

## Synthesis and Characterization of Sodium Acrylate and 2-Acrylamido-2-Methylpropane Sulphonate (AMPS) Copolymer Gels

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(Received February 10, 2004; Revised April 20, 2004; Accepted April 27, 2004)

**Abstract:** A series of superabsorbents based on acrylic acid (AA), sodium acrylate, 2-acrylamido-2-methylpropane sulphonic acid, N,N'-methylene bis-acrylamide (MBA) were prepared by inverse suspension polymerization. These hydrogels were further crosslinked on the surface with polyethylene glycol-600 (PEG-600). The water absorbency or swelling behaviors for these xerogels in water and 0.9 % saline solutions, both under free condition and under load were investigated. Absorption characteristics of these hydrogels were found to depend on nature and concentration of crosslinker in the system. It was also found that the saline absorption was significantly improved as the incorporation of AMPS in the polymer was increased. The surface crosslinking introduced in the polymers was found to improve the absorption under load characteristics without lowering the free water absorption capacities of the polymer to a considerable extent.

**Keywords:** Superabsorbent, Hydrogel, AMPS, Sodium polyacrylate, 2-Acrylamido-2-methylpropane sulphonate

### Introduction

Superabsorbent polymers are lightly crosslinked hydrophilic polymers that can absorb, swell and retain large amount of aqueous solution. These hydrogels are used mainly for personal care and hygienic products [1]. In addition to healthcare products, they are also used as moisture barriers in construction, as soil conditioners in agriculture, as controlled release agents for pharmaceutical, as artificial snow for skiing areas and numerous other applications [2,3].

The commercially important superabsorbents are crosslinked polymers of partially neutralized acrylic acid. They are generally formed by free-radical cross-linking polymerization of hydrophilic acrylate or methacrylate monomers with small quantities of cross-linking agents containing two (or more) polymerizable double bonds [1-3].

The swelling and the elasticity of these polymers depend on the precise structure of the polymer network and primarily on the crosslink density [2]. With increase in crosslink density, the free swelling in water and saline decrease while the absorption under load increases. For the personal hygiene products the superabsorbent polymers are desired to have high saline absorption as well as high absorption under load (AUL). The techniques for synthesis of superabsorbents are all aimed at adjusting the balance of properties of these hydrogels through control of the network structure. The modification of these absorbent polymers was carried out to enhance their superabsorbency, gel strength, and absorption rate by some research workers [4-9].

Homopolymers of acrylic acid, however, show a sharp decrease in absorbency in presence of electrolytes usually present in physiological fluids. Novel salt tolerant co-monomers like AMPS, 3-dimethyl (methacryloyloxyethyl) ammonium

propane sulphonate (DMAPS) and trimethyl methacrylamidopropyl ammonium iodide (TMMAAI) are used to improve saline absorption [10-12]. This increase in saline absorption is due to the presence of sulphonic acid groups in the chain, which have a higher degree of ionization as compared to the carboxylate groups of acrylic acid. Also, the introduction of crosslinks on the surface of these hydrogel particles can be utilized to modify the crosslinked zones on the surface and in the core independently to obtain high saline absorption as well as high AUL. By introducing crosslinks, on the surface of these hydrogels it can be made in such a fashion that the fluid does not saturate the surface (as the surface swelling is less due to higher crosslink density) but at the same time, the final absorption remains high due to lightly crosslinked core [13-16]. Superabsorbent polymers thus produced have higher mechanical properties while maintaining high absorption properties giving both high absorption under load and free absorption. However the degree of surface crosslinking needs to be optimized and carefully carried out, as crosslinks tend to decrease the free absorption. The amount of surface crosslinker which will give optimum absorption, both in free condition and under load is therefore of interest.

This article is a systematic attempt to investigate the influence of (i) AMPS comonomer concentration and (ii) extent and nature of crosslinking on the absorption properties of superabsorbent polymers synthesized by inverse suspension polymerization technique. In the present study, surface crosslinking has been attempted with polyethylene glycol 600 (PEG-600) a cheaper alternative to ethylene glycol dimethacrylate (EGDMA) or ethylene glycol diglycidyl ether (EGDGE).

### Experimental

#### Materials

Glacial acrylic acid (AA) monomer and N,N' methylene

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bisacrylamide (MBA) crosslinker Span 60 (sorbitan mono-stearate) surfactant, supplied by Fluka were used without further purification. 2-acrylamido-2-methyl propane sulphonic acid (AMPS) by Lubrizol, Ohio was used as a comonomer. Potassium persulphate (KPS), by Merck and sodium hydroxide by Qualigen of analytical grade were used as initiator and neutralizer respectively. Sodium chloride, polyethylene glycol-600, cyclohexane, methyl alcohol by Merck were used as received.

### Methodology

In this study the following three parameters which affect the absorption properties of superabsorbent polymers have been selected.

Crosslinker concentration

Monomer: comonomer ratio

Bulk and surface crosslinker ratio

### Selection of the Parameter Levels

Based on these preliminary experiments the following conditions were selected for polymerization.

Chemicals/Conditions	Quantity
Organic: Aqueous	3:1
Suspending agent	0.3 %
Monomer concentration	33 %
Degree of neutralization	70 %
Initiator concentration	0.19 %
Temperature	70 °C
Time	1.5 hrs.
Stirrer speed	400 rpm.

Each of the parameters to be studied were set at three levels, equidistant from the centre point, that is to say at -1, 0, and +1 coded levels, the actual values of which were as shown below:

- (i) Crosslinker percentage: -1 = 0.233 % molar  
0 = 0.467 % molar  
+1 = 0.701 % molar
- (ii) Acrylic acid: AMPS ratio: -1 = 90:10 molar  
0 = 85:15 molar  
+1 = 80:20 molar
- (iii) MBA: PEG 600: -1 = 0.426 molar  
0 = 0.305 molar  
+1 = 0.184 molar

To carry out experimental runs, Box-Behnken design has been used. Box-Behnken design is a combination of  $2^n$  factorial and incomplete block designs. To build a Box-Behnken design, factors were taken in pairs followed by building  $2^2$  factorial for all possible pairs while holding the other factors at a center point. Box-Behnken design gives an added advantage of being rotatable. Through the use of this design, information

**Table 1.** Coded level of variables according to Box-Behnken design

Run. No	Coded factor levels		
	Crosslinker %	AA: AMPS	MBA: PEG 600
1	+1	-1	0
2	-1	0	+1
3	+1	0	+1
4	-1	+1	0
5	+1	+1	0
6	+1	0	-1
7	0	0	0
8	-1	-1	0
9	0	-1	-1
10	0	+1	-1
11	0	0	0
12	0	+1	+1
13	-1	0	-1
14	0	-1	-1
15	0	0	0

on single linear, quadratic effects along with the two factor linear interaction can be obtained.

A total of 15 experiments were carried out by changing the parameters according to the above table (Table 1). Care was taken to randomize the runs to eliminate the operational error.

### Synthesis Procedure

#### Preparation of Dispersed Phase

Sodium acrylate monomer was prepared by gently dropping sodium hydroxide solution (predetermined amount) to aqueous acrylic acid under cooling (ice bath). After complete dissolution required amount of AMPS (co-monomer), was mixed with this neutralized acrylic acid and used for polymerization. Separate solutions were made for crosslinker and initiator.

#### Preparation of Continuous Phase

Cyclohexane was used as the continuous phase. A 1-litre reactor was charged with 250 ml of cyclohexane and required quantity of surfactant (Span 60) was added to it. The temperature of the reactor was increased to 70 °C and was stirred while bubbling nitrogen. After complete dissolution of surfactant and nitrogen purging of 30 min, the polymerization was started.

#### Inverse Suspension Polymerization

The solution of the crosslinker and initiator were added to the neutralized monomer (under nitrogen bubbling), just before the polymerization. After that the solution was poured into a dropping funnel and it was charged in the reactor slowly (drop by drop). The feeding time was kept 45 to 50 minutes.

The stirrer speed was maintained at 400 rpm and the temperature of the reaction was controlled at  $70 \pm 1$  °C. The polymerization was continued for 1.5 hours. The polymer was separated as a lower layer, dehydrated and washed with methanol and dried in a hot air oven maintained at 60 °C for 24 hours. Finally it was dried in vacuum oven and stored in a closed container. Gravimetric yields of >95 % were obtained.

### Surface Crosslinking

Surface crosslinking of the polymer was carried out by charging the required amount of dry polymer (vacuum dried) to a round-bottomed flask, with four times its weight of methanol and 20 % of its weight of water. The crosslinking reaction was carried out under reflux condition for 1 hour, while a solution of crosslinker in methanol was added using a dropping funnel over the entire reaction period. The polymer was then taken out and dried in the vacuum oven at 70 °C for 1.5 hours.

### Absorption Properties of Super Absorbent Copolymers

#### Free Absorption [11]

0.2 gm. of the polymer was taken in a beaker and 300 ml. of distilled water was added to it. The polymer was allowed to absorb water for 30 minutes, while stirring occasionally and then it was sieved through a stainless steel (SS) sieve (100 mesh). The initial and the final weight of the sieve were taken to find out the absorption capacity in grams of water per gram of the polymer using the following formula.

$$\text{Absorption capacity} = \frac{(W_f - W_i) - 0.2}{0.2} \quad (1)$$

where,  $W_i$  = initial weight of the SS mesh.  
 $W_f$  = final weight of the SS mesh.

#### Saline Absorption

A 0.9 % solution of the sodium chloride was prepared as saline solution. 0.2 g of the polymer was taken in a beaker and 300 ml of saline water was added to it. The polymer was allowed to absorb saline water for 30 minutes, required occasional stirring and then it was sieved through a 100-mesh stainless steel sieve. The initial and the final weight of the sieve were taken to find out the saline absorption capacity of the polymer in grams of saline water per gram of the polymer by the formula shown above.

#### Absorption under Load

The absorption under load was determined using the following method. A porous filter plate is placed in a petri dish and 0.9 % sodium chloride solution is added so that the liquid level is equal to the top of the filter plate. A filter paper is placed on the filter plate and allowed to wet thoroughly with the saline solution. Superabsorbent polymer (0.9 g) is carefully

scattered onto the filter screen of the test device (a Plexiglas cylinder with 400 mesh stainless steel cloth in the bottom: cylinder diameter = 60 mm, height = 50 mm). A piston assembly, including additional weight to achieve a load of 0.3 psi (or 0.7 psi), is placed on top of the superabsorbent polymer. After weighing the assembled device it is placed on the filter plate, and absorption is allowed for 1 hour. After 1 hour, the entire device is reweighed and the absorbency under load is calculated by the following formula:

$$\text{AUL} = \frac{(\text{Mass of cylinder group after suction} - \text{mass of cylinder group dry})}{(\text{Initial sample mass of the superabsorbent})} \quad (2)$$

For this test, 0.8 g of the sample was taken and sprinkled evenly inside the AUL testing cylinder. This cylinder was then rested on a porous plate, which was kept dip in a vessel. The piston along with the 0.3-psi load was lowered onto it and 0.9 % saline solution was added to the outside container so that the porous plate was just dipped into saline. Then the sample was allowed to absorb through the porous plate for 1 hour.

The initial and the final weight of the AUL testing apparatus were measured to calculate the absorption under load of the polymer using the relation.

$$\text{AUL} = \frac{(W_{f(\text{AUL})} - W_{i(\text{AUL})}) - \text{Weight of dry polymer}}{\text{Weight of dry polymer}} \quad (3)$$

Where,  $W_{i(\text{AUL})}$  = initial weight of the AUL apparatus.  
 $W_{f(\text{AUL})}$  = final weight of the AUL apparatus.

### Characterization of Superabsorbent Polymers

#### FTIR Spectroscopy

Representative sample was studied for structural analysis using Micro Jasco Fourier Infrared Spectroscopy to ascertain the incorporation of comonomer. The dried superabsorbent copolymer was ground with dried KBr powder. The KBr disc was dried again and subjected to FTIR spectrophotometry. Result are taken from the range of 450 to 4400<sup>-1</sup> cm of wavelength.

#### Fraction of Soluble Polymer

The soluble content in the super absorbent polymer determined the amount of un crosslinked polymers, this was determined quantitatively by treating 0.8 g of vacuum dried polymer sample with 300 ml of 0.9 % sodium chloride solution for 72 hours with occasional stirring at room temperature. The crosslinked polymer or the gel was separated by filtration through sintered glass crucible. It was washed several times to retrieve the entire soluble polymer and finally washed with water/methanol to remove the entrapped salts, if any. The residue was dried to constant weight and the difference of the initial weight of the polymer and the residue were used to calculate the soluble content.

### Results and Discussion

#### Free Swelling

The results obtained from the experiments have been tabulated in Table 2. These values were then entered into systat to form contour diagrams, which is the plot of the free absorption as a function of two variables taken at a time. Figure 1(a), (b), and (c) are the plots of free absorption with the AA: AMPS ratio and MBA: PEG 600 ratio keeping the total crosslinker percentage fixed at 0.233, 0.467, and 0.701 mole percent respectively. As the MBA: PEG-600 ratio increases, there is drop in surface crosslinking (coded level decreases), the free absorption increases. The free absorption first increases marginally as the AA: AMPS ratio increases.

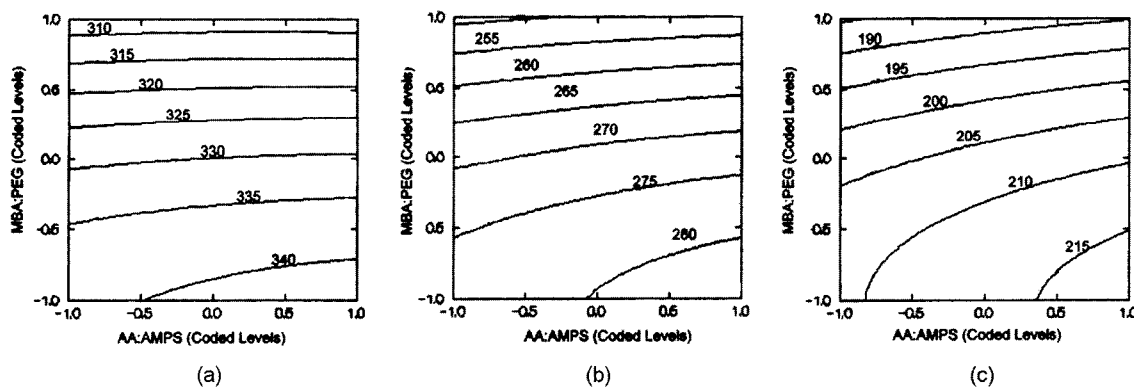
Figure 2(a), (b), and (c) are the plots for free absorption varying with the total crosslinker percentage on the x-axis and the MBA: PEG 600 ratio on the y-axis keeping the AA: AMPS ratio are fixed at 90:10, 85:15, and 80:20 molar ratio respectively. The curves clearly show that as the MBA: PEG-600 ratio increases (lower coded levels); there is a substantial increase in the free absorption. The free absorption, however, drops most significantly as the total cross-linker percentage increases.

Figure 3(a) and (b) are the plots of the free absorption with the total cross-linker percentage and the AA: AMPS ratio.

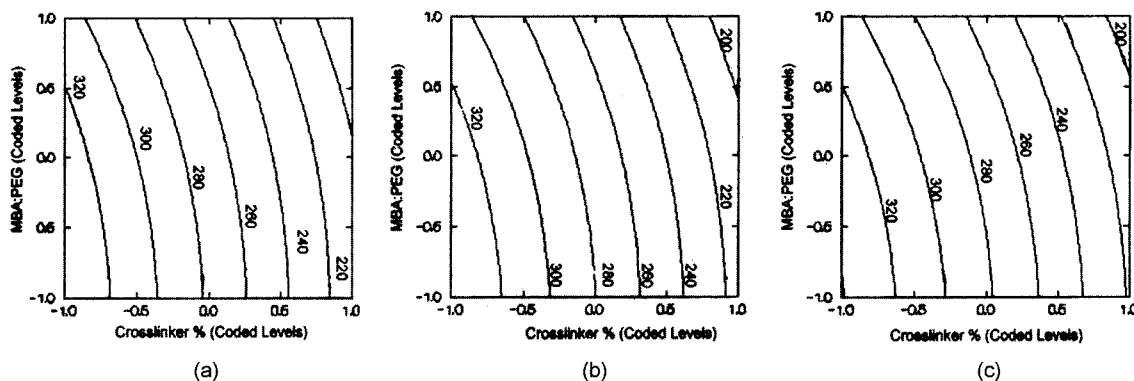
**Table 2.** Free absorption of super absorbent polymers

Sample No.	Crosslinker (mole%)	AA: AMPS (molar)	MBA: PEG-600 (molar)	Free absorption (g/g of Polymer)
1	0.701	4.000	0.305	207.80
2	0.701	9.000	0.305	198.50
3	0.233	4.000	0.305	333.80
4	0.233	9.000	0.305	331.75
5	0.701	5.667	0.184	187.45
6	0.701	5.667	0.426	219.60
7	0.233	5.667	0.184	302.60
8	0.233	5.667	0.426	339.65
9	0.467	4.000	0.184	253.20
10	0.467	4.000	0.426	279.55
11	0.467	9.000	0.184	251.75
12	0.467	9.000	0.426	275.35
13	0.467	5.667	0.305	268.30
14	0.467	5.667	0.305	271.85
15	0.467	5.667	0.305	273.85

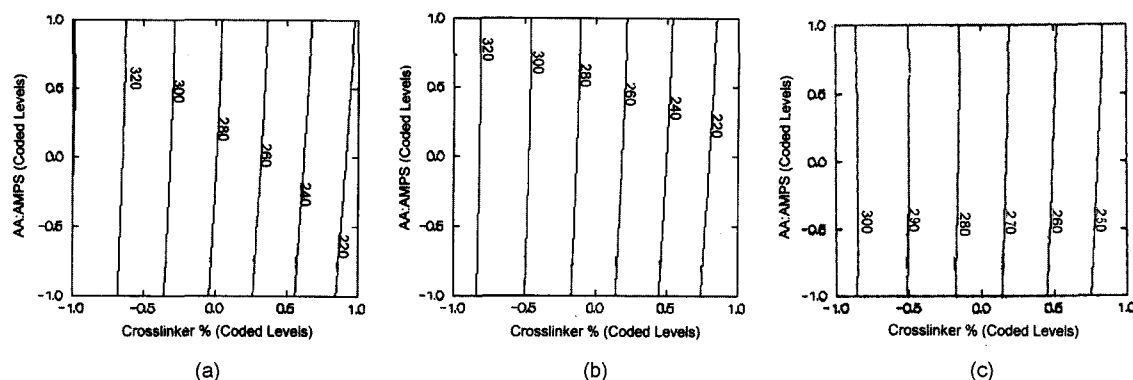
The MBA: PEG-600 ratio is fixed at 0.426, 0.305, and 0.184 respectively. Here again there is significant drop in free



**Figure 1.** Variation of Free Absorption with crosslinker at (a) -1 level, (b) 0 level, and (c) +1 level.



**Figure 2.** Variation of Free Absorption with AA; AMPS at (a) -1 level, (b) 0 level, and (c) +1 level.



**Figure 3.** Variation of Free Absorption with MBA; PEG at (a) -1 level, (b) 0 level, and (c) +1 level.

absorption with crosslinker percentage. With the AA: AMPS ratio there is not much change in the free absorption.

The above trends in free absorption with total cross-linker percentage, is predictable. It has been discussed earlier, as the amount of crosslinker in the polymer increases, the free absorption drops. The decrease of the free absorption with the MBA: PEG-600 ratio can be explained as the MBA: PEG-600 ratio decreases, the crosslinking at the surface becomes higher and hence the surface of the polymer becomes more rigid. The total amount of cross-linker in the system also increases. Hence there is a drop in free absorption.

Thus to maximize the free absorption, we must proceed by lowering the total crosslinker percentage and also reduce the MBA: PEG 600 ratio i.e. reduce the degree of surface crosslinking.

**Table 3.** Saline absorption of super absorbent polymers

Sample No.	Crosslinker (mole%)	AA: AMPS (molar)	MBA: PEG-600 (molar)	Saline absorption (g/g of Polymers)
1	0.701	4.000	0.305	88.40
2	0.701	9.000	0.305	71.35
3	0.233	4.000	0.305	143.70
4	0.233	9.000	0.305	126.25
5	0.701	5.667	0.184	77.75
6	0.701	5.667	0.426	82.30
7	0.233	5.667	0.184	135.15
8	0.233	5.667	0.426	137.65
9	0.467	4.000	0.184	114.10
10	0.467	4.000	0.426	116.80
11	0.467	9.000	0.184	100.85
12	0.467	9.000	0.426	104.35
13	0.467	5.667	0.305	112.15
14	0.467	5.667	0.305	114.55
15	0.467	5.667	0.305	110.70

### Saline Absorption

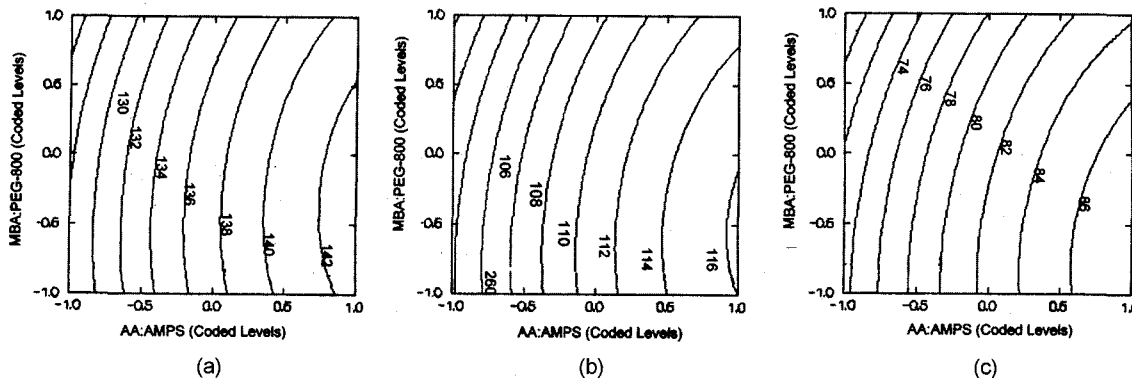
Saline absorption refers to the absorption of a standard 0.9 % NaCl solution by the polymer. This property is more significant especially when it comes to actual end use of superabsorbent polymers most of which are used in health and personal care products, where they are required to absorb physiological fluids. These physiological fluids are high in electrolyte content, which drastically lowers the absorption characteristics of the super absorbent polymers by common ion effect.

The results obtained from saline absorption test are displayed in Table 3. The first thing that comes to notice on comparison with Table 2 is the fact that saline absorption is far lower than the free water absorption. This is expected as explained above.

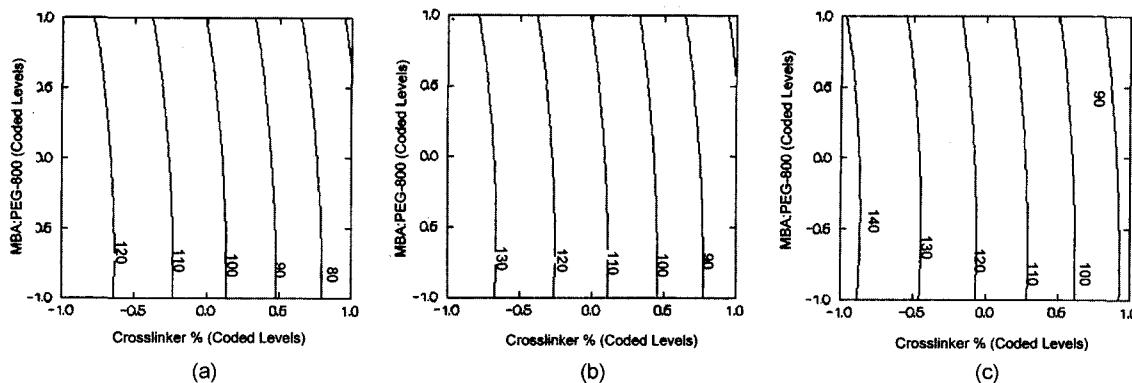
The data were fed into systat to obtain the contour diagrams.

Figure 4(a), (b), and (c) represent the saline absorption properties as a function of the AA: AMPS ratio and the MBA: PEG 600 ratio, fixing the total cross linker percentage at 0.233, 0.467, and 0.701 mole percent respectively. The most significant trend in these three graphs is the increase of saline absorption as the AA: AMPS ratio decreases or in other words as the incorporation of AMPS in the polymer increases. The saline absorption, however, decreases with higher level of surface crosslinking. The variation of the saline absorption with MBA: PEG 600 ratio is more significant at higher levels of surface crosslinking. Initially, at lower level of surface crosslinking it remains almost constant and then it starts falling as the degree of surface crosslinking increases.

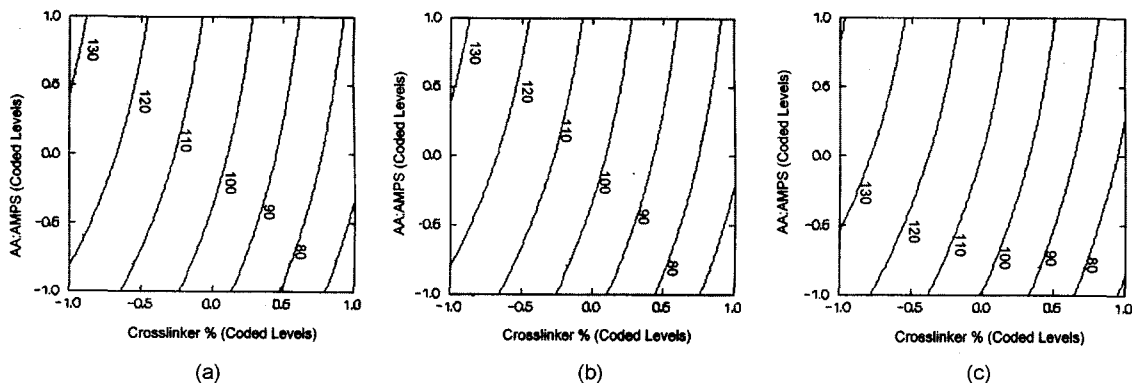
The next three figures (Figure 5(a), (b), and (c)) are the contours of saline absorption with the total crosslinker percent and the MBA: PEG 600 keeping the AA: AMPS ratio fixed at 90:10, 85:15, and 80:20 molar respectively. As is expected, saline absorption decreases both with the increase in the total crosslinker percent and increases in surface cross-linking. But the decrease of saline absorption with surface crosslinking is not as much as that with total crosslinker percent. Similar results on decrease of saline absorption with increasing crosslinking density were obtained by Omidian *et al.* [6]. In



**Figure 4.** Variation of Saline Absorption with Crosslinker at (a) -1 level, (b) 0 level, and (c) +1 level.



**Figure 5.** Variation of Saline Absorption with AA; AMPS at (a) -1 level, (b) 0 level, and (c) +1 level.



**Figure 6.** Variation of Saline Absorption with MBA; PEG at (a) -1 level, (b) 0 level, and (c) +1 level.

the same study the authors also showed that with increase in salinity, the amount of swelling became independent of the crosslinking density. This however is beyond the scope of the present study as we are using a fixed 0.9 % saline solution for testing purposes.

Figure 6(a), (b), and (c) gives the plot of saline absorption with the total cross-linker and the AA: AMPS ratio. In these cases the MBA: PEG-600 ratio is fixed at 0.184, 0.305, and 0.426 respectively. The saline absorption shows a downward trend as the total crosslinker increases and an upward trend

as the amount of incorporation of AMPS in the polymer increases.

Thus we can see from all the nine graphs that saline absorption increases significantly as the AMPS incorporation in the polymer increases. This is because the incorporation of AMPS in the polymer causes a higher number of sulphonic acid groups replacing the carboxylic acid groups of acrylic acid. On partial neutralization this changes to  $\text{SO}_3^- \text{Na}^+$ .  $\text{SO}_3^- \text{Na}^+$  has a higher ionization product; hence the common ion effect is less. The higher osmotic pressure inside the polymer

**Table 4.** Absorption under load of Super Absorbent Polymers (at 0.3 psi)

Sample No.	Crosslinker (mole%)	AA: AMPS (molar)	MBA: PEG-600 (molar)	AUL (g/g of Polymer)
1	0.701	4.000	0.305	35.23
2	0.701	9.000	0.305	35.92
3	0.233	4.000	0.305	32.67
4	0.233	9.000	0.305	32.35
5	0.701	5.667	0.184	40.32
6	0.701	5.667	0.426	31.71
7	0.233	5.667	0.184	36.13
8	0.233	5.667	0.426	30.31
9	0.467	4.000	0.184	38.25
10	0.467	4.000	0.426	31.17
11	0.467	9.000	0.184	37.72
12	0.467	9.000	0.426	30.85
13	0.467	5.667	0.305	34.75
14	0.467	5.667	0.305	33.97
15	0.467	5.667	0.305	34.18

in case of the  $SO_3^-$  incorporated chains results in higher saline absorption. The total amount of crosslinking lowers the saline absorption playing a similar role, as during free absorption, of restricting the degree of swelling of the polymer.

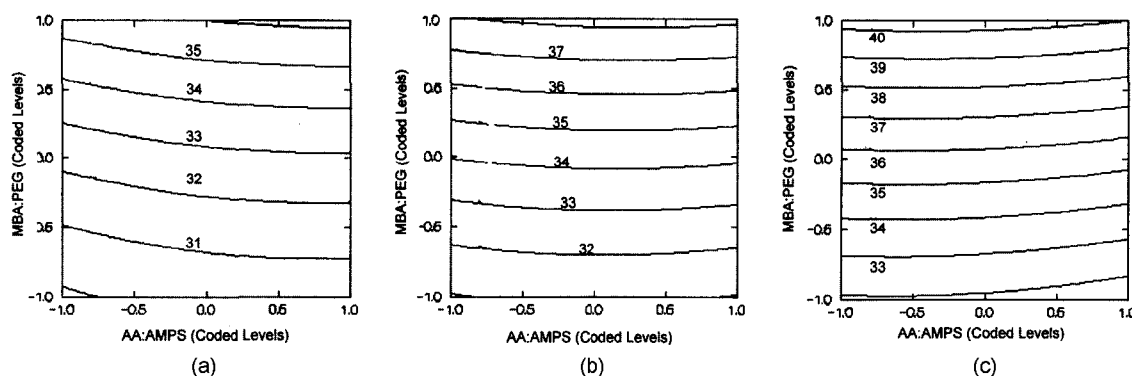
Thus to maximize the saline absorption, AMPS incorporation should be increased, while at the same time the total amount of crosslinker and the amount of surface crosslinking should be decreased. The first two factors cause a greater effect than the third factor.

**Absorption under Load**

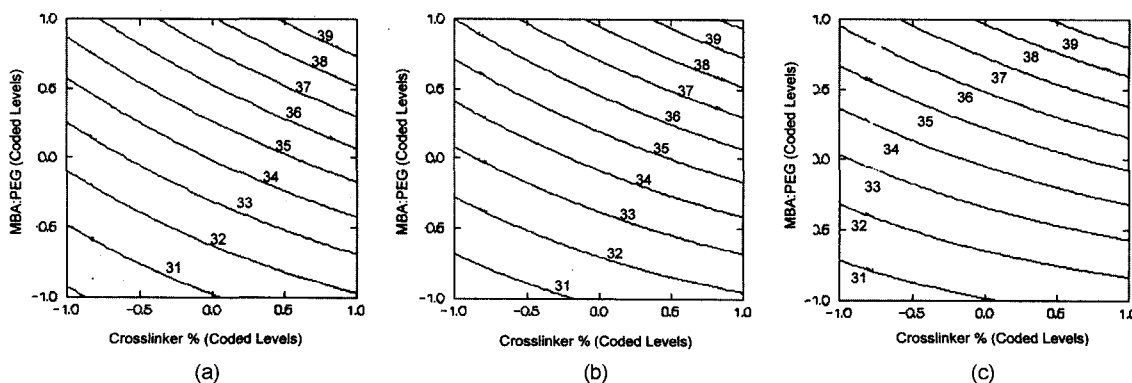
The absorption under load refers to the amount of 0.9 % saline solution absorbed by a known quantity of the polymer (usually 1 g) when kept in contact with the saline solution under a standard load of 0.3 psi. This is by far the most important absorption property of superabsorbent polymers since in most cases of their application; they need to absorb physiological fluid while under a compressive pressure.

The results of the absorption under load tests are given in Table 4.

Figure 7(a), (b), and (c) are the contour plots of the absorption under load as a function of the AA: AMPS ratio on the x-axis and the MBA: PEG-600 ratio on the y-axis keeping the



**Figure 7.** Absorption under load with crosslinker at (a) -1 level, (b) 0 level, and (c) +1 level.



**Figure 8.** Absorption under load with AA; AMPS at (a) -1 level, (b) 0 level, and (c) +1 level.

total crosslinker amount fixed 0.233, 0.467, and 0.701 mole percent respectively. The general trend shows that the absorption under load increases as the MBA: PEG-600 ratio decreases i.e. as the surface cross-linking amount increases. There is also a little increase in the saline absorption under load as the amount AMPS incorporated in the polymer increases.

Figure 8(a), (b), and (c) show the variation of the absorption under load with the total crosslinker amount and the MBA: PEG-600 ratio. In each case, the AA: AMPS ratio has been kept at 90:10, 85:15, 80:20 molar ratio respectively. The trend follows an increase of absorption under load as the total crosslinker in the system increases. The absorption under load is found to be increasing as the amount of surface crosslinking in the polymer increases. Both these trends are expected. This is because increasing the amount of crosslinker in the system will make it more rigid, and hence compressive forces are not able to squeeze them thoroughly. The higher degree of surface crosslinking will mean polymer granules with stiffer surface and hence more rigid.

The contour plots of the absorption under load as a function of the total amount of crosslinker and the AA: AMPS ratio are shown in Figure 9(a), (b), and (c). In these cases the MBA: PEG-600 ratio is fixed at 0.426, 0.305, and 0.184 molar ratio respectively. The contour plot shows an increase of the absorption under load as the total amount of crosslinker in the system increases. The absorption under load also shows an increasing trend as the amount of AMPS incorporated in the polymer increases initially.

The increase in the absorption under load with the increase in the amount of AMPS incorporated in the polymer may be

explained if we keep in mind that by absorption under load, we actually mean the saline water absorption under load. This in turn will increase with the higher and higher incorporation of AMPS in the system.

Therefore, for optimization of the saline absorption under load, we will have to increase the total crosslinker percent, the amount of AMPS incorporated in the system and the amount of surface crosslinking. AA: AMPS ratio should be kept at around 87:13 to 83:17 depending on the amount of total crosslinking agent. Out of these three parameters the effect of surface cross-linking is the maximum supported by the regression equation coefficients and the graphs.

The above discussions and graphs were based on equations obtained from systat by feeding in the data. The regression equations are of the general form:

$$\text{Property} = C_0 + C_1X_1 + C_2X_2 + C_3X_3 + C_4X_1^2 + C_5X_2^2 + C_6X_3^2 + C_7X_1X_2 + C_8X_2X_3 + C_9X_3X_1 \quad (4)$$

Where,  $X_1$  = coded levels of total cross linker percent

$X_2$  = coded levels of AA: AMPS ratio

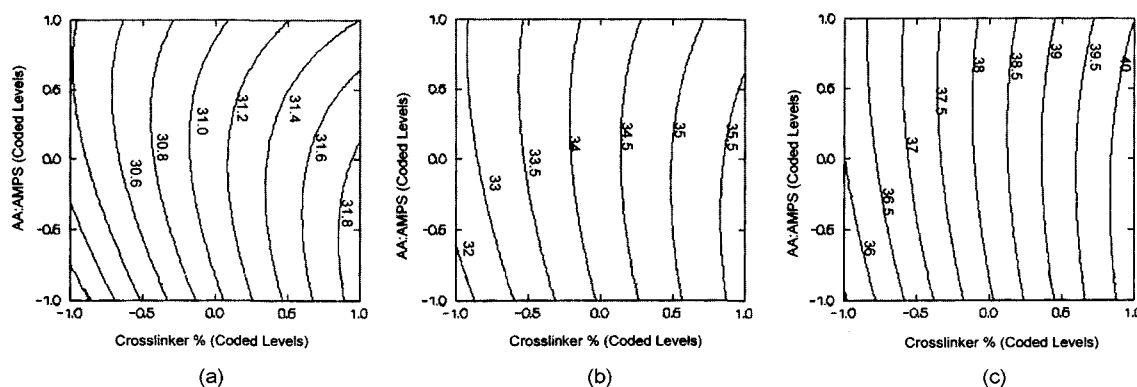
$X_3$  = coded levels of MBA: PEG-600 ratio

$C_0 - C_9$  = coefficients of regression

The coefficients of regression are given in Table 5.

### Effect of Surface Crosslinking

The incorporation of crosslinks by polyethylene glycol-600 (PEG-600) on the surface of the polymer is expected to improve the absorption under load of the polymer significantly without



**Figure 9.** Absorption under load with MBA: PEG at (a) -1 level, (b) 0 level, and (c) +1 level.

**Table 5.** Coefficients of regression equation

Property studied (g/g of polymer)	Coefficients									
	$C_0$	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$	$C_6$	$C_7$	$C_8$	$C_9$
Free absorption	271.333	-61.806	2.125	-14.894	-3.004	-0.367	-6.004	1.813	-0.688	1.225
Saline absorption	112.467	-27.869	7.463	-1.719	-2.990	-2.052	-1.265	-0.100	0.325	-0.512
Absorption under load	34.300	1.465	0.060	3.548	-0.069	-0.189	0.386	-0.253	0.053	0.697



**Table 6.** Effect of surface crosslinking on the absorption properties of super absorbent polymers

Sample No.	Crosslinker (mole%)	AA: AMPS (molar)	MBA: PEG-600 (molar)	Free absorption (g/g of polymer)		Absorption under load (g/g of polymer)	
				Before surface cross-linking	After surface cross-linking	Before surface cross-linking	After surface cross-linking
1	0.701	4.000	0.305	213.75	207.80	33.86	35.23
2	0.701	9.000	0.305	203.30	198.50	32.89	35.92
3	0.233	4.000	0.305	336.75	333.80	27.35	32.67
4	0.233	9.000	0.305	340.15	331.75	26.12	32.35
5	0.701	5.667	0.184	236.50	187.45	33.12	40.32
6	0.701	5.667	0.426	225.75	219.60	33.07	31.71
7	0.233	5.667	0.184	339.05	302.60	26.77	36.13
8	0.233	5.667	0.426	341.35	339.65	26.41	30.31
9	0.467	4.000	1.184	273.90	253.20	31.13	38.25
10	0.467	4.000	0.426	285.60	279.55	31.02	31.17
11	0.467	9.000	0.184	308.25	351.75	39.08	37.72
12	0.467	9.000	0.426	311.15	275.35	29.30	30.85
13	0.467	5.667	0.305	297.40	268.30	30.56	34.75
14	0.467	5.667	0.305	296.40	371.85	29.73	33.97
15	0.467	5.667	0.305	302.10	273.85	30.11	34.18

much affecting the free absorption properties of the polymer. To study this the free absorption and absorption under load properties of the polymer were evaluated before and after surface crosslinking. The results are shown in Table 6.

It is evident from the table that the effect of the surface cross-linking causes a significant increase in the absorption under load of the polymer varying from 0.5 % to 3.5 % depending on the initial crosslinker percentage and the final amount of surface crosslinking. The AA: AMPS ratio does not appear to influence the absorption under load characteristics much.

It can be seen from the graphs, that in all cases there is an increase in the absorption under load after surface cross-linking. This is because of the increased mechanical rigidity of the hydrogels as a result of higher degree of cross-linking at the surface. At the same time, it is also evident from Table 6, that though there is a decrease in free absorption capacity of the hydrogels after surface crosslinking, the drop is not drastic, and can be argued to be tolerable keeping in view the increase in absorption under load obtained by the same.

Another feature that is to be noticed from the graphs is that the increase in the absorption under load after surface crosslinking is higher as the amount of surface crosslinker is increased in the system. Also the absorption under load increases as the total amount of crosslinker increases in the system. This can be explained by the effect of crosslinking, which makes the hydrogels more rigid and hence less prone to squeezing action by applied load.

#### Soluble Fraction

The fraction of soluble polymer was found to be in the

range of 1.5 %-3.5 % for the entire series of experiments. The soluble content was found to decrease with increase in the concentration of MBA. The fraction of the soluble polymer depends on the crosslinking density, and the initial monomer concentration. In our experiments the initial monomer concentration was fixed therefore the variation in soluble content can be attribute to change in crosslinker concentration.

#### Conclusions

Superabsorbents based on acrylic acid were prepared via inverse-suspension polymerization method. The effects of polymerization conditions on absorbency were systematically investigated using Box-Behnken design. Superabsorbents for specific end application can be designed by suitable selection of process conditions. The incorporation of surface crosslinking can be utilized to improve the absorption under load characteristics without seriously affecting the free water absorption capacity of hydrogels.

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