can be calculated using the Flory–Rehner equation [25] which relates the average molecular weight of the effective strands between cross-links in the network, $\bar{M}_e$, and the equilibrium water uptake from immersion in liquid water by

$$\bar{M}_e = -\frac{\rho V_w[(1-\phi_w)^{1/3} - (1-\phi_w)/2]}{\ln\phi_w + (1-\phi_w) + \bar{\chi}(1-\phi_w)^2} \qquad (8)$$

where V_w is the molar volume of water and ρ the density of the polymer. The values of the apparent interaction parameter thus calculated are shown as open symbols in Fig. 3. It can be observed that the three different points corresponding to the three different networks seem to fall on the same line, which would be a common prolongation of the three tendency lines obtained at the lower water content (open symbols in Fig. 2). The decreasing trend, which on the whole Fig. 3 shows for the apparent interaction parameter, is surprising and can be explained as follows: the Flory–Huggins interaction parameter should, in principle, be independent of composition, but it was already observed by Flory [24] that this condition, required by the theory, was only exceptionally met in experimental behavior. The interaction parameter is a normalized interaction enthalpy that supposes the nature of the pair interaction is not altered when the concentration of one of the components of the system changes. However, in a hydrogel, one must concede that the interaction of a given water molecules with other water molecules or with one of the polymer units might be different depending on the intensity of that molecule's link to a polymer chain (i.e., whether it is adsorbed in the first or in successive layers, or not adsorbed at all) or on the degree to which the polymer unit is screened by the surrounding water molecules, and this depends on concentration. This certainly introduces a dependence of $\bar{\chi}$ on water volume fraction.

3.5. Sorption kinetics

For the three PVA networks investigated here, the variations of the amount of sorbed water versus time at different water activity (identical with RH) were measured. A representative reduced sorption rate curves, as plot of M_t/M_∞ versus $(t/\delta^2)^{0.5}$ are given in Fig. 5; M_t is the amount of water sorbed in time and M_∞ corresponding limiting value at equilibrium (taken as the weight gain when the sample reach equilibrium water uptake); δ is the thickness of the dry film, presumed constant over the whole sorption process. The curves show an initial linearity followed by a curvature convex to the abscissa axis. The dependence of the initial slope of the curves with the initial water content of the sample indicates a significant dependence of the diffusion coefficient, D, on water concentration. The explanation here runs parallel to that given for the interaction parameter: the environment seen by a diffusing water molecule is different depending on the degree of hydration of the medium. This feature indicates that the diffusion process is not Fickian. The apparent diffusion coefficient, $\bar{D}$, were calculated from the linear part of the curve in the region were $M_t/M_\infty < 0.5$ using the relationship [29]:

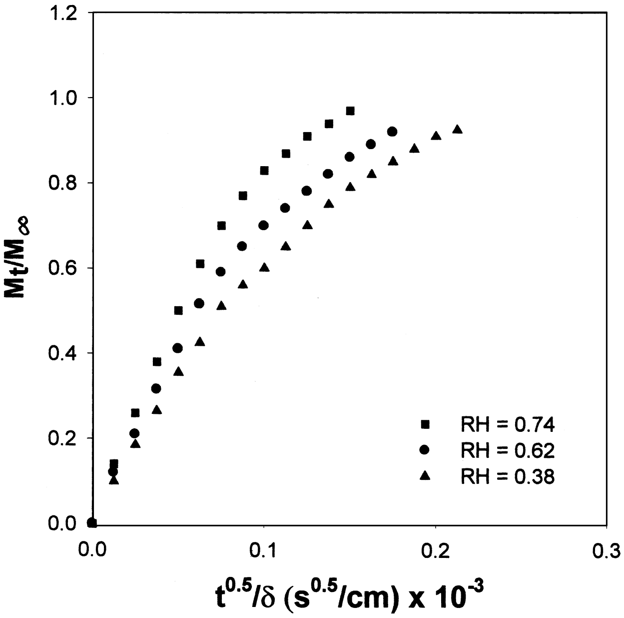


Fig. 5. Reduced sorption curves of 5 mol% cross-linked PVA network at 25 °C in sorption experiments with different RH.

$$\bar{D} = \frac{\pi}{16}\left[\frac{d(M_t/M_\infty)}{d(\sqrt{t}/\delta)}\right]^2 \qquad (9)$$

The values of $\bar{D}$ for the 5 mol% samples are given in Table 3 at different water activity. The same values are valid for the 1 and 10 mol% samples. The apparent diffusion coefficients for all of the structurally modified PVA samples show similar trends, $\bar{D}$ increases with increasing water activity. This type of behavior is typically interpreted in terms of plasticization of the polymer by water molecules and is common in hydrophilic polymers.

Table 3
Apparent diffusion coefficient, $\bar{D} \times 10^7$ cm^2 s^{-1}, calculated for the 5 mol% cross-linked PVA network from sorption mode

Relative humidity	$\bar{D} \times 10^7$ cm^2 s^{-1}
0.38	0.94
0.61	1.40
0.74	2.40

4. Conclusions

Water sorption isotherms, sorption from liquid water and dynamic-mechanical analysis have been used to investigate the interaction between water molecules and hydrophilic polymer network of cross-linked PVA. The calculated Flory–Huggins interaction parameter $\bar{\chi}$ decreases with increasing the volume fraction of water in the hydrogel and increases slightly with increasing cross-linking density. This has been attributed to the decreasing hydrophobicity of the network with increasing content of the hydrophobic cross-linking agent. From the parameter of the GAB equation a number of 0.15 water molecules directly attached (first sorption layer in the GAB model) to the polymer segment could be calculated. This means that not all the hydroxyl groups are active as primary sorption sites. The apparent diffusion coefficient was determined from dynamic sorption experiments, which increase with increasing water activity.

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