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Swelling of sodium chloride filled polybutadiene networks in water, water/acetone and water/THF mixtures

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The swelling of polybutadiene (PB) networks of different cross-link densities filled with finely divided sodium chloride (NaCl) particles are studied in water, water/acetone and water/THF mixtures. Swelling over periods of 2 months are recorded. The degree of swelling was observed to increase continuously in water during this period, whereas in water/acetone mixtures it reached a peak followed by deswelling and it converged to a maximal value in water/THF mixtures. The highly cross-linked samples exhibited unusually high degrees of swelling, and calculations indicated full stretching of the network chains. The enthalpic contribution to the chemical potential of the networks in equilibrium with solvent was determined using the phantom network model of rubber elasticity theory. The swollen network–salt system was approximated by the lattice model of polymer solutions. The positive contributions of water and acetone to the chemical activity of the swollen network were offset by the negative contribution of dissociation of salt in water, resulting in a small negative enthalpy of mixing. The highest rate of diffusion of solvent was observed for the PB/water/THF ternary system. Diffusion rates of pure water and water/acetone mixture were much smaller and of comparable magnitude. Mechanical measurements of stress and strain at break, and dynamic mechanical measurements of storage and loss moduli of filled and unfilled samples showed that filling with NaCl did not change the mechanical properties of the networks significantly, in spite of the dramatic change in the swelling behaviour. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polybutadiene/water/acetone system; polybutadiene/water/THF system; sodium chloride filler)

INTRODUCTION

Some years ago results of observations on the absorption of water by butyl rubber were reported[1]. Recently, a more detailed account of the same study was given[2]. According to these observations, cross-linked butyl rubber absorbed significant amounts of water when small amounts of salt were added to the samples during cross-linking. No systematic study of this phenomenon have been made since then, although there have been reports of high water absorption by rubber in the literature[2]. The present study is undertaken with the purpose of further understanding the mechanisms of water absorption by cross-linked rubbery systems. Considering the everyday importance of water wettability and water absorption of polymeric materials[3], we thought that a detailed study of polybutadiene networks with different amounts of NaCl would be timely.

The elastic activity of polymeric networks depends strongly on the type, size and amount of filler particles[4]. Conventional fillers such as carbon black or mica are osmotically inert in the sense that they do not interact directly with the solvent molecules with which the network may be in contact. It is well known that a polymer network filled with carbon black swells to a much lesser extent than the unfilled network. This is due to the negative contribution of the filler to the elastic activity of the network, a fully entropic contribution resulting from the constraining action of the filler on the fluctuations of the polymer chains. On the other hand, a network with fillers that have favourable enthalpic interactions with solvent presents an opposite example, and is the subject of the present work. Here, we consider polybutadiene (PB) networks filled with finely divided sodium chloride (NaCl) particles. Due to the favourable interaction of such filler particles with water, the networks exhibit a high degree of swelling in aqueous solvents. The relationship of the rate and extent of swelling to the type of solvent and degree of cross-linking, and the changes in the mechanical properties such as storage and loss moduli are the entities considered in the present work.

EXPERIMENTAL

Materials and sample preparation

The polymer, high *cis*-polybutadiene (PB), CBR 1203, was obtained from Petkim and used as it was. Dicumyl peroxide (DCP), used as cross-linking agent, was coded as Petkadox BC-ff, obtained as 99% peroxide content and no carrier. The diameter of NaCl particles, used as filler, was about 70 μm. NaCl was predried at 120°C in a vacuum oven for 12 h. PB, DCP and NaCl were mixed on a two-roll mill. Vulcanization was done at 180°C on a hot press for 30 min. The cross-linked samples were immersed in chloroform for 3 days to remove the uncross-linked polymer. Weight loss upon extraction was negligible.

Four sets of networks were prepared, differing in their cross-linking density and their amount of filler. The compositions of the networks are listed in *Table 1*. The sample description is given in column 1 according to the

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Table 1 Composition and codes of samples

Sample code	NaCl[a]	DCP[a]
30/1	30	0.005
30/2	30	0.010
30/3	30	0.050
30/3	30	0.080
30/5	30	0.100
15/1	15	0.005
15/2	15	0.010
15/3	15	0.050
15/4	15	0.080
15/5	15	0.100
5/2	5	0.010
5/5	5	0.100
0/1	0	0.005
0/2	0	0.010
0/3	0	0.050
0/4	0	0.080
0/5	0	0.100

[a] Grams per 100 g of PB.

Table 2 Volume fraction of polymer at equilibrium swelling (v_{2m}), average molecular weight between junctions (M_c), maximum elongation of polymer chains (λ_{max}) and maximum swelling ratio (Q_{max}) of the networks in the absence of NaCl

Sample code	v_{2m}	M_c (g mol^{-1})	λ_{max}	Q_{max}
0/1	0.0717	8200	6.48	271.8
0/2	0.0739	8000	6.37	259.0
0/3	0.1353	2900	3.83	56.1
0/4	0.1551	2500	3.55	44.9
0/5	0.1971	1500	2.79	21.7

format *x*/*y*, where *x* is the weight in grams of salt per 100 g of PB, and *y* ranging from 1 to 5 refers to the weight of DCP used per 100 g of PB, listed in the third column of *Table 1*.

Swelling measurements

Strips of dimensions 0.2 × 0.5 × 2 cm^3 were immersed in solvents having various compositions of water/acetone and water/THF at room temperature for several weeks. The changes in the lengths of the samples were measured in the immersed state by a traveling microscope (Gaertner 7109-C-46) with an accuracy of 0.005 cm. Measurements were repeated for at least three samples in each case and the results were averaged.

Mechanical experiments

Mechanical experiments were performed under two loading conditions. (1) Quasi-static mechanical tests, carried out at room temperature and cross-head speed of 5 mm s^{-1} in the static mode of a Zwick 1464 machine equipped with an incremental extensiometer. (2) Dynamic mechanical tests, carried out on a Polymer Laboratories dynamic mechanical testing analyser (DMTA), over a temperature range of $-100°C \le T \le 50°C$ at a frequency of 1 Hz. Tests were also performed at room temperature for frequencies of 1, 3, 5 and 10 Hz.

Characterization of molecular weights and maximum extensibilities of network chains

The average molecular weight M_c of network chains between cross-links was obtained by two sets of experiments: (i) equilibrium stress–strain isotherms on dry unfilled networks, and (ii) swelling isotherms of unfilled samples in chloroform. In the first case, the large deformation equilibrium moduli were determined for samples with five different degrees of cross-linking and the values of M_c were calculated from the expressions

$$M_c = \frac{1}{2}\frac{\rho RT}{[f^*]_{ph}} \tag{1}$$

where ρ is the density of dry polymer and $[f^*]_{ph}$ is the so-called 'phantom network modulus' obtained at large deformations. The values of M_c obtained by this equation were plotted as a function of the amount of DCP used, and a master curve was obtained from which the value of M_c for any given network can be found as a function of the amount of DCP. In the second set of experiments, equilibrium swellings of PB networks in chloroform were determined for the samples used in the stress–strain isotherms, and their M_c values calculated from equation (1) were used in the expressions[5]

$$M_c = \frac{\rho(1-2/\phi)V_1 v_{2c}^{2/3} v_{2m}^{1/3}}{\ln(1-v_{2m}) + \chi v_{2m}^2 + v_{2m}} \tag{2}$$

to evaluate the χ parameter for the PB-chloroform system. In equation (2), ϕ is the average junction functionality (ϕ = 4 in the case of cross-linking with DCP), V_1 is the molar volume of solvent (V_1 = 81 cm^3 for chloroform), v_{2c} is the volume fraction of polymer during cross-linking (taken as unity in the present case), v_{2m} is the experimentally determined volume fraction of polymer at equilibrium swelling and χ is the Flory interaction parameter. The value of the χ parameter giving the best agreement with stress–strain isotherms was obtained as 0.15 at room temperature. Values of M_c obtained from equation (2) for the five unfilled samples are presented in the third column of *Table 2*. In the interpretation of results below, the M_c values for the unfilled samples are assumed to hold for the filled samples, as well. The fifth column of *Table 2* gives the maximum extensibility λ_{max} of the network chains. This is the ratio of the maximum stretched length $n l \cos(\theta/2)$ of a PB chain of n bonds each of length l, to its root-mean-square end-to-end length $\langle r^2\rangle^{1/2} = (C_n n l^2)^{1/2}$, i.e. $\lambda_{max} = (n/C_n)^{1/2}\cos(\theta/2)$, where C_n is the characteristic ratio and θ is the supplement of backbone bond angles averaged over the three bond angles of the repeat unit. For the PB chains, C_n and θ are taken, respectively, as 4.9 and 62° in the calculations[6]. The fifth column of *Table 2* gives the maximum swelling ratio Q_{max} of the networks, calculated as $Q_{max} = \lambda_{max}^3$. The values of Q_{max} estimated in this manner help in understanding the extent of swelling of networks relative to maximum chain extensibilities.

Characterization of mechanical properties of filled samples

Results of quasi-static stress–strain experiments are presented in *Table 3* for the sample with the highest amount of filler. The values of stress and strain at break, σ_{max} and ε_{max}, are given in the second and third columns, respectively. These are normalized with respect to the

Table 3 Normalized stress and strain at break values for samples containing 30% NaCl, and the storage moduli of filled systems relative to unfilled samples, for samples containing 30 and 15% NaCl

DCP (%wt)	Stress: $\frac{\sigma_{\max}(30)}{\sigma_{\max}(0)}$	Strain: $\frac{\varepsilon_{\max}(30)}{\varepsilon_{\max}(0)}$	$E'(30)/E'(0)$	$E'(15)/E'(0)$
0.005	1.25	0.59	1.95	0.79
0.010	1.00	0.83	2.40	1.07
0.050	1.20	1.00	1.74	1.05
0.080	1.33	1.01	1.17	0.89
0.100	1.18	1.30	1.62	1.07

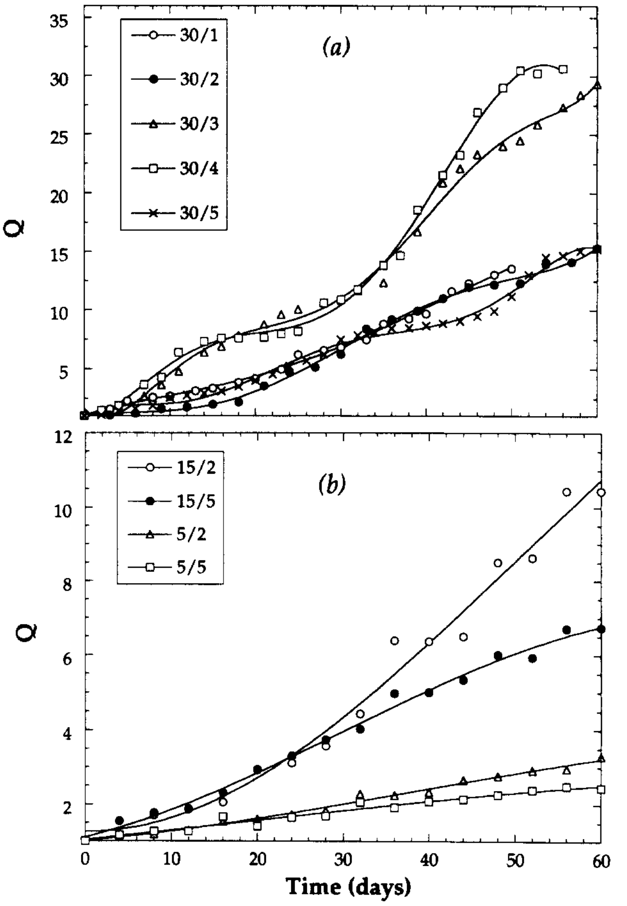

Figure 1 Swelling ratio (Q) of samples having different cross-linker amounts, plotted against time. Experiments are performed in pure water (a) for samples containing 30% NaCl filler, and (b) for samples containing 15 and 5% NaCl filler

corresponding values for unfilled samples. The values 30 and 0 in parentheses refer to weight per cent of filler (*Table 1*). The ratios obtained in this manner are around unity, indicating that inclusion of salt as a filler does not produce reinforcing effects, contrary to those observed with carbon black or mica. Results for other amounts of filler are qualitatively similar to those shown and are not presented.

Changes in the storage modulus E' with the degree of cross-linking are presented in the last two columns of *Table 3* for 30 and 15% NaCl filled samples, at 1 Hz. In order to compare with the behaviour of unfilled samples, the ratios of the storage moduli of the filled systems to that of the unfilled one are presented. For 15% NaCl filled sample, (and for 5% not shown here) the ratio is around unity, indicating that filling by NaCl particles does not change the elastic activity of the network chains, contrary to carbon black reinforcement, for example. For the 30% NaCl filled sample, this ratio varies between 1 and 2. One may conclude that the change in the elastic activity of the NaCl filled PB networks relative to that of the unfilled network is relatively weak.

RESULTS AND DISCUSSION

Swelling of filled networks in different solvents

Time evolution of swelling experiments are reported here for networks immersed in (i) pure water, (ii) various water/acetone mixtures, and (iii) water/THF mixtures. Swelling degrees are reported in terms of swelling ratio Q defined as the ratio of the swollen volume of network to the dry network. For unfilled networks, $Q = v_2^{-1}$ where v_2 is the volume fraction of polymer in the swollen network at a given time during the course of the experiment.

We note that, in the present experiments, we have a heterogeneous system, that is particles of solid NaCl are dispersed in voids in the PB matrix, with these particles becoming droplets of NaCl solution as the water uptake takes place. The v_2 values evaluated from the macroscopically measured Q values should then be corrected so as to eliminate the contribution of the water uptake by NaCl to the observed swelling ratios, as will be shown in the subsection on enthalpic contributions below.

Swelling in pure water. Results are presented in *Figure 1*(a) and (b), where Q is plotted as a function of time. Parts (a) and (b) refer to different degrees of cross-linking as identified in the figure legend. Best-fitting curves are drawn through experimental data points in this and following figures to guide the eye. In *Figure 1*(a), the swelling behaviour of the largest amount of filler is shown. Interestingly, the samples with intermediate cross-linking densities, 30/3 and 30/4, exhibit the highest swelling ratio. Q values as high as 30 are reached by these samples within the first 60 days of immersion. The curves in *Figure 1*(a) exhibit a double-sigmoidal shape, indicating an accelerating uptake of water at the initial stages, a slowdown at intermediate times followed by again an accelerating uptake and then a slowdown. Equilibrium degrees of swelling for these samples were not reached within the time scale of measurements. In *Figure 1*(b), results for samples 15/2, 15/5, 5/2 and 5/5 are shown. The Q values reached for these samples are significantly smaller than those shown in *Figure 1*(a), indicating that the presence of NaCl filler enhances the degree of swelling.

At long times, one would expect eventual diffusion of the salt solution inside the networks back into the surrounding solvent, as a result of which the volumes of the samples should start decreasing. The curves presented in *Figure 1*(a) and (b) do not exhibit a decrease in Q. We therefore conclude that the 'leaching out' of the salt solution into the surrounding solvent is not of important extent within the first 60 days of immersion in water.

In order to compare the degrees of swelling of the networks relative to their maximum possible swelling, *Figure 1*(a) is replotted as *Figure 2*. Here the ordinate is the ratio $Q/Q_{\max}$. $Q_{\max}$ values are taken from *Table 3*. The time evolution of $Q/Q_{\max}$ provides a measure of the rate of swelling, irrespective of the equilibrium degree of swelling.

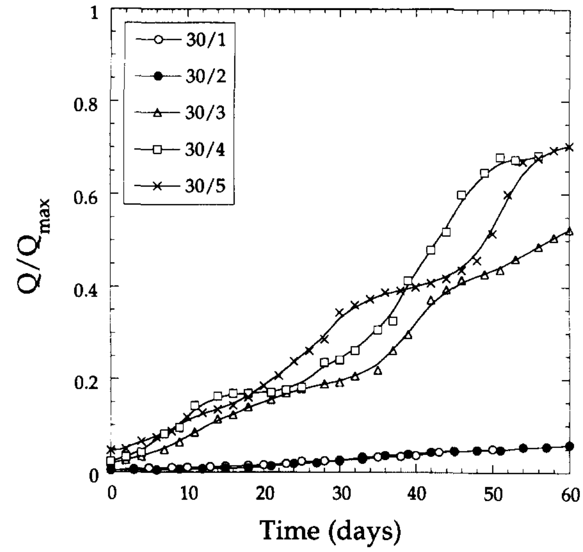

Figure 2 Time evolution of swelling ratio (Q) in pure water, divided by the maximum possible swelling (Q_{max}), for samples 30/1–30/5. See *Table 1* for sample identification

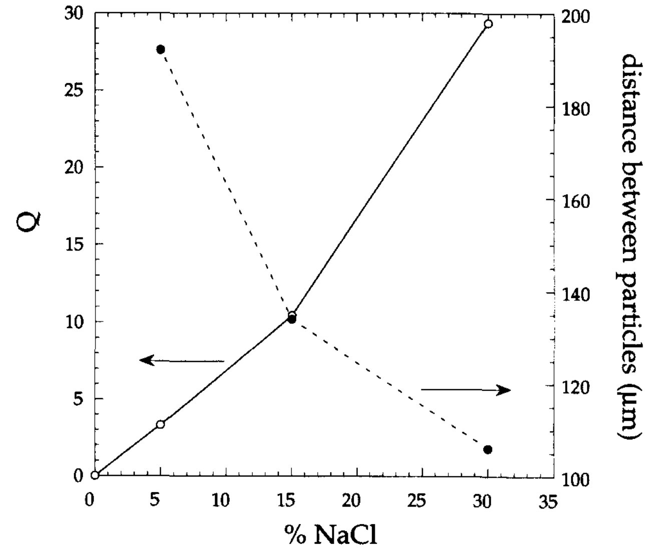

Figure 3 Maximum swelling ratio reached at the end of the experiments in pure water for each sample containing different amounts of NaCl (left ordinate), and distance between NaCl particles in these samples (right ordinate) plotted against the filler concentration

The curves show that the rate of diffusion of water into the samples is correlated with the degree of cross-linking. The equilibrium swelling ratio is attained faster as the cross-linking density exceeds a certain threshold value. It should be noted that the values of Q presented in *Figure 1*(a) do not exhibit this trend, and that normalization with respect to maximum swelling is required for visualizing this effect.

The extent of swelling at the end of 60 days is displayed in *Figure 3* as a function of the amount of NaCl in the network. Results for the samples having 0.01% DCP are presented by open circles connected by the solid curve. The three samples, containing 0, 5 and 15% NaCl exhibit an approximately linear dependence on salt content. The sample with 30% salt content, on the other hand, exhibits a swelling twice as large than would be expected from the extrapolation of the linear relationship. We note that the distance between centres of salt particles decreases with salt content. The dashed curve, obtained under the assumption

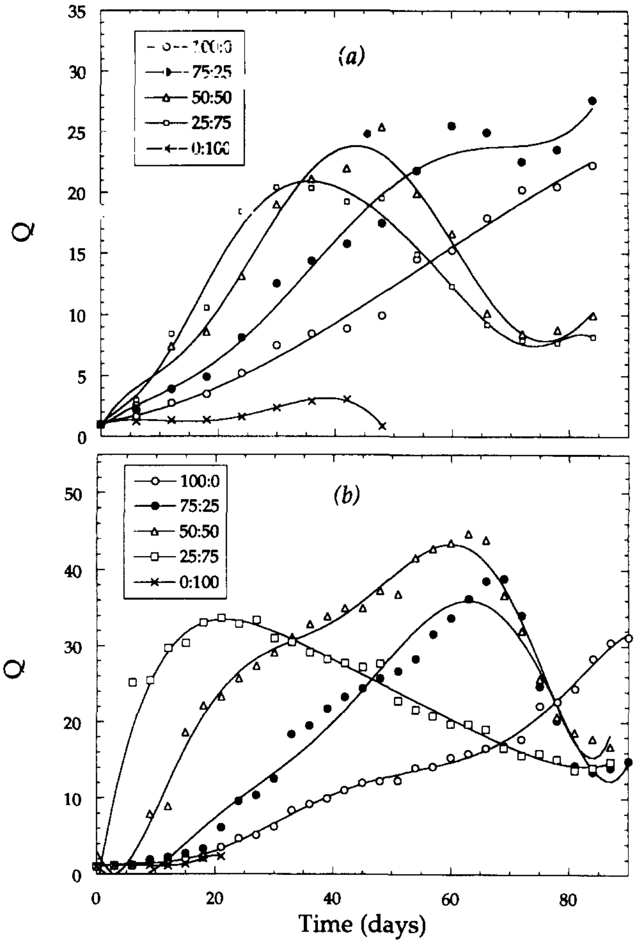

Figure 4 Time dependence of swelling ratio for samples (a) 30/5 and (b) 30/2 in various water/acetone mixtures. The compositions of the solvent are indicated in the legends, in terms of the volume ratios of water to acetone

of uniform particle size and body-centred cubic arrangement, illustrates this dependence. The particles are in contact when the distance is 70 μm, i.e. the diameter of salt particles. For 30% NaCl, the interparticle distance is about 100 μm. This distance is sufficiently small, and water molecules penetrating into the network do not have to travel large distances between salt particles in the rubber phase.

Swelling in water/acetone mixtures. Swelling measurements of networks immersed in various water/acetone mixtures are presented in *Figure 4*(a) for the sample 30/5. In as much as acetone is a poor solvent for PB, the sample immersed in pure acetone exhibited a small degree of swelling, which continued for 40 days. After this time deswelling started; all osmotic activity was lost and the sample deteriorated completely. For direct comparison, the curve for the sample immersed in pure water (indicated by the label 100:0) is also shown in *Figure 4*(a). This sample continued to swell steadily, even at the end of 80 days.

Interestingly, the samples in pure water or pure acetone exhibit much lower degrees of swelling at the initial stages of the experiment than those immersed in mixtures of the two solvents. Such a synergistic effect is observed in all compositions of water/acetone mixtures. Among them, the samples immersed in 75 and 50% acetone by volume continued swelling until 30 and 50 days, respectively, and started deswelling from then on, as may be observed from *Figure 4*(a). The sample immersed in 25% acetone, on the

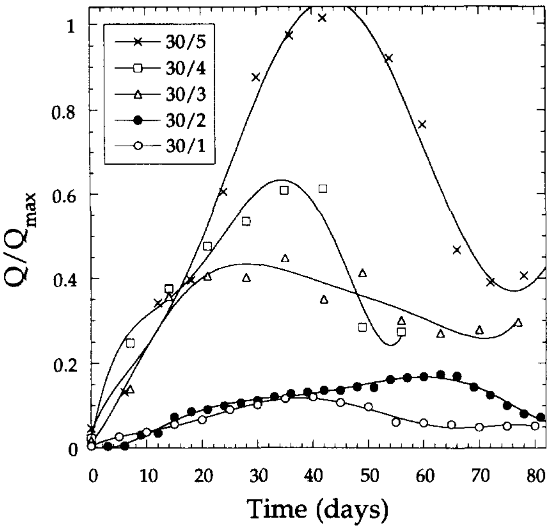

Figure 5 Swelling ratio (Q) obtained in 50% acetone mixture, divided by the maximum possible swelling (Q_{max}), plotted against time for samples 30/1–30/5

other hand, exhibited an intermediate behaviour between 50% acetone and pure water systems.

In *Figure 4*(b), the same type of data is shown for the sample 30/2, i.e. the dicumyl peroxide amount (or the cross-linking density) is now reduced by a factor of 10, compared to the samples displayed in *Figure 4*(a), while the salt content is unchanged. Higher swelling ratios are attained in this case, as expected. The peaks are well pronounced for the sample with 25, 50 and 75% acetone. The initial sigmoidal part of the curves results from the fact that the time required for the solvent to diffuse into the unswollen network is larger at the initial stages of swelling, and diffusion becomes progressively easier as the network swells.

In *Figure 5*, Q/Q_{max} values are presented as a function of immersion time for the samples 30/1–30/5 for 50% acetone solutions. Comparison with *Figure 2* shows that in the present case of water/acetone mixtures, the networks reach relatively higher swelling ratios at earlier times which are followed by strong deswelling, while in pure water swelling continues. In particular, the sample with the highest cross-linking density (30/5) is observed to attain its maximum extensibility ($Q \approx Q_{max}$) in *Figure 5*. It is also to be noted that, although there is not, in general, a smooth dependence of Q values on the degree of cross-linking for the filled samples, a smooth increase of Q/Q_{max} values are observed with increasing degree of cross-linking.

Swelling in water/THF mixtures. Representative results of swelling measurements for the samples in various water/THF mixtures are presented in *Figure 6*(a) for sample 30/5 and in *Figure 6*(b) for sample 30/2. A significant departure from the behaviour in water and water/acetone mixtures is observed. In water/THF mixtures, the samples reach their maximum swelling at short times (~10 days) after which no significant deswelling takes place. In contrast, samples immersed in water were found to continue swelling within the same time span, and those immersed in water/acetone exhibited significant deswelling after reaching a peak value. In *Figure 7*, the values of Q/Q_{max} for samples 30/1–30/5 in 50% THF are presented as a function of time. The curve for 30/5 shows that the network 30/5 has reached its maximum swelling in about 6 days. In fact, in the figure the value of Q/Q_{max} exceeds unity slightly, which may result from approximations involved in the calculation of Q_{max}.

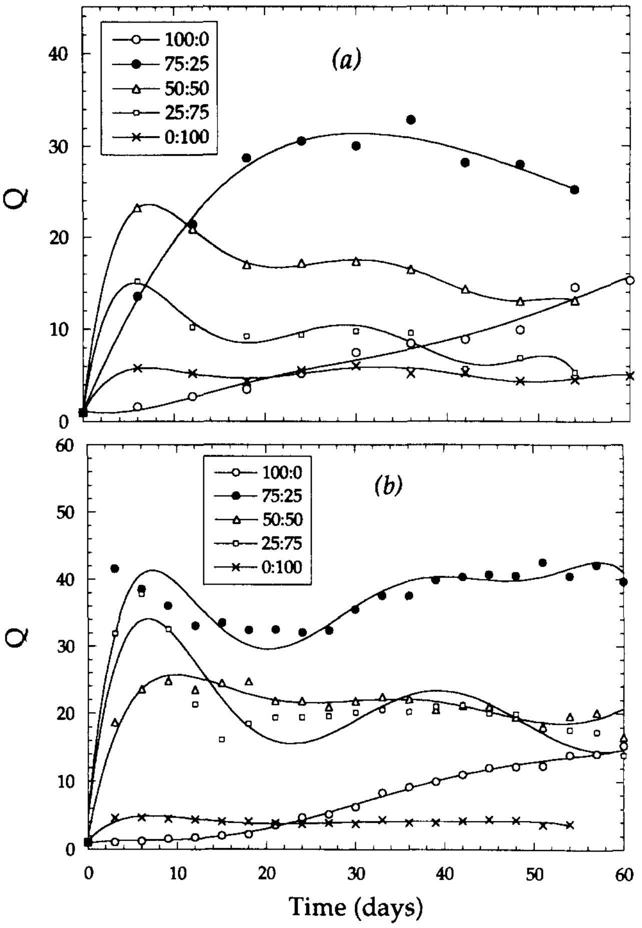

Figure 6 Swelling ratio (Q) obtained for sample (a) 30/5 and (b) 30/2 in various water/THF mixtures plotted against time. The volume ratios of water and THF are shown in the legends

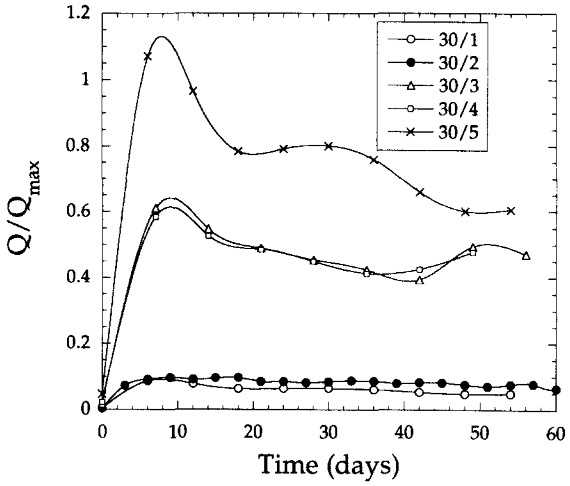

Figure 7 Swelling ratio (Q) of samples 30/1–30/5 in 50% THF mixture, divided by the maximum possible swelling (Q_{max}), plotted against time

An important observation in both water/acetone and water/THF solutions is that the samples immersed in a pure solvent (water, THF or acetone) exhibit a moderate degree of swelling, whereas swelling is significantly enhanced in mixtures of two solvents. This synergistic effect is observable in both *Figure 4*(a) and (b), illustrating the behaviour of the respective samples 30/5 and 30/2 in water/

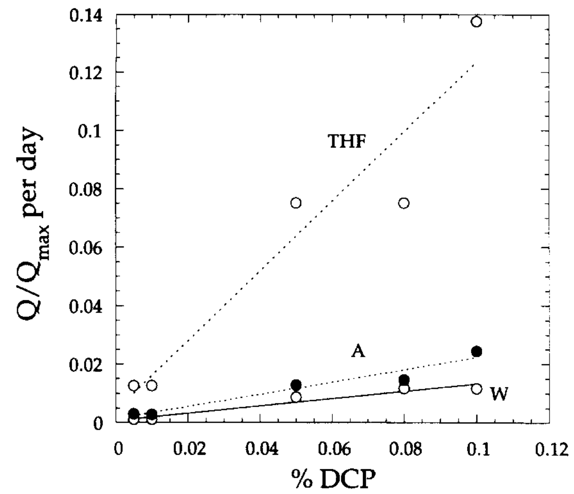

Figure 8 Dependence of the ratio Q/Q_{max} on the amount of cross-linker for three different solvent mixtures: 50% acetone (A), 50% THF (THF) and pure water (W)

acetone solutions, and in *Figure 6*(a) and (b), displaying the behaviour of the same samples in water/THF solutions. Highest degrees of swelling are attained at the compositions 50% acetone and 25% THF, with the sample 30/2 having highest content of NaCl and moderate amount of cross-linker.

Rates of diffusion of solvent and comparison of the three solvents

The networks exhibit two features that depend on the type of solvent: (i) the highest Q/Q_{max} values and (ii) the rate of diffusion of the solvent. The former is an equilibrium property, the latter reflects the kinetics of the swelling process. These two variables differ significantly from solvent to solvent and also show strong dependence on the degree of cross-linking. In *Figure 8*, the swelling rate of the samples in the three different solvents are compared. The ordinate values are obtained by dividing the experimentally obtained highest Q value attained, by the time required to reach this state, and by the expected Q_{max} value. These give an idea on what fraction of maximum possible swelling is reached at the end of 1 day immersion. Results for 50% acetone and 50% THF solvent are shown, only, together with that observed in pure water. Results for the other compositions are qualitatively similar. The dependence of the rate on the degree of cross-linking is linear in all cases, as seen from *Figure 8*. The behaviours in water and water/acetone are close to each other; both exhibit a weak dependence on the amount of cross-linking; whereas the swelling rate in water/THF shows a substantial increase with the degree of cross-linking.

Enthalpic contribution to chemical potential of solvent

The chemical potential for the diluent in the swollen network is given by the expression[7,8]

$$(\mu_1 - \mu_1^0)/RT = \ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^2 + (RT)^{-1}\left(\frac{\partial \Delta A_{el}}{\partial n_1} + \Delta\mu_i\right) \qquad (3)$$

Here μ_1 and μ_1^0 are the chemical potentials of the solvent in the presence and absence of the polymer, respectively, χ is the polymer–solvent interaction parameter, ΔA_{el} is the elastic free energy of the swollen network, n_1 is the number of solvent molecules and $\Delta\mu_i$ is the chemical potential of ionic groups in the network. When the network is in thermodynamic equilibrium with solvent, the expression given by equation (3) equates to zero.

In the present study, we have a four-component system consisting of PB, NaCl, water and acetone or THF. The interaction parameter χ between the solvent and the polymer cannot be evaluated by the usual methods due to the existence of salt particles. For this reason the terms containing the interaction parameter and the ionic contribution in equation (3) are evaluated together and named as enthalpic contribution ΔH_1 to the chemical potential of the solvent in the swollen system, i.e.[5]

$$\Delta H_1/RT = \chi v_{2m}^2 + \Delta\mu_i/RT = -\left[\ln(1 - v_{2m}) + v_{2m} + (RT)^{-1}\frac{\partial \Delta A_{el}}{\partial n_1}\right] \qquad (4)$$

The first two terms on the right-hand side of equation (4) follow from the theory of polymer solutions, and the third term denotes the potential due to the elastic activity of the network. Within the accuracy of the theory of polymer mixtures and the theory of rubber elasticity, ΔH_1 may be evaluated if the equilibrium swelling is measured and the degree of cross-linking of the network is known. According to the molecular theory, the elastic free energy of a swollen network may satisfactorily be represented by that of the phantom network model[9]. The latter is given by

$$\Delta A_{el} = \frac{3\xi kT}{2}\left[\left(\frac{v_{2m}}{v_{2c}}\right)^{2/3} - 1\right] \qquad (5)$$

where ξ is the cycle rank of the network. For usual cross-linking in the dry state, the volume fraction of polymer during cross-linking, v_{2c}, equates to unity. In the present study, it departs from unity because of the presence of NaCl particles.

Substituting equation (5) into equation (4) and differentiating with respect to the number of solvent molecules results in

$$\Delta H_1/RT = \Delta\mu_i/RT + \chi v_{2m}^2 = -\left[\ln(1 - v_{2m}) + v_{2m} + \frac{V_1\rho}{M_c}(v_{2m}/v_{2c})^{1/3}\right] \qquad (6)$$

where V_1 is the molar volume of the solvent, evaluated from the molar volumes of acetone (73.43 cm^3 mol^{-1}) and THF (81.94 cm^3 mol^{-1}). ρ is the density of the network (ρ = 1.01 g cm^{-3} for PB 1203). The volume fraction v_{2m}, of polymer at equilibrium swelling is defined as the ratio of polymer in the dry state to that in the swollen state. Taking into consideration the solvent uptake of the salt particles in the spatially heterogeneous PB/NaCl mixture, the value of v_{2m} may be obtained from the measured Q values by the expression

$$v_{2m} = [Q(1 + c) - cr]^{-1} \qquad (7)$$

where c is the volume ratio of dry NaCl to dry polymer and r is the ratio of the volume of NaCl mixture to the volume of dry NaCl. The value of c is set during cross-linking. However, the amount of solvent uptake by the salt particles at

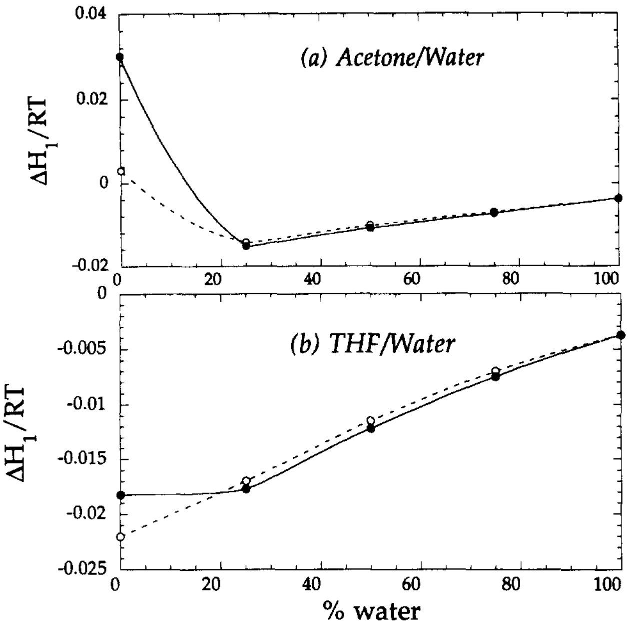

Figure 9 (a) Enthalpic contribution to chemical potential of solvent for sample 30/5 in water/acetone mixtures. The solid and dashed curves refer to the cases where the uptake of solvent by NaCl is neglected, and taken into consideration, respectively. The two cases are represented by equations (9), () and (8), respectively. (b) The same results for sample 30/5 in water/THF mixtures

equilibrium swelling is not known, and is expected to be different for each system. The ratio r may vary in the range $1 \leq r \leq Q$. The limit $r = 1$ is obtained for the case when the filler remains dry. For this case,

$$\nu_{2m} = [Q + c(Q - 1)]^{-1} \qquad (8)$$

The upper limit for r is for the case when the swelling of the filler equates to that of the macroscopic sample. For this case,

$$\nu_{2m} = 1/Q \qquad (9)$$

The enthalpic contribution for samples 30/5 containing 30% NaCl and 0.1% DCP in water/acetone and water/THF are plotted against solvent composition in *Figure 9*(a) and (b), respectively. The dashed curve in each figure is obtained by using equation (8), and the solid curves are obtained with equation (9). The two curves almost coincide in mixtures having ≥ 20% water by volume, which shows the remarkable independence of the results at higher water contents from the use of equation (8) or equation (9). Both acetone and water are poor solvents for PB. For this reason the χ parameter between PB and these solvents is large and positive. Consequently, large positive values are observed for the enthalpic contribution in pure acetone. Pure THF, on the other hand, is a good solvent for PB, leading to a negative enthalpic contribution. Upon dilution of the solvent with water, a negative (favourable) enthalpic contribution to mixing (swelling) occurs in both cases.

CONCLUSION

Experiments on PB networks containing different amounts of NaCl particles showed widely varying degrees of swelling in different solvents. In general, a synergistic effect has been observed, in the sense that the extent and rate of swelling is significantly higher in solvent mixtures compared to those in pure solvents. Moreover, the long time behaviour of swelling was significantly different for the different co-solvents. In particular, the large degrees of swelling obtained in the THF/water system persisted for over 2 months without deswelling. In the water/acetone system, the networks either continued swelling or exhibited deswelling after reaching a maximum swelling, depending on the composition of the solvent. The rates of diffusion of solvent into the networks also showed significant dependence on the type of solvent. These results invite attention to the possible use of the hydrocarbon–NaCl networks as super-absorbent polymeric systems. The latter, based mostly on polyacrylates, play a major role in absorbing body fluids as personal care products[10]. The use of hydrocarbon systems, such as in the present case may also be considered as possible alternatives for biotechnological applications such as drug or pesticide release.

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