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A model for the swelling of superabsorbent polymers

H. Omidian[a], S. A. Hashemi[a,]*, P. G. Sammes[b] and I. Meldrum[b]
[a]*Polymer Research Centre of Iran, P.O. Box 14185/458 Tehran, Iran*
[b]*Department of Chemistry, Brunel University, Uxbridge, Middlesex UB8 3PH, UK*

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When dry superabsorbent polymers are immersed in water they swell by two or three orders of magnitude. Both the ultimate degree of absorption and rate of absorption are important in practical applications. Experimentally they depend on the type of polymerisation, e.g. suspension or solution; the monomer composition, e.g. proportions of acrylic acid, sodium acrylate and acrylamide; and on the type of cross-linker, e.g. water or oil-soluble. In this paper relationships between the various parameters are investigated in order to improve understanding and to identify the basic limiting factors. Plots of swelling against time have been found to fit mathematical relationships which are based on spring and dashpot models and are applied in the polymer field to viscoelastic systems. By associating the spring element with resistance to expansion by the absorbent and the dashpot element with resistance to permeation and by relating the behaviour of the elements to the polymerisation system, underlying molecular factors influencing absorption behaviour could be identified. Relationships were also established between the ultimate degree of swelling and the ratio of cross-linker to monomer for the different polymerisation systems. © 1998 Elsevier Science Ltd. All rights reserved

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INTRODUCTION

Superabsorbent polymers can swell up to thousands of times their own weight in aqueous media[1]. Their swelling behaviour is characterised mainly by the amount of water they absorb and the rate of absorption[2–5]. Both are important in practice and most applications, such as diapers, require them to be optimised[6]. They are determined by thermodynamic and kinetic factors respectively but the cross-link density is particularly influential[7,8]. Although these materials have been commercialised for some time there would appear to be considerable scope for gaining more insight than has been published so far into relationships between these swelling characteristics and molecular structure.

The work reported here is an exploratory investigation of the influence of cross-linking agents on the capacity for absorbing water and on the rate of absorption for acrylate polymers using both inverse suspension and solution polymerisation which are the main processes used industrially. The data are examined to seek relationships between polymerisation variables and swelling characteristics.

EXPERIMENTAL

Materials

The monomers and toluene were supplied from Merck. Acrylic acid was purified by steam distillation through a column packed with copper gauze to inhibit polymerisation. Acrylamide was crystallised from methanol. Methylene bisacrylamide was also recrystallised from methanol. Sodium hydroxide (AnalR) was supplied from BDH chemicals. Ethyl cellulose (degree of substitution ranging from 2.42–2.53, N-14) was purchased from Hercules. Sorbitan mono-oleate was supplied by Aldrich. Potassium peroxydisulfate was recrystallised from distilled water.

PROCESSES

Inverse suspension polymerisation

S1 series of experiments (ethylene glycol dimethacrylate as cross-linker). To a 1 litre round-bottomed five-necked flange flask fitted with mechanical stirrer, dropping funnel, an efficient condenser, nitrogen inlet and thermocouple was added toluene (150 g), and solutions of sorbitan mono-oleate (0.8 g in 23.6 g toluene) and ethyl cellulose (3.0 g in 50 g toluene). The mixture was heated to 80°C under a head of nitrogen in an oil bath and constantly stirred (400 rpm-paddle type mechanical stirrer) until a bright yellow solution was obtained (approximately 15 min). A 20 ml volume of a toluene solution of ethylene glycol dimethacrylate (cross-linker) (0.4654, 2.2963 and 4.5836 mol% on monomer for the S1.1, S1.2 and S1.3 preparations respectively) was subsequently added to this mixture to yield the continuous phase of the inverse suspension.

A binary mixture of aqueous solutions (the discontinuous phase) of acrylic acid (monomer; 30 g in 7.5 g water) [previously partially neutralised with sodium hydroxide (12.52 g in 36.18 g of water, density of this solution is about 1.2815 g cm^{-3}) to achieve 75% conversion to the sodium acrylate] and potassium persulphate (0.15 g in 6 g of water) was introduced to the stirred, pre-heated continuous phase over 10 min whereupon it was observed that the mixture became rapidly turbid. The reaction mixture was stirred at 80°C for 90 minutes from the moment monomer was introduced to the continuous phase after which the reaction liquor was allowed to cool to room temperature. Supernatant liquor was subsequently decanted to waste and the

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* To whom correspondence should be addressed

insoluble polymer washed first with methanol (400 ml) for 30 minutes then dried at 60°C in a forced air oven overnight before being stored in an air-tight container until required.

S2 series of experiments (methylene bisacrylamide as cross-linker). The S1 experiment was repeated using the following reagents:

Continuous phase: toluene (170 g); sorbitan mono-oleate (0.8 g in 23.6 g toluene); ethyl cellulose (3.0 g in 50 g toluene).

Dispersed phase: The preparation for the cross-linker solution was as follows. Into 4.0 g of doubly-distilled water, the methylene bisacrylamide (0.0, 0.0467, 0.0779 and 0.109 mol% to the total monomer for S2.0, S2.1, S2.2 and S2.3 respectively) was dissolved at room temperature with frequent shaking for 30 min. The same amount of water was used to dissolve the initiator. The cross-linker solution was combined with the other aqueous solutions (acrylic acid/ sodium acrylate monomers and potassium persulphate initiator) just before starting the reaction.

S3 series of experiments. The S1 experiment was repeated using the following reagents:

Continuous phase: 145.6 g of toluene; sorbitan mono-oleate (0.72 g in 23.6 g toluene); ethyl cellulose (2.7 g in 50 g of toluene).

Dispersed phase: acrylic acid monomer (15 g in 7.5 g of water) neutralised with sodium hydroxide (6.26 g in 18.11 g water); acrylamide monomer (15 g in 13.39 g water); methylene bisacrylamide cross-linker (0.0, 0.0467, 0.0779 and 0.109 mol% to the total monomer in 4.0 g water for S3.0, S3.1, S3.2 and S3.3, respectively); potassium persulphate (0.15 g in 4.0 g water).

Solution polymerisation

B1 series of experiments. Aqueous solutions of the acrylic acid monomer (15 g in 7.5 g water) neutralized with sodium hydroxide (6.26 g in 18.11 g water), acrylamide monomer (15 g in 13.39 g water), methylene bisacrylamide cross-linker (0.0, 0.0077, 0.0155, 0.0467 and 0.0779 mol% to the total monomer in 4.0 g water for B1.0, B1.1, B1.2, B1.3 and B1.4 respectively) and potassium persulphate (0.15 g in 4 g water) were prepared. Into a 1 l open beaker immersed in an oil bath and heated up to 80°C, the combined above solutions were poured in under magnetical stirring (400 rpm). The reaction mixture was left stirring until gel point when the magnetic stirrer follower bar was stopped due to the high viscosity of the reaction mixture. The oil bath was removed at this moment and the beaker contents were allowed to reach room temperature. The resulting rubbery gel was removed from the reaction vessel and cut into small pieces (dimensions of 2–5 mm) using a pair of scissors. The pieces were dehydrated in methanol, and after decanting the supernatant spread over an aluminium foil and heated overnight in an air-circulating oven at 60°C to dryness. The presumably dried gels were ground by a hammer type minigrinder (laboratory scale), then screened using a robot sifter. The classified particles were stored in tightly-stoppered bottles until required.

Swelling measurements

A 1 gram (±0.001 g) polymer sample under test (50–60 mesh) was dispersed into 2 l of doubly-distilled water and allowed to swell with mild agitation. The steady state uptake of water or equilibrium swelling was determined by allowing overnight for absorption. The dispersion of water-swollen particles in water was filtered through a 100-mesh wire gauze and surface water of the filtered swollen particles dried carefully using a piece of a soft open-cell polyurethane foam until they no longer slipped from the sieve where it was held vertical. For measuring swelling kinetics or rate of absorption, the water-absorbed samples were taken from the solution at prescribed periods and then exposed to swelling measurements through the above procedure. To obtain a reliable value for swelling at any time, five values were averaged, although the value of standard deviation for this method is ±2.1 g of water absorbed per g of dry superabsorbent. The quantitative figures of swelling were calculated as follows:

$$W_t = [W_{ss} - W_{ds}]/W_{ds}$$

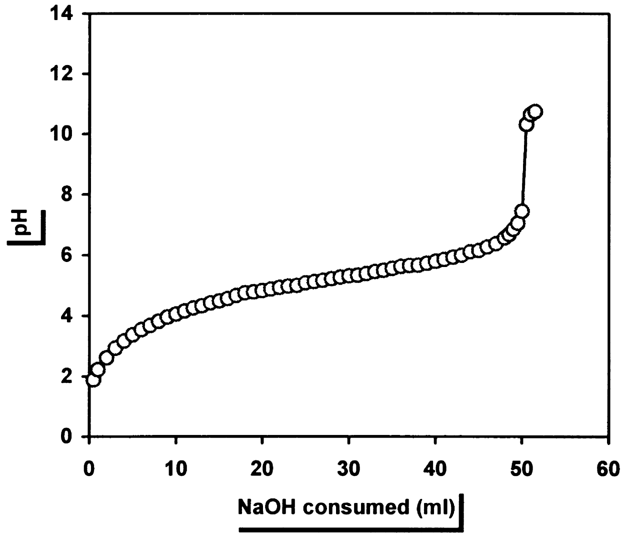
where:

(1) W_t = Swelling at time *t*.
(2) W_{ss} = Weight of the swollen or water-absorbed polymer at time *t*.
(3) W_{ds} = Weight of the original dry superabsorbent polymer.

All of the measurements were done on the original polymer without isolating its sol content.

Neutralisation

To obtain the desired degree of partial neutralisation of acrylic acid (i.e. the acid:salt ratio) the required amount of sodium hydroxide was determined by the following diagram. To sketch the latter, diluted acrylic acid (30 g in 7.5 g doubly-distilled water) was titrated by 25.4% w/w NaOH solution. According to the diagram, 75% neutralisation degree (acid:salt molar ratio of 1:3) is obtained when the pH assumes a value of 5.73.



Sol content measurement

To a 1 l beaker containing 500 ml of 1.0% sodium chloride solution, 0.5 g (±0.0001 g) of dried superabsorbent (50–60 mesh) was poured. The dispersion was kept aside at room temperature for a period of 72 h. After several shaking and standing cycles to homogenise the liquid phase, the dispersion was allowed to settle. The supernatant liquid was subsequently filtered through a sintered glass, and examined using a PU 8800 UV/VIS (double beam) spectrophotometer and 1 cm quartz cells. A 1% NaCl solution was used as reference and the scanning was performed through the range of 250–190 nm. With our acrylate superabsorbents the λ_{max} appears at about 206 nm.

Water content measurement

A PL-TGA 1500 was used. Samples were examined under a nitrogen atmosphere at an isothermal temperature of 200°C, for a period of 30 min. By this time all the water contained into the polymer was isolated.

RESULTS

The scope for modifying the swelling behaviour of superabsorbents was investigated by making changes to the polymerisation process and conditions of polymerisation. Two kinds of polymerisation process were used. One was by inverse suspension and the other was in solution. For the inverse suspension process both oil and water-soluble cross-linkers were tested. The monomers comprised acrylamide, acrylic acid and sodium acrylate. The monomer concentration in the aqueous phase was 40.0% by weight throughout. In each case acrylic acid and sodium acrylate were present in the molar ratio of 1:3. In some cases acrylamide was present. The relative proportions of the monomers and cross-linkers were varied. The degree of swelling at different times was measured for each set of conditions. The features of the processes and observed swelling measurements for all the polymerisations are given in *Table 1*.

The swelling behaviour of the polymers, were characterised by measuring the initial fast rate of swelling, measured as gram of water absorbed per minute, the time taken to reach the steady state and the degree of swelling (water uptake) at this time. In *Table 1* the degree of swelling ranges from about 200 to 800 g/g whereas the time to reach a steady state ranges more widely from about 1.6 to 40 min and the initial rate of swelling ranges from about 90 to 1200 g min^{-1}. The highest degrees of swelling were obtained for inverse suspension polymerisation with an oil-soluble cross-linker at its lowest concentration and for solution polymerisation at the lowest concentration of cross-linker. For each set of polymerisation conditions the steady state swelling decreased as the concentration of cross-linker was increased.

The first two sets of polymerisations (*Table 1*), S1 and S2, differed only in the nature of the cross-linker. Ethylene glycol dimethacrylate and N,N-methylene bisacrylamide were used as oil-soluble and water-soluble cross-linkers, respectively. A much higher concentration of the oil-soluble cross-linker was required to form a gel and prevent the polymer from dissolving, presumably because it partitioned primarily into the oil phase. For example, comparing samples S1.3 and S2.1 indicates that about 100 times as much oil-soluble cross-linker as water-soluble cross-linker was required to give a steady state swelling of 500 g/g. Also, increasing the concentration of oil-soluble cross-linker by a factor of 10 decreased the steady state swelling to 65% of its previous value whereas increasing the concentration of water-soluble cross-linker by a factor of only 2.3, in the S2 set of polymerisations, cut the swelling by half.

The S2 and S3 polymerisations differ only in that acrylamide was present in S3 and not in S2. Although the steady state swelling was somewhat higher for S2, there was a much more striking difference of an order of magnitude in the initial rate of increase of swelling and in the time taken to reach a steady state, i.e. acrylamide speeded up swelling by this extent. The S3 and B1 polymerisations both contained acrylamide but differed in the type of process. This affected the rate of swelling much more than the final degree of swelling. Polymer made by the inverse suspension process swelled faster than that obtained from the solution process by a factor of about 8.

Although the rate of change of swelling with time falls off rapidly, simple power law expressions did not fit the

Table 1 Feature of inverse suspension and solution methods as well as parameters fitted to experimental swelling data

Exp.No.	Process type	X^a type	M^b Present (mol ratio)	[C]/[M] mol%	Initial slope g min^{-1}	Time to constant swelling min	Steady state swelling g/g	σ_0/E g/g	τ_0 min	Sol^c content	Water content
S1.1			AAc	0.2375	89.7	38.67	756.2	760	7.3	—	6.254
S1.2	I.S.	O.S.	NaA	2.2963	99.0	28.08	617.0	620	5.3	1.931	5.281
S1.3			(1:3)	4.5836	86.0	23.84	487.5	490	4.5	1.828	5.316
S2.0				0.0	—	—	—	—	—	2.080	—
S2.1	I.S.	W.S.	AAc	0.0467	123	16.95	517.4	520	3.2	1.047	5.169
S2.2			NaA	0.0779	82.5	15.36	288.5	290	2.9	0.959	4.812
S2.3			(1:3)	0.109	86.0	13.24	253.7	255	2.5	0.901	4.649
S3.0			AAc	0.0	—	—	—	—	—	2.645	—
S3.1	I.S.	W.S.	NaA	0.0467	1178	1.58	422.8	425	0.3	1.623	8.605
S3.2			AAm	0.0779	825	1.85	218.9	220	0.35	0.872	6.707
S3.3			(1:3:4)	0.109	785	1.74	203.9	205	0.33	0.786	7.707
B1.0				0.0	—	—	—	—	—	4.440	6.114
B1.1			AAc	0.0077	162	21.19	779.5	783.5	4.3	3.70	6.407
B1.2	S	W.S.	NaA	0.0155	144	15.89	505.9	508.5	3.0	—	6.417
B1.3			AAm	0.0467	123	12.18	323.4	325	2.3	2.682	6.805
B1.4			(1:3:4)	0.0779	95	10.59	228.8	230	2.0	2.652	6.343

[a] Cross-linker
[b] Monomer(s)
[c] As UV absorbance in arbitrary units
Abbreviations: I.S. – Inverse suspension; S – Solution; O.S. – Oil-soluble; W.S. – Water-soluble; AAc – Acrylic acid; NaA – Sodium acrylate; AAm – Acrylamide

experimental data satisfactorily. A sharper transition from the high initial rate to the slow rate towards the end of the swelling process needed to be explained. This was provided by using a Voigt model[9,10] which consists of a spring and dashpot in parallel. When a stress σ_0 is applied at time t_0 the strain response ε of the model with Young's modulus E is given at time t by an expression of the form:

$$\varepsilon(t) = \sigma_0/E[1 - \exp\{(t_0 - t)/\tau_0\}] \qquad (1)$$

where τ_0 is known as the retardation time and determines the influence of the dashpot. Using this expression a better fit was obtained to the experimental data for all the polymerisations.

So, the experimental swelling data follows a typical exponential relationship which has two characteristic constants, i.e. σ_0/E and τ_0. The quantitative value of the former can be estimated from the values of the steady state swelling of the individual samples, since the water transport is diffusion-controlled. For the latter, the reciprocal value of the slope of the plot of Ln[1-W_t/W_∞] against time has been used (W_∞ is equilibrium or steady state swelling). Since such a plotting is a typical first order kinetics, the slope is a measure of the characteristic time (τ_0) for the individual superabsorbent polymers. The theoretical curves sketched using these two characteristic parameters, i.e. σ_0/E and τ_0 were used to obtain the values of the initial slope and the time needed to reach constant swelling quoted in *Table 1*. With the former, the slope of the line passed the point zero and the point of 70% fractional swelling was determined. For the latter, the point in which the swelling value diverged from the value of the σ_0/E was considered.

For each of the sets of polymerisations the steady state swelling decreased as the ratio of cross-linker to monomer was increased. The relationship was explored further by testing different functions. For this purpose, the extent of swelling was assumed to be zero when only cross-linker was present and not monomer. Moreover, in order to obtain a more reliable fit, another experimental point was obtained for each inverse suspension series. So that, at 0.05 molar percent of cross-linker to monomer in S1 series, an equilibrium swelling value of 789 g/g was obtained. On the other hand, at 0.0155 molar percent of cross-linker to monomer, the equilibrium swelling values of 752 and 573 g/g were respectively obtained for S2 and S3 series. So, it is evident from the data for S1 polymerisations, that any relationship between cross-linker concentration and equilibrium swelling was quite indirect. The best fit (equation (2)) was obtained with a power law plotting W_∞ against [C]/[M] having an exponent in [C]/[M] of about 0.1 (*Figure 1*).

$$W_\infty = 616/\{[C]/[M]\}^{0.1}\,\text{g/g} \qquad (2)$$

where W_∞ is equilibrium (steady state) swelling.

For the S2 and S3 inverse suspension and B1 solution polymerisations, with the water-soluble cross-linker, the following relationship was obtained in which the power law exponent was found to be about 0.6 (equation (3)):

$$W_\infty = A/\{[C]/[M]\}^{0.6}\,\text{g/g} \qquad (3)$$

where A = 64 g/g for S2, 49 g/g for S3 and 41 g/g for B1. The relationships were plotted in *Figure 2* for the two first and in *Figure 3* for the last one.

DISCUSSION

In the polymer field the spring and dashpot model is best known for its use in modeling creep and relaxation in viscoelastic materials. The spring and dashpot elements respectively provide the immediate elastic and delayed viscous strain responses to an externally applied stress. Any number of arrangements of these elements can be devised to simulate a particular kind of time dependence, however complex. In molecular terms the elastic responses are the

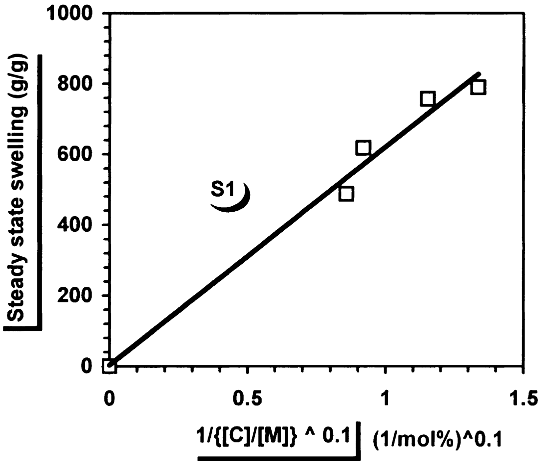


Figure 1 Relationship between steady state swelling and ratio of cross-linker to monomer for S1 samples of inverse suspension polymerisation

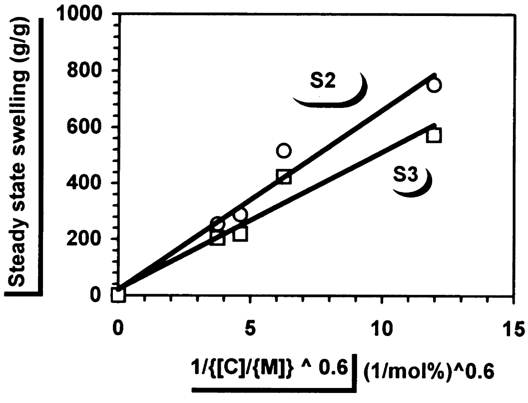


Figure 2 Relationship between steady state swelling and ratio of cross-linker to monomer for S2 and S3 samples of inverse suspension polymerisation

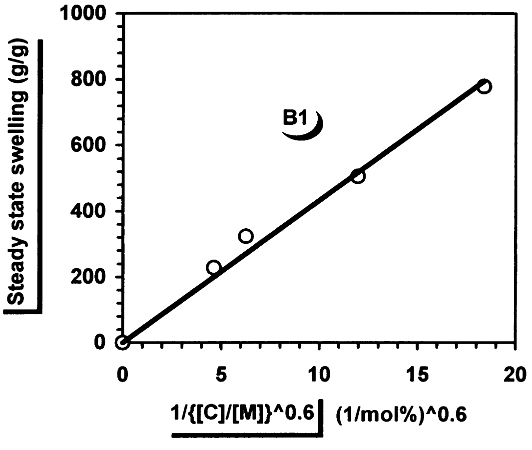


Figure 3 Relationship between steady state swelling and molar ratio of cross-linker to monomer for B1 samples of solution polymerisation

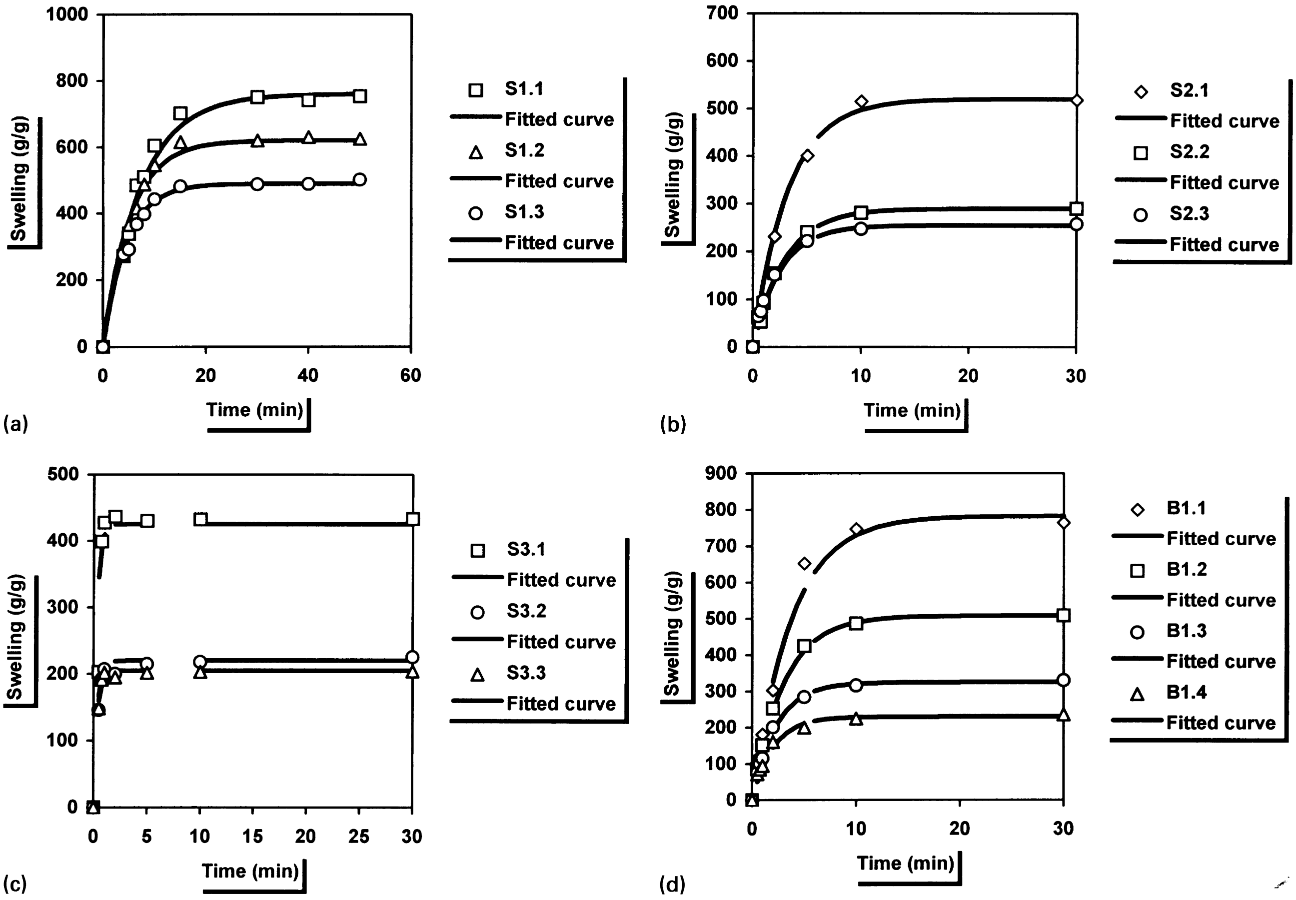


Figure 4 Curves fitted to the experimental swelling values of the individual samples

fast, reversible changes in bond length, shape and orientation which occur when stress is applied to a polymer chain. The viscous responses are the slower, irreversible, energy dissipating processes which occur as a result of the molecular movements. Elastomers show particularly large effects.

For the absorbent application one of the simplest arrangements of elements, a spring and dashpot in parallel, known as the Voigt model, has been found to suffice for most of the swelling *VS* time observations [*Figure 4a–d*]. In this case there is no externally applied stress. Instead stress is exerted on the network of polymer chains in the absorbent by the interaction with water. The system differs fundamentally from the stretching of a dry rubber in that the volume increases a lot with time and the chains become separated from each other. Consequently the modulus in equation (1) cannot have the same significance for absorbents. Although Flory[11], in describing the thermodynamics of swelling, referred to an inverse relationship between the equilibrium swelling of a rubber by a solvent and the 'modulus' of the rubber, this was for a dry rubber[11] and the time dependence of swelling was not discussed. Also the absorbents were dried before coming into contact with water and were, therefore, presumably in a glassy state.

When water comes into contact with an absorbent, which is initially in the glassy state, it has to penetrate between the chains and separate and mobilise them for swelling to occur. The process becomes self accelerating and a sheath of swollen polymer can be envisaged to form. Water then has to travel through the sheath to reach the interior of dry polymer. This description suggests the possibility of replacing the resistance to stretching, or modulus, in the viscoelastic model with a resistance to permeation and swelling for absorbents.

In general, permeation is governed by Fick's laws of diffusion and the degree of absorption by a material obeying these laws is proportional to the square root of time. This is known as Case I sorption but in some cases the amount of absorption is observed to be directly proportional to time and this is known as Case II sorption. Case I occurs when the rate of advance of permeant is determined by the rate of diffusion and Case II occurs when the rate of advance is determined by the rate of expansion of the material[12]. In Case II sorption the permeant front is much sharper than in Case I, and high stresses are generated at the sharp boundary between the swollen and non-swollen material. By identifying the type of diffusion which takes place when absorbents swell, the rate limiting factor becomes known and this is what has to be tackled for absorption to be made faster.

The rate of swelling for all of the absorbents can readily be obtained from equation (1) for the Voigt model and is given by the expression:

$$d\varepsilon/dt = (\sigma_0/E\tau_0)\exp\{(t_0 - t)/\tau_0\} \qquad (4)$$

In the early stages of swelling when $t_0 – t \ll \tau_0$ the exponential term is close to 1 and so the rate changes slowly with time, i.e. it approximates to Case II sorption.

For the B1 series of polymers (in *Table 1*) which were prepared by the solution process at the lowest cross-linker ratio of 0.0077 g/g the degrees of swelling calculated using the parameters given in *Table 1* for equation (1) at times of $\tau_0/4$ and $\tau_0/8$ are respectively 22.2% and 11.75% of the steady state value. These values are much closer to being proportional to time^1 than to time$^{1/2}$ and they demonstrate that Case II sorption applies over a substantial part of the swelling. The same applies to the other members of this series B and to the other series as well, because it is only the ratio $(t_0-t)/\tau_0$ that matters. At longer times the ratio increases and swelling changes more slowly with time. For example at times of τ_0 and $2\tau_0$ the degrees of swelling for the same B1 polymer as before become 63.2% and 86.5%. These values are close to a square root relationship and so it follows that the overall swelling behaviour changes progressively from Case II in the early stages to Case I in the second half. The same Case II sorption process might even persist to a late stage of swelling for the last dry material to be reached by the water but on too small a scale to be detected.

It also follows that the rate of swelling is restricted in the early stages by the resistance of the polymer molecular structure to diffusion or expansion. Diffusion could be resisted by unfavourable interactions between the water and polymer chains or by close packing and low chain mobility. Expansion could be opposed by bonding between chains and by lack of mobility within chains. These factors may also be expected to influence the polymer behaviour at an earlier stage when it is dried prior to testing and because this comes before the swelling stage their influence in the drying process may well predetermine the swelling behaviour. The experimental data provide information about the effect of changes in cross-linking, monomer composition and type of polymerisation process on the degree and rate of swelling.

The fastest rates of swelling by far occurred for the inverse suspension polymerisation process with acrylamide present as a monomer, i.e. in the S3 series. The time taken to reach constant swelling (1.58–1.85 min) and the initial rate of swelling (1178–785 g min^{-1}) were about an order of magnitude faster than for the S2 series (13.24–16.95 min and 86.0–123 g min^{-1}) which differed only in the absence of acrylamide. Clearly the presence of acrylamide (half the total molar monomer concentration) speeds up absorption. As may be seen in *Table 1* the first parameter of the Voigt model is a little lower for the S3 series than for S2 but the second parameter for S3 is an order of magnitude lower than for S2 and so, although the effects are opposing, it is the second parameter which dominates and is associated with the higher rate of swelling for S3.

For viscoelastic systems the second parameter which is also known as the retardation time determines the magnitude of the viscous component in the Voigt model and the extent to which the spring element is retarded by the dashpot. This suggests that just as the spring element and first parameter in the model are thought to represent the resistance to expansion of the polymer network in the absorbent, the dashpot element and second parameter may represent the resistance to permeation by water. If so, it follows, from the values of the parameters for the S2 and S3 series, that introducing acrylamide into an acrylic acid/sodium acrylate copolymer speeds up absorption by lowering resistance to permeation. The replacement of ionic monomer segments by non-ionic ones would be expected to reduce the stress responsible for the expansion of the polymer network by decreasing the number of ionic repulsions and accounts for the reduction in the first parameter since this is the ratio of stress to modulus for the absorbent system. Neither is measured on its own, unlike the viscoelastic system where the stress is applied externally and is readily measured.

The general observation of increased rate of permeation of water (through decrease in τ_0) with increase in cross-linker concentration can be described as follows. If the polymer network acted only as a barrier against diffusing water molecules, the decreased mobility of water is expected for highly cross-linked networks. Thus, rate of water uptake should be increased by decreasing in cross-link density[13]. However, an acrylic-based superabsorbent is strongly hydrophillic polymer, which attracts water molecules instead of repelling them. It must generate a strong thermodynamic force that makes water diffuse so as to cancel the gradient. As a result, it may be expected that a denser network offers a higher rate for water uptake. Moreover, it has been described that the swelling process of a polyacrylamide gel is in fact the polymer network diffusion into water rather than by that of water molecules into the polymer network[14]. Since the local motion of a polymer network increases with increasing the elastic modulus of the network, the diffusion coefficient of water is expected to increase with increasing the cross-link density. This relationship has been already found for the sodium acrylate gels[15].

The increase in permeability resulting from the introduction of acrylamide into the polymer is attributable to higher chain mobility or more free volume. On completion of polymerisation there is sufficient water present to permit a high level of mobility but this changes as drying progresses.

According to data quoted in *Table 1*, all the absorbents contain a substantial amount of water in their network even after the drying process. This type of water can be called presumably bound water which cannot be readily isolated from the polymer. In studying the thermal stability and degradation mechanism of poly (acrylic acid) and its salt, thermogravimetry analysis indicated that the initial weight loss below 100°C is due to the release of water absorbed by the polymer which is free water[16]. In other work, the TGA curves of four different samples of polyacrylamide displayed one thing in common: the loss of water up to a temperature of approximately 250°C[17]. Using the same technique, it was found that this type of water can not escape from the network at temperatures below 200°C, of course, in a short period of time.

On the other hand, the transition from glassy to rubbery state in the polymer is characterised by a threshold concentration of water which is the minimum local concentration of water required for the glassy state to be transformed into rubbery state[18]. The threshold concentration of water can be measured for instance using various compositions of water/acetone mixture. All series of absorbents here, are insoluble in acetone but swellable in water. Increased contribution of water in binary mixture of these two solvents results in gradual or sudden glass-to-rubber transition. Based on our findings, at a same cross-linker concentration, swelling in medium of 7:1 volume ratio of the acetone/water for the S2 samples was ignorably low in contrast to obtaining an appreciable amount of swelling for the S3 samples. In swelling medium of 1:1 volume ratio of the two solvents, S3 samples could swell up to 10 times more than that of their S2 counterparts. These observations showed us that the threshold concentration of water which affects the glass-to-rubber transition should be much lower for the S3 samples compared to their S2 counterparts. On the other hand, at a same cross-linker concentration, S3 samples contained a larger amount of bound water than their S2 counterparts (1.6 times), i.e. 8.605, 6.707, 7.707 against 5.169, 4.812, 4.649 respectively. If the bound water can in part contribute to the threshold concentration of water, it can be expected that the polymer which is originally contained in higher amount of bound water (say S3 samples) assumes shorter times to reach its transition point. The other point is that the mobility arises due to incorporation of acrylamide into the polymer chain. Acrylamide screens the acrylate anions by which the polymer chain assumes more coiled conformations than extended alternative. Another point of consideration is as the water level drops and interaction between chains becomes increasingly important the difference in polarity between the sodium acrylate and acrylamide groups suggests the likelihood of segregation which would affect chain packing and perhaps the free volume.

Another feature of the S3 series is that the second parameter did not become smaller with more cross-linking as the others did. Since a decrease in the second parameter is interpreted as a lowering of resistance to permeation it follows that cross-linking lowered this resistance for series S1, S2 and B1, presumably by preventing the chains from packing as closely in the drying step. Cross-linking also reduced the first parameter but this has the opposite effect of slowing the rate of absorption, presumably by increasing the resistance of the network to expansion. The net result of the opposing effects was for the initial rate of absorption to become slower with more cross-linking for all the series.

The semi-quantitative values of sol content of individual series of samples were plotted against cross-linker concentration (*Figure 5*). With any superabsorbents we studied so far, whether home-made or commercial, the efficiency of cross-linking has not been complete. So that, some part of the polymer chains can not be incorporated into the cross-linked network depending on the amount and efficiency of the cross-linker used. These chains can be extracted from the network using water or saline as a solvent. The term sol content refers to the amount of the water-soluble or saline-soluble fraction of the original network. Although the data obtained from UV spectroscopy cannot offer the quantitative value of the soluble chains, it has been used here as a semi-quantitative mean to assay cross-link density of the networks. Generally speaking, the sol content decreased with increase in cross-linker amount as the swelling did, according to the data in *Table 1*. The initial rate of swelling can partly be related to the amount of soluble material in the network, although the rate also depends on the maximum capacity of absorption. This behaviour can be attributed to an initially large chemical potential or osmotic driving force for swelling due to the presence of solute within the gel[19].

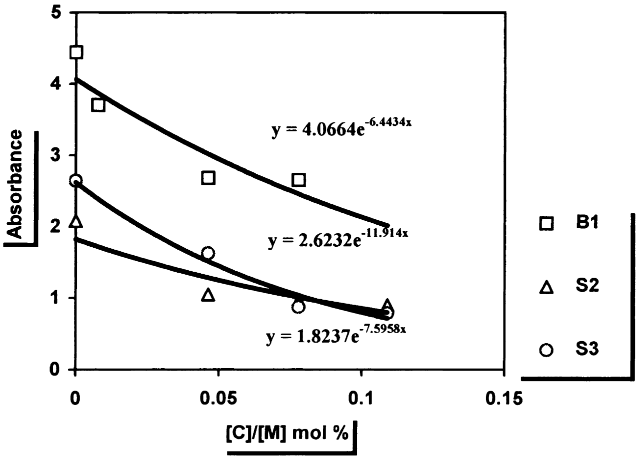


Figure 5 The UV absorbance of the sol samples against cross-linker to monomer concentration for the individual series

Through the range of cross-linker concentration which was studied here, samples were obtained by solution polymerisation offered higher concentration of soluble materials. In addition, decreasing trend of sol content with increased cross-linker concentration follows a rather similar rate with S2 and B1 series which is more or less similar to the decreasing trend in values of retardation time. A different position can be observed for S3 series. Any reduction in sol content is strongly dependent on cross-linker concentration as can be seen in its trend line (comparing the exponent 11.91 with the exponents 6.44 and 7.59 for the two other series).

Comparison of the S3 and B1 series in *Table 1* shows that the solution process gave much slower absorption than the inverse suspension process. The data show that this was mainly associated with the second parameter being lower for S3 although the first parameter also contributed by being smaller at the same level of cross-linker. This indicates that permeation is slower for products made by the solution process. If the polymer particles formed in the inverse suspension process gave a porous structure after drying and the solution process gave a continuous mass then this would account for the difference. The other reasons can be found somewhere in the process of manufacturing. The big difference was the atmosphere under which the polymerisation was carried out. With all the inverse suspension formulations, a nitrogen blanket was used, whilst with the solution systems, the reacting mixture was open to the free atmosphere. The other difference was the time of reaction, which was much too long for the suspension system. Moreover, at a same cross-linker concentration, the extractable materials within the solution products were more than of the inverse suspension products. These can be responsible for a decreased swelling characteristics in the solution products.

The longest times to reach steady state swelling were taken by the S1 series in which the cross-linker was oil-soluble. The last member, S1.3, of this series had almost the same steady state swelling as the first member, S2.1 of the S2 series, which differed only in the water solubility of the cross-linker. The first parameter was a little lower for S1.3 indicating less resistance by the polymer network to expansion since the monomer composition was the same. The retardation time for S1.3 was longer than for S2.1 indicating lower permeability. Overall the permeability effect was more pronounced and made swelling slower. Although some of this effect may be attributable to a lower degree of cross-linking another factor may have been the distribution of cross-linker. As the cross-linker became consumed during polymerisation more could diffuse from the oil phase in the case of the oil-soluble cross-linker but not in the case of the water-soluble one. This could have resulted in a higher degree of cross-linking at the outside of polymer particles than at the centre for the oil-soluble cross-linker.

The finding that, the steady state swelling was inversely proportional to about 0.6 power exponent of the molar ratio of cross-linker to monomer for S2, S3 and B1 polymerisations is quite close to the 0.6 relationship derived thermodynamically[11]. The relationship between the steady state swelling and cross-linker to monomer ratio was different for the inverse suspension polymerisations in the presence of an oil-soluble cross-linker. When the cross-linker was oil-soluble, swelling became less dependent on the amount of cross-linker than for the water-soluble counterpart, presumably as a result of most of the cross-linker existing in the oil phase.

CONCLUSIONS

Measurements of the rate of swelling of absorbent polymers in water from a dry state showed substantial differences depending on the type of polymerisation process, monomer composition and amount of cross-linker. The fastest swelling was given by inverse suspension polymerisation of acrylic acid with sodium acrylate and acrylamide. A good fit to the swelling data was obtained using a two parameter Voigt model which consists of a spring and dashpot in parallel. By assigning the spring parameter to the resistance to expansion of the polymer network and the dashpot parameter to the resistance to permeation, the swelling characteristics of the different absorbents could be accounted for in more fundamental terms.

The model approximates to Case II sorption in the early stages of the swelling process and to Case I in the later stages. This shows that the rate controlling process occurring in the early stages is the advance of a water front through the polymer with a sharp profile which generates high stresses on the polymer network and that swelling is restricted by the rate at which water can permeate into the dry polymer network or by the rate at which the network can expand. The inclusion of acrylamide as a monomer substantially improved the permeability. Over the range of cross-linking investigated, permeability increased with cross-linking, probably by restricting the collapse of the polymer network during the drying process. Faster swelling for absorbent made by inverse suspension polymerisation compared with the solution process is attributed to porosity resulting from the formation of the polymer as small particles and intrinsic differences in the nature of the two processes.

For the solution and inverse suspension polymerisations, in the presence of MBA as a cross-linking agent, the steady state swelling was inversely proportional to the exponent of about 0.6 of the molar ratio of the cross-linker to monomer. This was very close to the thermodynamically derived 0.6 power relationship obtained by Flory, for the non-ionic polymers. In the case of EGDMA-cross-linked materials, the dependence was much weaker. This can be attributed to the partitioning of the oil-soluble cross-linker mainly into the continuous organic phase.

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