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The Effect of Monomers Molar Ratio on Degree of Absorptivity of Poly (AAc -co -AAm) as a Super Absorbent Polymer in Different Aqueous Solutions

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Abstract In this research the Super Absorbent Polymers (SAPs) were prepared by free-radical crosslinking copolymerization with different molar ratios of acrylamide (AAm) with partially neutralized acrylic acid (AAc) in aqueous solutions in the presence of potassium persulfate (KPS) as initiator and N,N'-methylene-bisacrylamide (MBA) as crosslinking agents at temperature 60 °C for 2 hours. The structure of the prepared SAP was confirmed using FTIR spectroscopy. The degree of swelling then was measured for all prepared samples in different types of water. The results showed that the degree of swelling of SAP samples as a function of AAc:AAm ratio were arranged as following: 1:2 > 1:3 > 1:1. In addition, as a function of water type, the different SAPs have greater absorbency of distilled water than deionized water, where tap water was recorded as a medium of lowest absorbency.

Key words: Super absorbent polymers, Free radical polymerization, Acrylic acid, Acrylamide.

تأثير المعدل المولي للمونومرات على درجة امتصاصية البوليمر المشاركة Poly (AAc-co-AAm) فائق الإمتصاص في محاليل مائية مختلفة.

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الملخص في هذه الدراسة جرى تحضير بوليمرات فائقة الإمتصاص (SAPs) بإستخدام البلمرة المشتركة بالجذور الحرة بمعدلات مولية مختلفة من الأكريلاميد AAm وحمض الأكريليك AAc المعتدل جزئيا في محلول مائي بوجود بيرسلفات البوتاسيوم KPS كبادئ، ومركب MBA كعامل تشبيك عند درجة حرارة 60 درجة مئوية لمدة ساعتين. بعدها تم التأكد من التركيب الكيميائي للبوليمر الناتج بواسطة مطياف FTIR وقياس درجة الامتصاصية في أوساط مائية مختلفة لجميع العينات المحضرة. أظهرت النتائج درجة الانتفاخ للعينات إعتماد على معدل AAm:AAc ورتبت كالتالي: 1:2 > 1:3> 1:1، كما انه بإختلاف الوسط المائي إختلفت الامتصاصية حيث أن SAPs كان لديها إمتصاصية للماء المقطر أعلى من الماء منزوع الأيونات، ويأتي ماء الحنفية كأقل وسط للإمتصاص.

كلمات مفتاحية: بوليمرات فائقة الإمتصاص، بلمرة الجذور الحرة، حمض الأكريليك، أكريلاميد.

1. Introduction:

Polymeric hydrogels (PHs) are cross-linked hydrophilic polymers absorbing large quantities of water without dissolving. PHs which can hold up to hundreds to thousand times of their existing weight of water are called as Super Absorbents Polymers (SAPs) [1]. This type of polymers contains long polymeric chains which are slightly cross-linked. Their ability to absorb water arises from hydrophilic functional groups attached to the polymer backbone, while their dissolution resistance arises from the cross-links between network chains[2]. Water inside the SAP allows free diffusion of some solute molecules, while the polymer material serves as a matrix to hold water together. These polymers are synthesized by using water soluble monomers through a free radical polymerization in the presence of a suitable cross-linking agent [2]. Among these hydrogels polyacrylamide (PAAm) is one of the most popular [3, 4]. In addition, partially neutralized polyacrylic acid (PAAc) has also been proven to give high performance [5]. This was attributed to the interaction between the solute ions i.e. COO^- and Na^+ ions with the solvent molecules which are polar water molecules. Hydrogen bonds has also a major contribution in water absorption process by the interactions between molecules, occurring in molecules that have hydrogen atoms attached to small electronegative atoms such as N or O [5].

Different preparation methods, raw materials, experimental conditions and other factors cause tremendous gaps in the performance of SAPs [6, 7]. Some of the resultant SAPs called "intelligent" or "smart" hydrogels because they are respond to the external conditions such as pH, temperature, ionic strength, etc. Such responsive hydrogels attracted an increased attention in many areas like biotechnology, pharmacy, drug delivery systems, separation processes and in the field of agriculture[8].

In this work, SAPs from Acrylic acid and acrylamide copolymer were prepared by free radical polymerization, and their swelling characteristics will be studied. The purpose of our recent research is to modify and upgrade the produced SAPs to obtain an ecofriendly hydrogels with an ultimate absorptivity in order to apply them in many fields such as agriculture or medical fields.

2. Experimental:

2.1. Materials:

Acrylic acide (AAc), Acrylamide (AAM), N, N'-methylenebisacrylamide (MBA), and Potassium persulphate (KPS) are analytical grades and were purchased from; LOBA CHEMIE Co. India and used as received. All other used agents were analytical grade, and all solutions were prepared with distilled water.

2.2. Preparation of Poly (AAc-co-AAm):

poly(acrylic acid – acrylamide) copolymers with different molar ratios of monomers were prepared as following: Different amounts of Acrylamide as given in table (1) were dissolved in 50 ml distilled water and mixed in a three necked round bottom flask and heated to 40 °C under nitrogen protection in a water bath. The solution is then mixed for 20 mins, then 2.5 ml acrylic acid was added to the solution. 0.05 g of MBA as crosslinking agent were added into the flask. The solution was stirred for 20 min under nitrogen. An amount of 0.1 g KPS as initiator dissolved in 10 ml distilled water, was slowly added into the flask to initiate the polymerization process. The solution was then heated at 80 °C while mixing for 2 hours. The polymer thus formed is cross linked poly(AAc- co-AAm) super absorbing polymer (SAP). The obtained SAP was dewatered using ethanol and then poured into a petri dish and dried in the oven of 80°C for 24 h to a constant weight then crushed under mortar and pestle.

Table 1: Composition of different prepared SAPs

SAP Type	AA:AAm	AA:AAm (mole:mole)	AA:AAm (g:g)
A	1:3	0.05:0.15	2.5:10.66
B	1:2	0.05:0.10	2.5:7.11
C	1:1	0.05:0.05	2.5:3.55

2.3. Structural analysis:

For structural analysis and as a conformation of polymerization reaction the FTIR spectra of SAP samples were dispersed in KBr pellets using a FTIR spectrophotometer (Tensor27) scanned in the range 400-4000 cm^{-1}.

2.4. Degree of swelling measurement:

The degree of swelling of SAPs represents the percentage increase of the volume of SAPs in water. Weighted quantities of the as prepared Poly (AAm-co-AAc) dry samples were immersed in excess deionized water, distilled water and tap water at room temperature to reach an equilibrium of swelling. Swollen samples were then separated from unabsorbed water by filtered over a 0.25 mm screen. Degree of swelling (g/g) was determined by weighting the swollen samples and then calculated using the following equation:

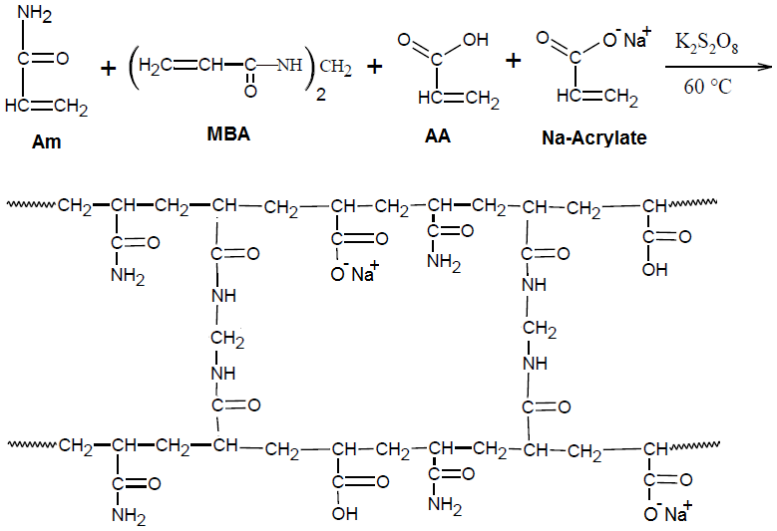
$$Ds = W - W_o / W_o$$

Where; W, W_o are the weights (g) of swollen and dry samples respectively.

3. Results and discussion:

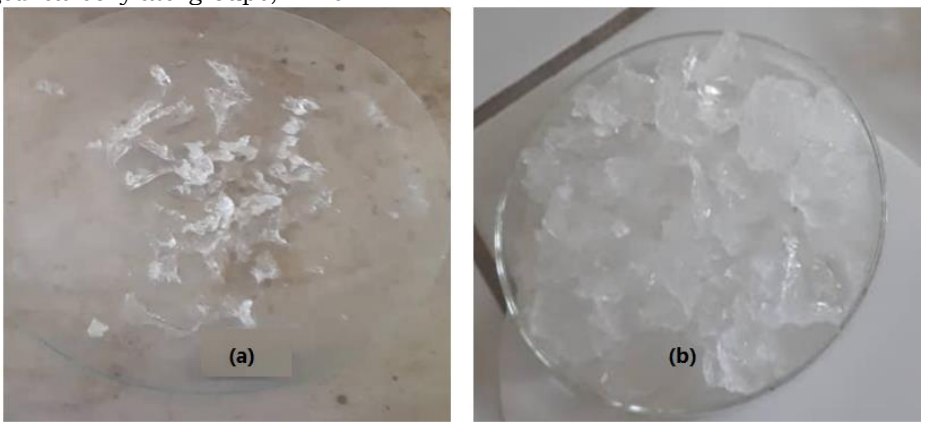
3.1. Preparation of Poly (AAc-co-AAm):

Crosslinked copolymers of acrylamide and acrylic acid were synthesized by free radical polymerization using acrylamide and partially neutralized acrylic acid as monomers, in presence of MBA as crosslinking agent and potassium persulphate KPS as an initiator for the polymerization reaction. Scheme (1) shows the chemical equation of this polymerization reaction.



Scheme (1): Chemical equation showing the preparation of Cross-linked Poly (AAc-co-AAm).

The performance of poly(acrylamide-acrylic acid) copolymer [Poly(AAc-co-AAm)] hydrogels depends on their molecular structure. These gels are made from monomers whose structure consists of a carbon double bond and the $CONH_2$ and -COOH groups respectively, as well as suitable amounts of a cross-linker. Causing repulsion between the resulting charged carboxylate groups, which will extend the polymer chains. This creates large spaces within the gel to absorb water molecules and increase swelling [9, 10]. Figure (1a) shows a photograph image of the as prepared dry SAP, it seems like a hard crystal particles while Figure (1b) represents the same sample after swelled with water.



Figure(1): Photograph images of dry (a) and swelled (b) SAP.

3.2. FTIR spectra analysis:

Figure (2) represents FTIR spectra of Poly (AAm-co-AAc) scanned in the range 400-4000 cm^{-1}. The characteristic a bands due to (C=O) are appeared between 1600-1700 cm^{-1}, and the characteristic peaks (1300-1400cm^{-1}) are due to the presence of a (C-N) vibration. The peak at around 2932 cm^{-1} is due to (C-H) stretching of the polymer backbone and the abroad absorption band due to (N-H) stretching is observed between 3200-3500 cm^{-1} [11, 12]. Absorption bands from 2960-3400 cm^{-1} were assigned to the -OH from the carboxylic group [13, 14]

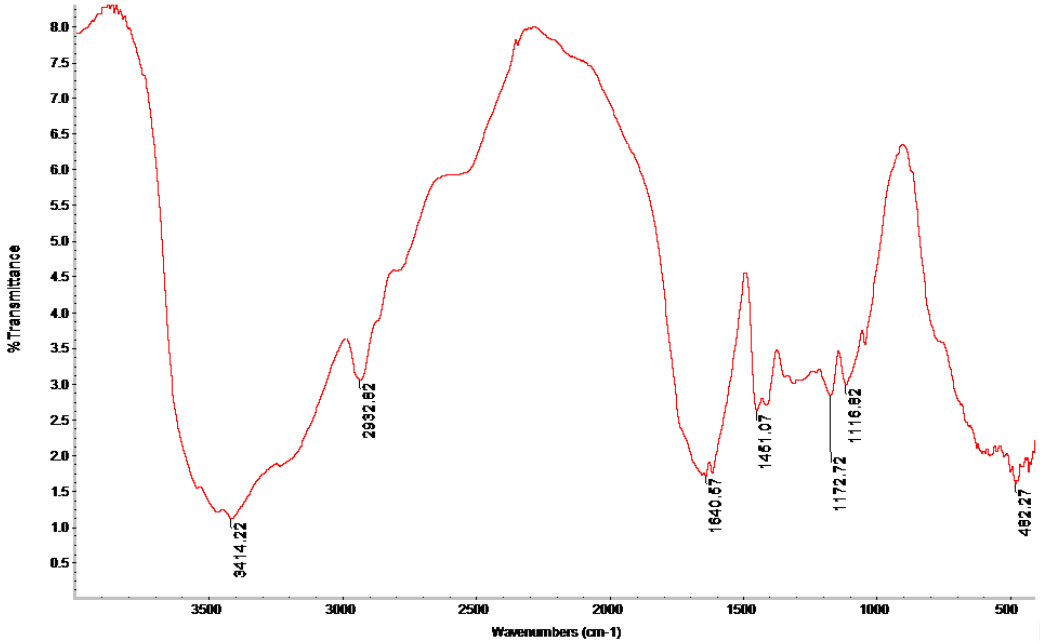


Figure (2): FTIR spectra of Poly (AAm-co-AAc) in the range 400-4000 cm^{-1}.

3.3. Swelling measurements:

The swelling property of SAPs is of interest for many applications. The swelling behavior depends on the functional groups present. This is primarily owing to the fact that the hydrophilic groups adsorb water molecules which are immobilized in the three-dimensional cross-linked network [15]. Swelling experiments were carried out at room temperature to evaluate the swelling capacity of the prepared SAP in tap water and compare it with swelling capacity of the same sample in distilled water and deionized water. The effect of variation of monomers molar ratio were investigated related to the swelling behavior of the prepared SAP under investigation. Table 2 Shows the effect of variation of AAc:AAm molar ratio on degree of swelling of SAP.

Table 2: Degree of swelling (g/g) of the prepared SAPs in different types of water

SAP Type	Degree of swelling, Ds (g/g)		
	Deionized water	Distilled water	Tap water
A	58.0	73.8	32.6
B	64.4	103.8	53.6
C	24.0	38.2	14.2

It is shown that degree of swelling of SAP increased by decreasing AAc:AAm molar ratio from 1:3 to 1:2. In deionized water it increased from 58.0 g/g to 64.6 g/g, in distilled water Ds increased from 73.8 g/g to reach 103.8 g/g, while in tap water it increased from 32.6 g/g, to 53.6 g/g. Further decrease in AAc:AAm molar ratio to 1:1 causes decrease in degree of swelling up to 24.0 g/g in deionized water, 38.2 g/g in distilled water, and 14.2 g/g in tap water. Thus, the optimum degree of swilling is 103.8 g/g at molar ratio of 1:2 (AAc:AAm) in distilled water. Figure (3) shows the dependence of the swelling of Poly (AAc-co-AAm) on monomers molar ratio of different samples (A, B, and C) according to their composition as listed in table 1.

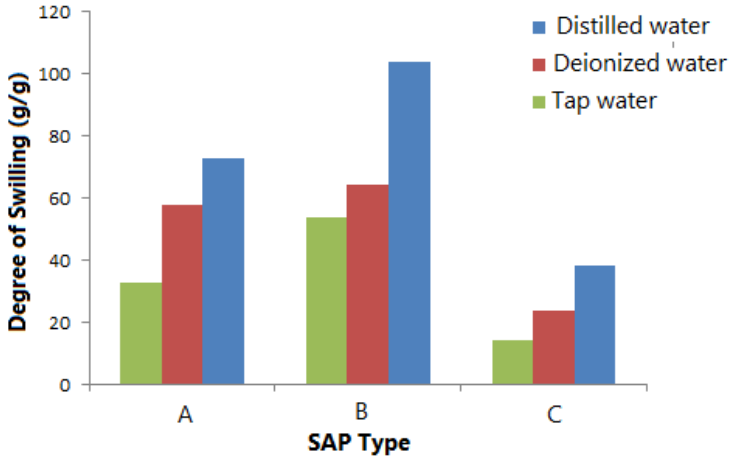


Figure (3): The effect of monomers molar ratio and water type on the degree of swelling of Poly (AAc-co-AAm).

4. Conclusion and future work:

Superabsorbent polymer (SAP) hydrogels of poly(acrylic acid - acrylamide) copolymer [poly (AAc-co-AAm)] are synthesized and tested as water absorbent granules which swell to many times their original size when they come in contact with water. The effect of variation of AAc:AAm ratio of the as prepared SAPs was investigated related to their swelling behavior in different types of water (deionized water, distilled water, and tap water). The optimum Degree of swelling was 103.8 g/g which is by SAP of 1:2 AAc:AAm molar ratio in distilled water.

More investigations on the structural and behavioral properties and their effect on water absorbency of the as prepared SAPs, as well as their nano-composites, will be as our future work in order to have more efficiency and eco-friendly applications as polymeric hydrogels in many fields such as in the field of agriculture, in oil industries, or in medical field etc.

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