Synthesis of Superabsorbent Polymer (SAP) via Industrially Preferred Route

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Abstract: The assigned study is dedicated to the synthesis, improvement and characterization of acrylic-based superabsorbent polymers (SAPs) which can be used in versatile applications notably in disposable diapers and pharmaceutics. The industrially preferred solution polymerization route and low cost monomers were used to synthesize SAPs. Homopolymer and copolymer based SAPs were prepared with varying amount of cross-linker and initiator concentrations and compared for swelling rate with a commercially available SAP sample. Swelling capacity linearly decreases with increase in cross-linker content for both the synthesized SAPs samples whereas it first increases and then decreases with initiator content for the synthesized copolymer SAP. Swelling kinetics of the synthesized and commercial SAPs were modelled using model equation proposed by Omidian *et al.* Both the synthesized SAPs showed substantial increase in swelling capacity whereas copolymer SAP exhibited the highest swelling rate (rate parameter 2.78 min) when compared to homopolymer SAP and the commercially available SAP samples. Accordingly, the copolymer SAP may find its application in disposable diapers or pharmaceutics where the higher swelling rate is of prime importance. Copolymer and commercially available SAPs depicted significant decrease in swelling capacity even at very low saline solution concentration (0.01 %).

Keywords: Copolymer, SAP, swelling capacity, swelling rate, solution polymerization.

INTRODUCTION

Hydrophilic polymers having capability of absorbing and retaining enormous amount of water, saline and physiological solutions are known as superabsorbent polymers (SAPs). SAPs are sometimes mentioned as “xerogels” or “xerogellents” owing to their dryness and gelling nature [1,2]. SAPs were developed in mid 1970s and find applications in personal care, hygienic products, agriculture, controlled delivery of drugs, artificial snow for skiing areas and many others [1-4]. Monomer concentration, initiator concentration, cross-linker concentration, polymerization temperature and particle porosity are some of the major factors that affect the final properties of the SAPs [5]. On the other hand, high swelling capacity, high swelling rate and good swollen gel strength are some of the desired properties of a good superabsorbent [6]. To prevent infinite swelling of polymer chains in water three dimensional structures or networks commonly known as cross-links are employed between polymer chains of a SAP. As polymer (SAP) is immersed in water, random coils of polymer become more aligned on swelling which reduces the entropy of the chains. There is a direct relationship between cross-link density and polymer characteristics, as increase in cross-link density decrease swelling capacity and increase gel strength of the polymer [7-9].

SAPs can be synthesized using either solution [10] or inverse suspension/emulsion polymerization [11, 12] techniques. Both of the polymerization techniques have their own advantages and disadvantages. However the solution polymerization is industrially preferred in consequence of its economical process [13, 14].

It is well documented that superabsorbent polymers are ordinarily polyelectrolytes which contain carboxylic groups and cross-link sites. Dissociation of carboxylic groups results in the extension of polymer coils because of osmotic pressure and electrostatic forces [1,2]. Many kinds of raw materials, synthesis methods and properties of SAPs have been reviewed by many researchers [15-18]. However, acrylic acid and acrylamide are industrially preferred due to their high water absorbency and low cost [13, 14].

Majority of the reported research work is devoted to the high swelling capacity whereas the swelling rate is of prime importance for certain applications such as disposable diapers which alone accounts for 80-85% of the market share [19] and pharmaceutics [20]. On the other hand, currently in Pakistan no industry is involved in the production of SAPs.

The main purpose of this study is twofold: first, to explore SAP synthesis using low cost acrylic-based monomers and second to compare the swelling rate (water absorption rate) of the synthesized SAPs with a commercially available imported SAP sample.

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ISSN: 1814-8085 / E-ISSN: 1927-5129/16

Table 1:

Raw Material*	Type	Manufacturer
Acrylic acid	Monomer	Lab grade (Shafi Reso Chemicals Pvt. Ltd. – Pakistan)
Acrylamide	Monomer	Commercial grade
Methylene-bis-acrylamide	Cross-linker	Merck
Potassium peroxide	Initiator	Commercial grade
Sodium hydroxide	Neutralizer	Analytical grade (Merck)

*All the raw materials were used as received.

EXPERIMENT

Materials

Sample Preparation

All the solutions were prepared in distilled water. Two different SAP samples namely homopolymer SAP (Poly-SAP) and copolymer SAP (copolySAP) were synthesized and compared with a commercially available imported SAP sample.

The commercial SAP sample was purchased from the local market in the form of disposable baby diaper. The SAP resins were separated from the diaper wrapping materials. The separated SAP resins were used for comparison purpose in this study and named Commercial-SAP hereafter.

Synthesis of Homopolymer SAP (Poly-SAP)

In a typical recipe of homopolymer SAP, acrylic acid solution (50 % V/V) was neutralized up to 75 % using 0.15 M NaOH solution. The resultant exothermic mixture was left for about 2 to 3 hours at room temperature. Cross-linker solution ranging from 0.75 % to 1.75 % (W/V) was added to the above mixture in a separate beaker. The beaker was gradually heated on a silicon oil bath under continuous stirring using magnetic bead. The initiator solution of constant concentration (3.75 % (W/V) was added to the mixture when the final temperature of 55 °C was reached. The beaker was left for reaction until the gelation was reached. The gelation was practically observed when the stirring magnetic bead stopped working.

Synthesis of Copolymer SAP (copolySAP)

In a typical recipe of copolymer SAP, acrylic acid solution (50 % V/V) was neutralized up to 75 % using 0.15 M NaOH solution. The resultant exothermic mixture was left for about 2 to 3 hours at room temperature. In a separate beaker cross-linker solution ranging from 0.75 % to 1.75 % (W/V) and the acrylamide solution (0.115 % W/V) of constant concentration were mixed under continuous stirring using magnetic bead. The mixture of the two beakers were mixed in a large beaker and left for approx. 30 min under continuous stirring to homogenize the content of the beaker. The beaker was gradually heated on a silicon oil bath. The initiator solution in the range of 1.88 % to 5.75 % (W/V) was added to the mixture when the final temperature of 55 °C was reached. The beaker was left for reaction until the gelation was reached. The gelation was practically observed when the stirring magnetic bead stopped working.

RESULTS AND DISCUSSIONS

Effect of Cross-Linker Concentration on Swelling Capacity

Figure **1** shows the effect of cross-linker concentration on the swelling capacity of Poly-SAP and copolySAP samples. It is apparent from the figure that Poly-SAP shows higher swelling capacity, for all cross-linker concentrations, than copolySAP. The higher swelling capacity of the Poly-SAP sample is attributed to the high absorption capacity of acrylic acid due to the repulsion of negatively charged carboxylic groups present in the main polymer chains [1]. The lower values of the swelling capacity of copolySAP might be attributed to the increase number of cross-links per polymer chain which relatively results in a strong molecular structure. Consequently, when the cross-linking density increases, the swelling capacity will decrease [7-9, 21-23]. However it is interesting to note that the swelling capacity decreases faster in case of Poly-SAP samples, see regression lines slopes in the Figure **1**.

Effect of Initiator Concentration on Swelling Capacity

It is evident from the Figure **2** that the swelling capacity of copolySAP first increases with the initiator

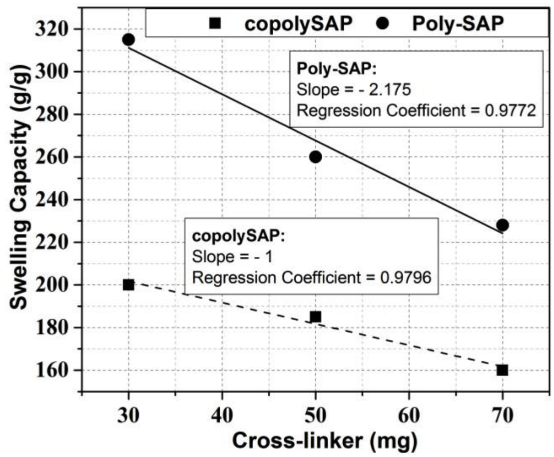

Figure 1: Effect of the cross-linker content on the swelling capacity of homopolymer SAP (Poly-SAP) and copolymer SAP (copolySAP) at 30 °C and constant initiator content of 150 mg.

concentration and then decreases. Similar Gaussian distribution behavior is also reported by other studies [24-26]. The initial increase in the swelling capacity might be attributed to the optimum amount of radicals to produce high molecular weight SAP with sufficient density of hydrophilic groups (-COOH, -CONH, $-COO^{-}$) and gel strength [25]. The decrease in the swelling capacity after optimum swelling capacity (228.45 (g/g)) could be due to the synthesis of low molecular weight SAP [27] which caused low gel strength [18,22,23] and hence, fast dissolution.

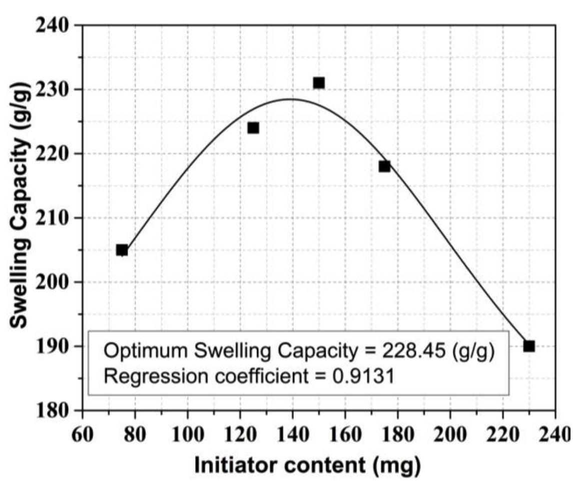

Figure 2: Effect of the initiator content on the swelling capacity of the copolymer SAP (copolySAP) at 30 °C and constant cross-linker content of 10 mg. The line is the Gaussian fit to the data.

Swelling Kinetics of the Synthesized and Commercial SAPs

The rate of distilled water (pH = 7) absorption (swelling rate), measured on the same range of particle size, is compared for the synthesized and commercial SAP samples in Figure **3**. All the samples show faster absorption in the initial stage and levels of at the later stages. The highest initial absorption rate is observed for the copolymer sample which might be due to the presence of amide groups [28]. Kabiri *et al*. also reported similar results for their copolymer samples [29].

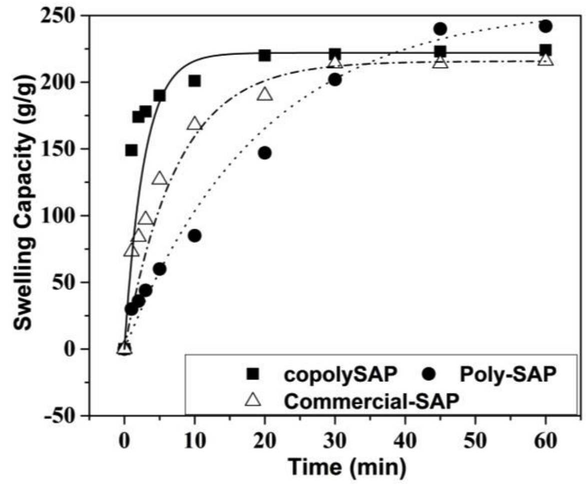

Figure 3: Swelling kinetics (rate of distilled water absorption, pH = 7) of the synthesized (homopolymer SAP (Poly-SAP) and copolymer SAP (copolySAP)) and Commercial SAP (Commercial-SAP) at 30 °C. Contents of the initiator and the cross-linker are 150 mg and 10 mg, respectively, for both the synthesized SAPs. The lines show the model fitting (see equation 1).

The swelling kinetics of the synthesized and commercially available SAPs can be modelled via following equation [30]:

$$SC(t)= SC_e\,[1- \exp(-t/R)] \quad (1)$$

Where SC(t) is the instantaneous swelling capacity (g/g), SC_e (equilibrium swelling capacity) is the swelling capacity (g/g) at infinite time, t is the swelling time (min), and R (the rate parameter) is the time (min) required to reach 63 % of the equilibrium swelling capacity.

A typical curve is shown in Figure **4** to determine the model parameters.

The model parameters were determined by non-linear curve fitting using OriginPro 9.1® and are shown in Figure **5**. It is evident that the lowest rate parameter is obtained for the copolySAP and the highest swelling capacity for Poly-SAP. The lower value of the rate parameter [31] suggests the higher swelling rate of the copolySAP. Accordingly, the copolySAP may find its application in disposable diapers or pharmaceutics where the higher swelling rate is of prime importance.

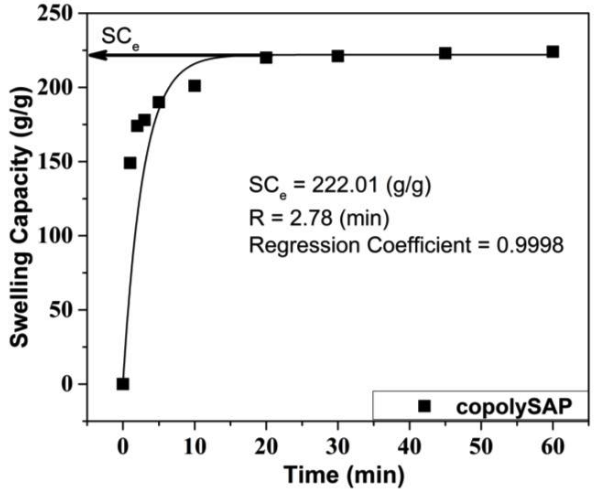

Figure 4: A representative curve of the copolymer SAP (copolySAP) for the determination of model (equation 1) parameters.

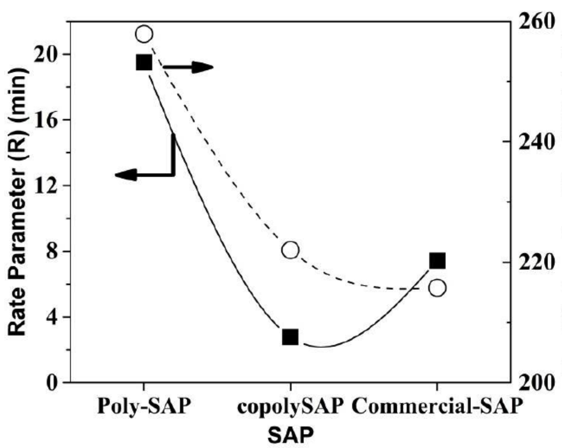

Figure 5: Rate parameter and equilibrium swelling capacity versus type of SAP. The lines are drawn to guide the eye of the reader.

Effect of Ionic Strength on Swelling Capacity

The effect of saline solution concentration on the swelling capacity is compared for the copolySAP and Commercial-SAP samples in Figure **6**. The swelling capacity of copolySAP and Commercial-SAP in distilled water is about 3 times and 2.4 times more than 0.01 % saline solution, respectively. The decrease in the swelling capacity might be due to the increase of sodium ions outside the SAP gel which leads to lowering in osmotic pressure. The observations made in this research are in accordance with the findings of the other researchers [32-34].

CONCLUSIONS

An attempt was made to synthesize acrylic-based superabsorbent polymers, homopolymer SAP and copolymer SAP, using low cost monomers (acrylic acid

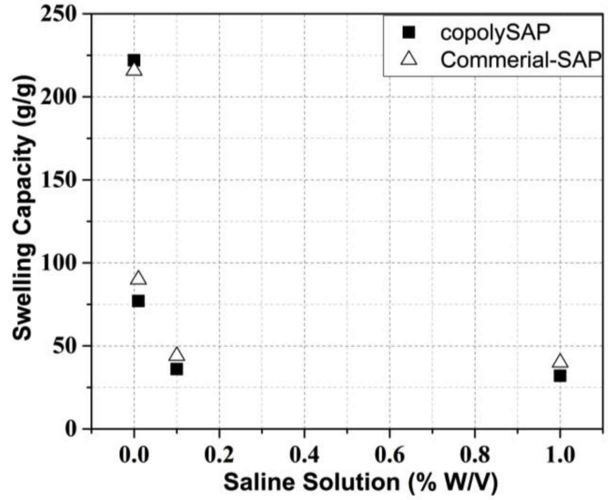

Figure 6: Effect of the saline solution concentration on the swelling capacity of copolymer SAP (copolySAP) and commercially available imported SAP (Commercial-SAP) at 30 °C. Contents of the initiator and the cross-linker are 150 mg and 10 mg, respectively, for the copolySAP.

and acrylamide) and industrially preferred solution polymerization route. The aim was to produce SAPs with high swelling rate (water absorption rate) and high swelling capacity especially for disposable diapers and pharmaceutics applications. The findings of this study are:

- Higher cross-linker concentration leads to lower swelling capacity for both the synthesized samples.
- Swelling capacity of the copolymer SAP first increases and then decreases with the initiator content.
- The swelling kinetics was successfully modeled by Omidian *et al*. proposed model.
- Both the synthesized SAP samples showed higher swelling capacity when compared to commercially available imported SAP sample.
- The highest swelling rate (water absorption rate) was obtained for copolymer SAP when compared to homopolymer and commercially available SAPs samples.
- Substantial decrease in swelling capacity in saline solution, even at very low concentration (0.01 %), was observed for copolymer SAP and commercially available SAP samples.

The findings of this study suggest that the synthesized copolymer SAP will find its applications in disposable diapers or pharmaceutics where higher swelling rate is the foremost prerequisite of the final products.

ACKNOWLEDGEMENTS

The authors are very thankful to Dr. S.I. Ali for his valuable discussions throughout the research.

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Received on 12-05-2016 Accepted on 15-06-2016 Published on 27-09-2016

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