

Modified acrylic-based superabsorbent polymers (dependence on particle size and salinity)

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Received 19 November 1997; accepted 13 May 1998

Abstract

Superabsorbent polymers have been prepared by inverse suspension and solution polymerisation techniques using different acrylic monomer compositions and different amounts of crosslinking agents. The particle size distributions of products made by inverse suspension polymerisation were determined and the dependence of absorption characteristics on particle size was investigated. As the particle size became smaller, the rate of absorption and ultimate degree of absorption both increased. These observations drew attention to the importance of particle morphology in optimising superabsorbent performance. The experimental data provided further support for a two-parameter Voigt model of the rate of absorption. The effect of increasing the salinity of the water on absorption was also determined. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Acrylic-based superabsorbant polymers; Crosslinking agents; Particle size distribution

1. Introduction

In a series of investigations of the preparation and properties of superabsorbent polymers, a number of aspects have been explored, such as the ultimate capacity for absorbing water, rate of absorption and the dependence of absorption on monomer composition, degree of crosslinking, type of crosslinker and type of polymerisation process, as well as on temperature and initiator concentration [1–4].

In practice superabsorbents are made as powders. Industrially the preferred manufacturing process is based on solution polymerisation, mainly because of its simplicity and low costs. This route gives the product in the form of a continuous mass which is converted to particles by grinding. In the laboratory it is easier to control the polymerisation conditions using inverse suspension polymerisation and the product is obtained in a particulate form simply by drying.

The particulate nature of the product prompted an exploratory investigation of the interaction between particle size and other parameters which influence the overall behaviour of the absorbent. The findings of this investigation are reported here. The range of parameters included crosslinking and monomer composition during polymerisation and salinity during absorption.

2. Experimental

Polymerisation procedures are outlined in the following sections. Further details have been described previously [1–4]. The reactive components in all the polymerisation systems consisted of monomers, crosslinking agent and free radical initiator.

2.1. Inverse suspension polymerisation

Polymerisations were carried out in three series of experiments, denoted S1, S2 and S3. In the S1 and S2 series the monomers were acrylic acid and sodium acrylate in the molar ratio 1:3 and the proportion of crosslinking agent was changed. Sodium acrylate was prepared by partially neutralising diluted acrylic acid solution with a predetermined amount of aqueous sodium hydroxide solution which was added dropwise. In the S1 series the crosslinking agent, ethylene glycol dimethacrylate (EGDMA) was oil soluble and in the S2 and S3 series the crosslinking agent, N, N' methylene bisacrylamide (MBA) was water soluble. In the S3 series acrylamide was also present as a monomer and the molar ratios of the monomers, acrylic acid:sodium acrylate:acrylamide were 1:3:4. The total monomer concentration in the aqueous phase in all three series was kept the same, 40.0% w/w, throughout. Potassium persulphate was

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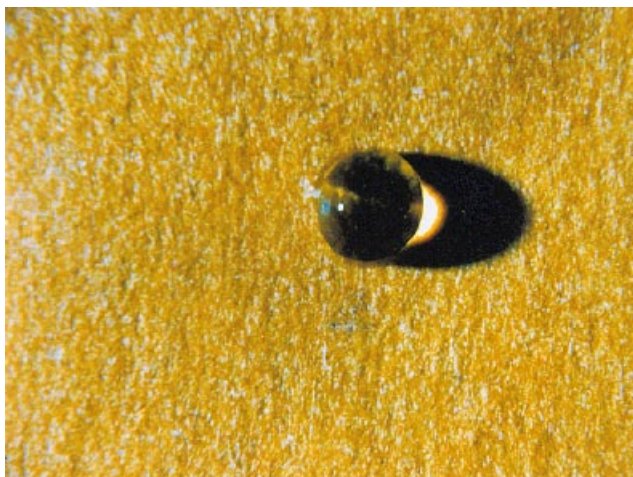


Fig. 1. Photograph of an isolated particle obtained from S2 inverse suspension polymerisations, in its slightly swollen state.

used as the initiator at a concentration of 0.5% w/w of the total monomer. The surfactant for stabilising the suspension was Span 80 (sorbitan monooleate). It was used at a concentration of 0.33% w/w of the continuous phase, toluene (243.6 g in the case of S1 and S2 series, 219.2 g in the case of S3).

Polymerisation was carried out in a five-necked flanged flask which was fitted with a stirrer, an efficient reflux condenser, nitrogen purging, a drip funnel and a digital thermocouple. Toluene, together with surfactant and, if appropriate, oil soluble crosslinker was poured into the reactor and heated to 80°C. Initiator was added to the aqueous monomer solution just before starting the reaction and the combined solutions were added dropwise to the contents of the flask. An addition rate of 10 g/min. prevented the formation of coagulum as the reaction product. Once all the monomer was added, stirring was continued for another 90 min to ensure completion of polymerisation.

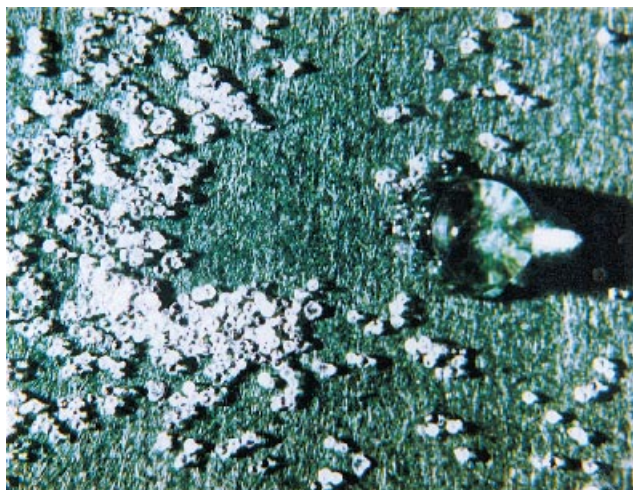


Fig. 2. Photograph showing a typical aggregation of fine particles onto coarser ones, in their swollen state.

2.2. Solution polymerisation

A series of polymers, denoted B1, was prepared in which the proportion of crosslinking agent, MBA, was changed. The monomer composition was the same as in the S3 series, i.e. acrylic acid:sodium acrylate:acrylamide in molar ratios of 1:3:4.

Monomer, crosslinker and initiator solutions were poured into a 1-l open beaker, immersed in an oil bath, and heated up to 80°C under magnetic 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.

2.3. Drying and classification

Once the reaction had been completed in the S1, S2 and S3 series of runs, the product was allowed to stand and cool. It settled out as a white mass and after decanting the supernatant liquid it was dehydrated with methanol, spread over aluminum foil and dried in an air-circulating oven at 60°C for 24 h. The dried product was sieved using an automatic sifter to obtain the mean particle size.

In the B1 series, the final product was a single rubbery mass. It was cut into pieces about 2–3 mm in size, spread over aluminum foil and oven-dried at 60°C for 24 h. The dried product was ground by a hammer-type laboratory grinder and classified.

2.4. Swelling measurements

A 1-g (± 0.001 g) polymer sample under test (250–300 μm) was dispersed into 2 l of doubly distilled water and allowed to swell with mild agitation. The steady state or equilibrium swelling was determined by allowing overnight for absorption. The swollen samples were filtered through a 100-mesh wire gauze and surface water dried carefully using a piece of a soft open-cell polyurethane foam until they no longer slipped from the sieve when 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 their swelling capacity was examined 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 gram of dry superabsorbent. The degree of swelling at a given time of immersion in water was determined as the fractional increase in weight of dry product after this time.

3. Results

As shown in Fig. 1 the particles formed by inverse suspension polymerisation were spherical and were mainly



Fig. 3. SEM micrograph of ground-up absorbent obtained from B1 solution polymerisation.

unattached to each other, although there were some aggregates of fine particles attached to coarse ones (see Fig. 2). Figs. 1 and 2 have the same scale. Particles from solution polymerisation were irregular in shape, as shown in Fig. 3. (The classified particles of 250–300 μm in size have been photographed.) They were obtained in too wide a size distribution (from dust to particles of 500 μm in size) than of their inverse suspension counterparts. Products from the S2 and S3 series of polymerisations were fractionated by sieving and the data are given in Table 1. In the S2 series more than 80% by mass of the particles were between 300 and 400 μm in diameter. The remainder was spread over a number of small fractions with diameters ranging from 300 to about 38 μm . In the S3 series the proportion of particles in the size range 300 to 400 μm was reduced to 50% or less and more particles appeared at smaller size ranges. The mean particle size in the S3 series (268 μm) was a little lower than in the S2 series (336 μm). There is some evidence of a bimodal distribution with a small peak at 100–180 μm .

The particle size distributions for both the S2 and S3 series were little, if at all, affected by changes in the level of the crosslinker.

Table 2(a, b) show the water uptakes for sieved products with particle sizes in the ranges 250–300 μm (Table 2(a)) and less than 250 μm (Table 2(b)) after different times of immersion in distilled water for different molar ratios of crosslinker to monomer and for all the series of runs, apart from S1 (EGDMA crosslinker) because of insufficient amounts of S1 fine samples to obtain their corresponding dynamic swelling values. The data show that absorption reached, or nearly reached a constant value within 10 min in all runs and for both ranges of particle sizes. For the smaller particle size range maximum absorption was reached after only 5 min. At the lowest ratio of crosslinker to monomer in the S2 series (0.000467) the coarser particles reached 44.6% of their ultimate absorption after 2 min, whereas the smaller particles reached 83%. As the proportion of crosslinker was increased, the degrees of absorption at 2 min for both the coarser (53.4 and 59.4%) and finer particles (90 and 95%) became lower. The final degrees of absorption for the smaller particles were a little higher than for the coarser particles. In order of increasing crosslinker concentration the ratios of the final degrees of absorption for the small particles to the final degrees for the coarse particles were 1.03, 1.12 and 1.11.

Introducing acrylamide into the monomer composition in the S3 series resulted in water being absorbed more rapidly than in the S2 series. By 1 min, the coarse particles had nearly reached their ultimate degrees of absorption and the smaller particles achieved this in only 0.5 min. At the lowest crosslinker concentration the coarse particles reached nearly half of their ultimate absorption in 0.5 min and the smaller particles nearly reached their ultimate absorption in the same time. At the higher crosslinker concentrations, absorption was faster and reached nearly 3/4 of the ultimate level in 0.5 min for the coarser particles, but was unchanged for the smaller particles. For the three

Table 1
Particle size distribution of the two series of samples (figures are in wt%)

Particle size (μm)	S2.1	S2.2	S2.3	S3.1	S3.2	S3.3
400–300	83.80	81.87	85.82	50.79	40.35	48.32
300–250	10.91	12.83	9.84	23.71	20.07	18.36
Total	94.71	94.7	95.66	74.5	60.42	66.68
250–180	2.18	2.24	2.16	4.54	9.25	6.30
180–150	1.91	2.03	1.57	13.04	12.40	11.95
150–106	0.72	0.61	0.39	3.75	10.82	6.52
106–75	0.18	0.20	0.00	4.15	4.72	5.86
75–53	0.00	0.00	0.00	0.00	0.19	1.18
53–45	0.09	0.20	0.19	0.00	0.00	0.00
45–38	0.21	0.02	0.03	0.02	2.20	1.51
Total	5.29	5.30	4.37	25.5	39.58	33.32
Mean particle size (μm)		336			268	
% Coarser than 250 μm		95.03 (averaged)			67.2 (averaged)	
% Finer than 250 μm		4.97 (averaged)			32.8 (averaged)	

Table 2
a: Dynamic swellings (in g/g)

Run no.	[C]/[M] mol%	0.5 min	1.0 min	2.0 min	5.0 min	10 min	Overnight (equilibrium)
(a) Coarse particles (250–300 μm)							
S2.1	0.0467			231	400	514	517
S2.2	0.0779			154	240	280	288
S2.3	0.109			151	221	247	254
S3.1	0.0467	202	427		430	454	423
S3.2	0.0779	146	207		214	217	219
S3.3	0.109	148	201		202	203	204
B1.1	0.0077	92	173	303		747	779
B1.2	0.0155	85	150	252		485	505
B1.3	0.0467	75	115	201		315	323
B1.4	0.0779	71	94	160		225	228
(b) Small particles (finer than 250 μm)							
S2.1	0.0467			444	530	534	531
S2.2	0.0779			290	322	323	323
S2.3	0.109			269	281	300	283
S3.1	0.0467	512	539		521	517	531
S3.2	0.0779	341	372		353	351	359
S3.3	0.109	296	314		301	306	306
B1.1	0.0077	406	433	538		627	600
B1.2	0.0155	204	348	410		469	470
B1.3	0.0467	199	226	266		291	285
B1.4	0.0779	139	161	196		208	204

crosslinker concentrations in ascending order the ultimate degrees of absorption were higher for the smaller particles than for the coarser ones by factors of 1.25, 1.64 and 1.5.

At the same crosslinker concentration (0.000467), the ultimate degree of absorption in the B1 series was lower than in the other series. Within the B1 series the ultimate degree of absorption decreased as the concentration of crosslinker increased. For a tenfold increase in crosslinker concentration the ultimate absorption decreased by a factor of 3.33 for the coarser particles and the absorption at 2 min decreased by a factor of 2.75 for the finer particles. The swelling values after 10 min and at equilibrium were found to be lower for fine particles than of their corresponding coarser counterparts. Comparing the degrees of absorption at 0.5 min shows that the rate of absorption for the finer particles at the lowest crosslinker concentration was more

than four times faster than for the coarser particles. The difference in absorption between the particle sizes became smaller as the crosslinker concentration increased. At the highest concentration the rate of absorption for the finer particles was only double that for the coarser ones.

The effect of adding salt to the water on the ultimate absorption of the coarse and fine particles produced in the S2 and S3 series is shown in Table 3. For each crosslinker concentration absorption decreased markedly as the salt concentration was increased. At all salt concentrations the ultimate swelling was higher for the small particles than for the larger ones. As shown in Table 4, the effect of reducing particle size was to increase absorption at all salt concentrations and the average increase for the S3 series (44.5%) was appreciably greater than for the S2 series (14.37%). There does not appear to be a dependence on the degree of crosslinking.

Table 3
Steady state swelling features of different particles at different swelling media

Size	[C]/[M] mol%	Size: 250–300 μm				Size: finer than 250 μm			
		Swelling (g/g) in saline of various molar concentration				Swelling (g/g) in saline of various molar concentration			
Run no.	[C]/[M] mol%	0.0	0.0015	0.015	0.15	0.0	0.0015	0.015	0.15
S2.0	0.0155	752	403	179	61	850	483	215	74
S2.1	0.0467	517	290	142	53	531	352	165	57
S2.2	0.0779	288	212	106	41	323	234	123	47
S2.3	0.109	254	196	105	39	283	220	114	48
S3.0	0.0155	573	328	134	60	750	544	197	68
S3.1	0.0467	423	261	99	50	531	331	130	41
S3.2	0.0779	219	183	85	31	359	247	115	42
S3.3	0.109	204	142	65	23	306	227	108	42

Table 4

Percentage increase or decrease in steady state swelling of different particles traveling from coarse to fine particles in swelling media of different salt molar concentration

Run no.	[C]/[M] mol%	0.0	0.0015	0.015	0.15	Average
S2.0	0.0155	+13.03	+19.8	+20.1	+21.3	
S2.1	0.0467	+2.70	+21.3	+16.2	+7.50	
S2.2	0.0779	+12.1	+10.3	+16.0	+14.6	
S2.3	0.109	+11.4	+12.2	+8.6	+23.0	
Average		+9.80	+15.9	+15.22	+16.6	+14.37
S3.0	0.0155	+30.9	+65.8	+47.0	+13.3	
S3.1	0.0467	+25.5	+26.8	+31.3	–	
S3.2	0.0779	+63.9	+34.9	+35.3	+35.4	
S3.3	0.109	+50	+59.8	+66.1	+82.6	
Average		+42.6	+46.8	+44.9	+43.7	+44.5

4. Discussion

4.1. Dependence of absorption on particle size

The size distribution of the polymer particles formed by inverse suspension polymerisation of acrylic acid and sodium acrylate in the S2 series was quite narrow. The spherical shape of the particles was as expected from suspension polymerisation [5–7]. A general lack of aggregation, except for some of the smaller particles, provided evidence for the effectiveness of the interfacial stabiliser. Surprisingly the effect of partially replacing the anionic acrylic acid and sodium acrylate monomers with nonionic acrylamide was to change the particle size distribution quite markedly. Since the stabiliser system was known to be near the limit for stability because decreasing the concentration of stabiliser (sorbitan monooleate plus ethyl cellulose) caused coagulation, it would appear that the acrylamide broadened the size distribution towards smaller particles by altering the hydrophilic–lipophilic balance and changing the behaviour of the interfacial stabiliser. The much lower concentration of crosslinker accounts for the lack of any effect on particle size distribution from changes in the

ratio of crosslinker to monomer. The irregular shape of the particles formed by solution polymerisation is as expected from the grinding step in the process.

Scanning electron micrographs of the two types of particles (which are 2.5 times different in their size) can be seen in Figs. 4 and 5. All the particles are spherical in shape and there are no serious differences between the two types of the particles, e.g. difference in aggregation, porosity and so on.

Absorption of water for all the products was rapid, requiring no more than 10 min to reach maximum uptake and it became more rapid as the particle size became smaller. The time taken to reach maximum absorption for particles with diameters between 250 and 300 μm was twice as long as for particles with diameters less than 250 μm . An increase in rate of absorption would be expected from the increase in surface area with decreasing particle size but more precise size distribution data would be needed to quantify the relationship and confirm this. The shift towards smaller particle sizes for products in the S3 series provides an explanation for absorption being faster than in the S2 series and a resulting increase in interstitial volume per unit mass of absorbent may also account for a higher ultimate degree of absorption (see Fig. 6). To explain this, two packages of swollen

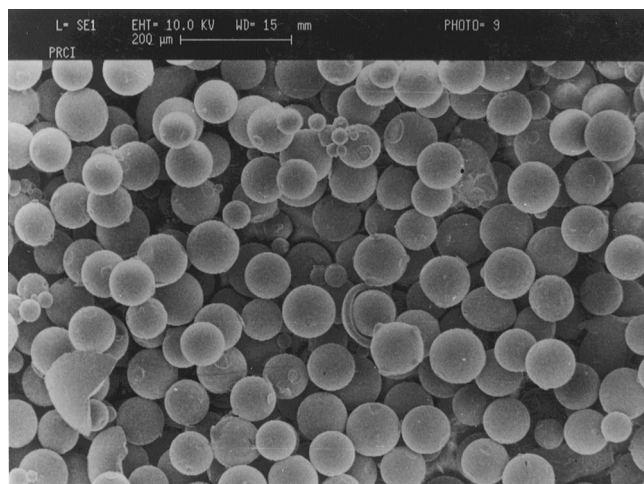


Fig. 4. SEM micrograph of an inverse suspension batch of small particles.

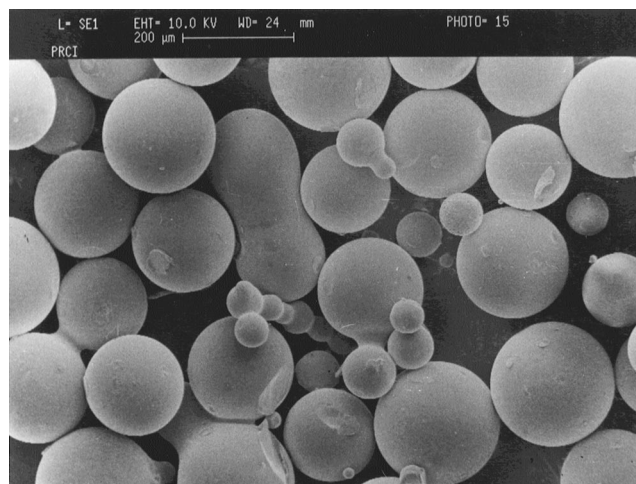


Fig. 5. SEM micrograph of an inverse suspension batch of coarse particles.

Table 5

Corresponding values of the model parameters for the fine and coarse particles in case of S2 and S3 series of samples

Particle size:	250–300 μm			Finer than 250 μm	
	σ_o/E (g/g)	τ_o (s)		σ_o/E (g/g)	τ_o (s)
S2.1	0.0467 ^a	520	192	530	65
S2.2	0.0779	290	174	325	60
S2.3	0.109	255	150	285	55
S3.1	0.0467	425	18	530	7
S3.2	0.0779	220	21	355	10
S3.3	0.109	205	19.8	310	10

^a Molar concentration of crosslinker to monomer (%).

particles can be imagined which differ only in terms of the size of the particles and hence, of swollen particles. If the particles laid side by side, some space could be left between the swollen particles, whether the particles are coarse or fine. This space can be called free or interstitial volume which serves to accommodate additional water by a typical capillary action. So the capillaries are expected to be wide and narrow in bore for coarse and fine swollen particles, respectively. Considering the two extremes for the size of the capillary bores, water drainage is presumably quite facile in case of extremely wide bore, i.e. coarser particles, whilst with the lowest size bores, i.e. finer particles, water is hardly drainable.

The highest degree of absorption for all the products was given by the lowest level of crosslinking in the B1 series and since this level was lower than in any of the others it seems very likely that this was the reason for the high absorption. The changes in ultimate absorption with crosslinking for S2, S3 and B1 series apart from S1 series suggest a roughly square root dependence. This would be consistent with the relationship derived by Flory [8].

$$\text{swelling}^{5/3} \cong (\nu M_c)(1 - 2M_c/M)^{-1}(1/2 - \chi_1)/\nu_1$$

where ν is the specific volume of the polymer, M_c is the chain length between crosslinks and ν_1 is the volume fraction of the polymer.

As for the S2 and S3 series of products the rate of absorption became faster as the particle size became smaller, but

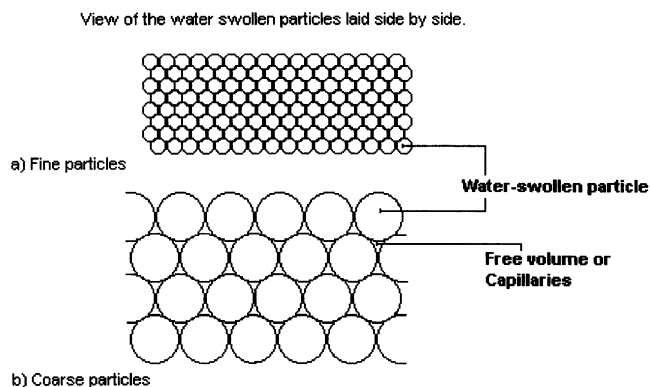


Fig. 6. A schematic diagram, showing interstitial volume between the water-swollen particles.

the ultimate degree of absorption became lower. This can be accounted for in terms of amount of water-extractable materials in B1 samples. We have already found [9] that B1 samples contain higher amount of water-extractable materials after immersion for a relatively long time in water. Moreover, water-extraction can be done faster for the fine particles compared to their coarse counterparts because of higher surface area or contact area of the former with water.

4.2. Application of absorption model to experimental data

As reported previously [9], the uptake of absorbents has been found to follow the same kind of exponential relationship as has been used to model creep in plastics. According to this relationship:

$$\varepsilon(t) = \sigma_o/E[1 - \exp\{(t_o - t)/\tau_o\}]$$

the swelling $\varepsilon(t)$ at time t depends on two parameters, one, σ_o/E , is both a measure of the resistance to expansion of the polymer network and is also the ultimate degree of absorption and the other, τ_o , is a measure of the resistance to permeation. Values of the parameters are given in Table 5 for the inverse suspension polymerisations at different levels of crosslinker and for the two ranges of particle size. For both series and for both ranges of particle size the expansion parameter decreased as the level of crosslinker was raised. This is interpreted as evidence of increasing resistance to expansion caused by the additional crosslinks.

For the S2 series, reducing the particle size did not affect the value of the expansion parameter at the lowest level of crosslinker but at higher levels of crosslinker the value of the parameter dropped less rapidly for the smaller particles. This indicates that crosslinking became less effective at resisting expansion as the particle size became smaller and that the ultimate degree of absorption also became larger, presumably as a result of the increase in surface area accessible to the water. Since the expansion parameter is also the ultimate degree of absorption, it follows that the degree of absorption increased as the particle size became smaller. This may be accounted for by an increase in interstitial volume with decreasing particle size. At the lowest level of crosslinker the expansion parameter for the S3

Table 6

Power law constants for swelling dependency of different samples to crosslinker concentration in different swelling media

Experiments	0.0 M		0.0015 M		0.015 M		0.15 M	
	<i>k</i>	<i>n</i>	<i>k</i>	<i>n</i>	<i>k</i>	<i>n</i>	<i>k</i>	<i>n</i>
S1.1–3	619	0.1	388	0.063	169	0.06	64	0.04
S2.1–3	72	0.58	83	0.38	53	0.29	23	0.24
B1.1–4	63	0.51	78	0.35	49	0.25	22	0.19

series was lower than for the S2 series. The effect of partially replacing the ionic monomers in the S2 series with a nonionic one, acrylamide, in the S3 series was to make the polymer more resistant to expansion for the larger particle size, as might be expected from the reduction in hydrophilicity. Surprisingly, the expansion parameter for the smaller particle size was unaffected by the monomer substitution at the lowest level of crosslinker and it dropped less rapidly with increasing level of crosslinker. It would appear that the substitution increased the sensitivity of the expansion to changes in particle size.

Whereas the expansion parameter became smaller with increasing level of crosslinker for both series of runs and for both particle sizes the permeation parameter changed in a more complex way. The highest values for the permeation parameters were in the S2 series, meaning that the highest resistance to permeation occurred in these runs. The fall in resistance with increasing level of crosslinker is attributed as before [9] to crosslinking preventing the network from collapsing as far when the polymer was dried. Reducing the particle size gave a much bigger drop in the permeation parameter than in the case of the expansion parameter. The resulting increase in surface area would be expected to increase the rate of permeation.

The permeation parameters for the S3 series were considerably smaller than for the S2 series and the effect of crosslinking was different. For both sizes of particles the permeation parameter changed little with increasing level of crosslinker. Evidently, partially substituting the ionic monomers with

acrylamide changed the permeability much more than crosslinking, although the mechanism is thought to be similar in preventing the structure from collapsing as far when the polymer was dried [9]. As in the case of the S2 series the parameter became smaller as the particle size was reduced.

4.3. Dependence of absorption on salinity

The sensitivity of polyelectrolyte superabsorbents to the addition of small amounts of ionic species to water is well known [10–12].

For all the series at different salinities the ultimate absorption was found to follow a power law relationship with the crosslinker concentration:

$$\text{Ultimate swelling} = k\{1/[\text{Crosslinker}]\}^n$$

The power law parameters are shown in Table 6. Moreover, at different crosslinker concentration, a power law relationship was also found for the dependency of the ultimate swelling to the saline concentration. The power law parameters are shown in Table 7.

$$\text{Ultimate swelling} = k\{1/[\text{Saline}]\}^n$$

For each series the exponent decreases with increasing salinity as expected from the well known effect of salinity on the diameter of polyelectrolyte molecules. In each series both of the parameters became smaller with higher levels of crosslinker.

The effect of increasing salinity on ultimate absorption for the different series at each level of crosslinker is shown in Table 8 by comparing the ratios of absorption at a given salinity to swelling in salt-free water. With the exception of S3.2, the increase in the ratio with increasing level of crosslinker shows that the sensitivity of absorption to changes in salinity decreased with crosslinking. This is to be expected since crosslinking prevents the network from expanding to its fullest extent, just as salinity does. The similarity of the ratios from one series to the next for a given level of crosslinker and salinity demonstrates that changes in crosslinker level are more important than changes in monomer composition and in method of polymerisation.

5. Conclusions

Absorbents produced by inverse suspension copolymerisation of acrylic acid with sodium acrylate had a narrow

Table 7

Power law constants for swelling dependency of different samples to salt concentration for different crosslinker concentration

Experiment	[C]/[M] mol%	<i>k</i>	<i>n</i>
S1.1	0.4654	33.4	0.398
S1.2	2.2963	31.48	0.389
S1.3	4.5836	27.77	0.383
S2.1	0.0467	27.43	0.366
S2.2	0.0779	21.67	0.354
S2.3	0.109	21.05	0.348
S3.1	0.0467	25.13	0.357
S3.2	0.0779	15.85	0.379
S3.3	0.109	11.60	0.381
B1.1	0.0077	24.48	0.445
B1.2	0.0155	23.96	0.408
B1.3	0.0467	18.29	0.402
B1.4	0.0779	19.36	0.352

Table 8
Dependency of the dimensionless swelling factor to crosslinker concentration

Experiment	[C]/[M] mol%	$\alpha_{0.0015}^a$	$\alpha_{0.015}$	$\alpha_{0.15}$
S1.0	0.055	0.573	0.248	0.09
S1.1	0.238	0.580	0.253	0.09
S1.2	2.30	0.632	0.282	0.10
S1.3	4.58	0.683	0.295	0.117
S2.0	0.0155	0.53	0.24	0.08
S2.1	0.0467	0.56	0.27	0.102
S2.2	0.0779	0.74	0.37	0.14
S2.3	0.109	0.77	0.41	0.15
S3.0	0.0155	0.57	0.23	0.1
S3.1	0.0467	0.61	0.23	0.12
S3.2	0.0779	0.86	0.39	0.14
S3.3	0.109	0.71	0.33	0.11
B1.1	0.0077	0.57	0.21	0.07
B1.2	0.0155	0.68	0.27	0.1
B1.3	0.0467	0.73	0.32	0.11
B1.4	0.0779	0.81	0.39	0.16
Series				
S1	0.055–4.580	0.57–0.68	0.25–0.29	0.09–0.12
S2	0.0155–0.109	0.53–0.77	0.24–0.41	0.08–0.15
S3	0.0155–0.109	0.57–0.86	0.23–0.39	0.1–0.14
B1	0.0077–0.0779	0.57–0.81	0.21–0.39	0.07–0.16

^a α : the ratio of swelling in saline to swelling in salt-free water. The subscripts denote the molar salt concentration.

size distribution. Increasing the level of crosslinking did not change the distribution appreciably but partially substituting the ionic monomers with nonionic acrylamide broadened the distribution considerably. The proportion by mass of particles in the size range 300–400 μm was reduced from more than 80% to about 50%. More particles were in the range 300–400 μm and there was some evidence for a bimodal distribution with a small peak at 150–180 μm . It is thought that altering the monomer composition modified the distribution by changing the partitioning of the suspension stabiliser between the aqueous and non-aqueous phases. Changes in the concentration of crosslinker were much smaller and did not affect the distribution appreciably.

Both the rate of absorption and the ultimate degree of absorption increased as the particle size became smaller. These effects are attributed to an increase in surface area of absorbent accessible to the water. The increase in rate of absorption is attributed to more water being absorbed for a given depth of permeation into the absorbent particles and the increase in ultimate degree of absorption is attributed to more water being held in the interstitial volume between the particles. It would therefore appear that control of the absorbent morphology at all levels of dimensions is potentially a route to improved performance.

Partially substituting ionic monomers with nonionic acrylamide made absorption a little faster but at the expense of ultimate absorption. Evidently the substitution prevented the polymer network from collapsing as tightly on drying so

that water could penetrate more rapidly but prevented the network from expanding as far on hydrating.

Applying a Voigt two-parameter exponential model to the rates of absorption gave a good fit to the data. The parameters, one representing resistance to expansion of the polymer network and the other resistance to permeation, could be meaningfully related to variables in the absorbent system such as crosslinking, monomer composition and particle size. This provides further support for the validity of the model and for its value in identifying the mechanism of a change in behaviour.

The extent to which absorption decreases with increasing salinity has been determined. As the level of crosslinking was increased the ultimate degree of absorption became smaller but was less sensitive to changes in salinity. Within the ranges of variables covered, changes in crosslinking at a given level of crosslinker and salinity were found to have more effect on absorption than changes in monomer composition and in method of polymerisation.

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