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RESEARCH ARTICLE

SSWELLING AND PHYSICO-MECHANICAL PROPERTIES OF SYNTHESIZED SODIUM POLYACRYLATE HYDROGELS.

Shanin Sultana[1], Md. Khayrul Islam Sumon[2], Husna Parvin Noor[1], Walliullah Md. Ajmotgir[2], Md. Khabir Uddin Sarker[1] and Md. Rashed Hasan[1]

1. Fiber & Polymer Research Division, BCSIR Laboratories Dhaka, BCSIR, Dhaka-1205, Bangladesh.
2. Department of Chemistry, Dhaka College, Dhaka, Bangladesh.

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Abstract

This research involves the synthesis of cross-linked sodium polyacrylate hydrogels by solution polymerization technique. Three products were selected from different types of synthesized cross-linked sodium polyacrylate polymers to investigate the physico-mechanical properties of sodium polyacrylate hydrogels. Reaction parameters such as time, temperature, concentration of initiators, concentration of activator, concentration of sodium acrylate solution and concentration of cross-linking agents were investigated for cross-linked sodium polyacrylate hydrogels. FT-IR spectroscopic analysis was done for the synthesized hydrogel and the results showed the evidence of positive reactions. Density, viscosity, solubility test, solid content and melting point were measured for all products. Polymer films of the synthesized polymers were made by solution casting method and the mechanical properties were studied. Mechanical properties (ultimate tensile strength, tensile modulus and elongation at break) were measured for all synthesized cross-linked sodium polyacrylate polymers. Swelling properties of cross-linked sodium polyacrylate hydrogels were measured in distilled water, tap water and aqueous sodium chloride solution respectively. Water absorbencies results indicate that this polymer was water-swellable but not water-soluble like super absorbent polymers.

Introduction:-

Hydrogels are crosslinked network polymeric materials that have received considerable attention in the past 50 years, due to their exceptional promise in wide range of applications. Researchers have defined hydrogels in many different ways. It is a water insoluble polymeric material that exhibits the ability to swell in aqueous conditions and retain a significant fraction of dispersed water within its structure [(1)]. The dissolution of a hydrophilic polymer in water can be prevented by adding cross-links via either a physical or a chemical process. Physical cross-linking gives reversible hydrogels. Chemical cross-linking gives permanent hydrogels. These cross-linked polymers are soft and rubbery in nature and referred to as "Super Absorbents".Highly swelling polymers, superabsorbent hydrogels are hydrophilic, three dimensional networks that can absorb water in the amount from 10% up to thousands of times their dry weight. They are widely used in hygienics, foods, cosmetics and agriculture. Hydrogels have vast potential applications, including biomedical applications, soil/water stabilization layers in farming, civil engineering

Corresponding Author:-Shanin Sultana.
Address:-Fiber & Polymer Research Division, BCSIR Laboratories Dhaka, BCSIR, Dhaka-1205, Bangladesh.

structures soil conditioners, controlled release of fertilizers, fiber and metallic cable sealing, in water technologies, diapers, thickening agents for cosmetics, in drug delivery systems and in many other fields [1, 2, 3]. Many materials, both naturally occurring and synthetic, fit the definition of hydrogels. During last two decades, natural hydrogels were gradually replaced by synthetic hydrogels which has long service life, high capacity of water absorption, and high gel strength. Various publications have discussed in detail synthetic methods and applications of hydrogels[1]. Sodium polyacrylate based hydrogels are playing a vital role in various types of industrial applications and it has the ability to absorb as much as 200 to 500 times its mass in water. Sodium polyacrylate is an anionicpolyelectrolyte with negatively charged carboxylic groups in the main chain. The hydrogels of PAA having properties of bioadhesive, biocompatible and antibacterial due to their pendent carboxylic groups. Polyacrylic acid and its copolymer is widely used in pharmaceutical processes due to its pH dependent swelling behavior. The pharmaceutical applications of PAA are in the sustained release of drugs in ocular, nasal, buccal, gastro-intestinal, epidermal and transdermal drug delivery system[4].Hydrogels are popular carriers for drug delivery applications due to their biocompatibility and resemblance to biological tissues. Synthetic hydrogel poly (acrylamide-co-acrylic acid) copolymeric hydrogel nanoparticles (HN) were prepared by precipitation polymerization technique using potassium per sulphate (PS) as reaction initiator and *N*, *N* - methylene-bis-acrylamide (MBA) as crosslinking agent. In future studies, drug can be entrapped and released from the submicron hydrogel nanoparticles due to its good swelling, bio degradability and size distribution properties (Ray *et al*). Sadeghi *et. al.* reported on chemically modified natural hydrogel kappa-carrageenan (C) polysaccharide. Graft copolymerization of acrylamide (AAm) and itaconic acid (IA) onto the polysaccharide substrate by alkaline hydrolysis produced a novel superabsorbent hydrogel. Yoshimura *et. al.* also reported on extracted polysaccharide based superabsorbent hydrogels prepared from ulva, green seaweed's polysaccharide crosslinked with divinylsulfone (DVS) under alkaline aqueous condition.

The aim and objective of the present work is to synthesis and investigate the physical, chemical and mechanical properties of crosslinked sodium polyacrylate hydrogels. In this work crosslinked sodium polyacrylate polymer was synthesized by solution polymerization method in aqueous media. Synthesized polymer was characterized by FT-IR spectroscopic analyses. Physico-mechanical properties of crosslinked sodium polyacrylate polymers and water absorbencies of crosslinked sodium polyacrylate polymers were carried out and reported in this paper.

Experimental Part:-

Materials:-

Starting material of this synthesis is reagent grade acrylic acid ($H_2C{=}CHCO_2H$) supplied by Loba Chemical Pvt Ltd, Mumbai, India. All other chemicals used in this research were supplied by Merck, Germany. Reagent grade initiator and crosslinking agent are ammonium peroxodisulfate and N, N'-methylene bis-acrylamide (MBA) respectively.

Synthesis of Cross-linked Sodium Polyacrylate Polymers by Solution Polymerization method:-

To prepare cross-linked sodium polyacrylate polymer, the cross-linking agent N, N'-Methylene bis-acrylamide (MBA) was added into the prepared sodium acrylate solution. Sodium acrylate solution was prepared by adding NaOH solution slowly into acrylic acid in a round bottom three-necked flask on an ice bath with continuous stirring for 1.5 hours. Then the reaction mixture in flask was fitted with condenser in a water bath. Initiator, activator and cross-linking agent were added into the reaction mixture and the solution polymerization reaction was carried out. The pH of the synthesized polymer was found 7.25 at 24^0C. The resulting polymer hydrogel was dried in oven at 80^0C. Optimum condition of the reactions was selected by changing the parameters such as time, temperature, concentration of initiator, concentration of activator, concentration of sodium acrylate solution and concentration of cross-linking agent. Product of cross-linked sodium polyacrylate with concentration of cross-linking agent (more than 0.004 %) was rejected for low quality. Three type products of synthesized crosslinked sodium polyacrylate polymers were selected for physico-mechanical analyses Table [1].

Table 1:- Selected three type products of cross-linked sodium polyacrylate polymers by changing concentration of cross-linking agent.

Selected cross-linked sodium polyacrylate product no.	Concentration of cross-linking agent on constant amount of starting material (%)
1	0.001
2	0.002
3	0.004

pH and Solubility test:-

pH of the products were measured after completion of reaction using Jenway pH & conductivity meter, (model-3540, UK). Solubility of all synthesized polymers in water was measured and presented in result and discussion section.

Measurement of solid content:-

This test is used to evaluate the solid material in the synthesized polymer solution (nearly equal polymer content). The sample was taken and weighted into a flat-bottomed glass dish. The sample was gently spread into flat-bottomed glass dish and dried for 3hrs in a ventilated oven maintained at 105±2ºC. The film was cooled and weighted; the non-volatile matter was calculated as follow:

Solid content % = (C-A) X 100 /B

Where, A: weight of empty flat-bottomed glass dish in gram, B: grams of sample taken, C: weight of dish and dried sample content after heating in grams.

Film Casting:-

The prepared different type polymer solutions were casted on a glass to make films. Casting solutions were dried at air first and after evaporation of the water at room temperature, the film was easily removed from the glass. The dried film was cut into sheets and finally the polymer films were dried in an oven at 80^0C.

FT-IR Spectral Characterization:-

The infrared spectrum of cross-linked sodium polyacrylate polymer was recorded on a FT-IR/NIR Spectrometer (Forntier, PerkinElmer, USA). IR spectra with all information about absorbance were obtained in the printed form. IR spectra obtained this study are presented in the result and discussion section.

Physico-mechanical properties of the Sodium Polyacrylate Polymers:-

In order to investigate the physico-mechanical properties of the prepared polymers the following tests were carried out; Melting Point, Density, Viscosity and Tensile properties.

Tensile test:-

Tensile tests were performed by a computerized Universal Testing Machine (Model-Titan 5, Brand- James Heal, UK) for all specimens. Tests were performed according to ASTM D 882-02[7]. The speed was 5 mm/min. The shape and the dimensions of the specimens are its length, width, thickness were 148 mm, 10 mm and 4 mm respectively. Eight to ten specimens of each composition were tested and the average values were reported by calculating of maximum five values. The load vs elongation curves were obtained from the instrument. The highest load in the tensile test gives the tensile, or ultimate strength. The tensile strength (σ_{UT}) is calculated from the following equation:

Tensile strength, $\sigma_{UT} = W / A_T$

Where W is breaking load and A_T is the cross sectional area.

Tensile stress and strain values were calculated from the load vs elongation curves. Then the tensile stress vs strain curves were drawn and tensile modulus were determined from the initial slope of the stress-strain curve.

Density Determination:-

Water insoluble polymers densities were measured according to ASTM D 972-01[8]. Density is calculated from the following equation:

Density, kg/m^3= (specific gravity) x (997.6)

Specific gravity= a / [(a+w)-b]

Where, a= mass of specimen in air

b= mass of specimen and sinker (if used) in water

w= mass of totally immersed sinker if used and partially immersed wire

Melting Point Determination:-

Melting points of the synthesized polymers were determined using dried solid particles of polymer in a Gallenkamp melting point apparatus, made in England.

Swelling test of Cross-linked Sodium Polyacrylate Polymers:-
Percentage swelling (or mass swelling) is the most important parameter in swelling studies for hydrogel polymers. The swelling behaviour of dried cross-linked sodium polyacrylate hydrogels were determined by immersion in distilled water at 25^0C in a water bath. The water absorbed was calculated by weighing the samples, after wiping, at various time intervals were followed over a long period of time for 24 hours. Swollen gels were weighed by an electronic balance (Denver Instron balance) and Percentage of swelling was calculated from the following equation:

$$\text{Percentage swelling (\% S)} = \frac{(Mt - Mo)}{(Mo)} \times 100$$

Where Mt is the mass (g) of the swollen gel at time t, and Mo is the mass (g) of the dry gel at time 0.
Swelling Studies of all of these hydrogels were also carried out in tap water and aquous sodium chloride solution containing 0.5%, 0.9% and 1.5% sodium chloride. Three replicate specimens were tested for each batch and the results were presented as average of the tested specimens in the result and discussion section.

Results and Discussion:-
In this work, cross-linked sodium polyacrylate polymers have been synthesized by solution polymerization method and their swelling and physico-mechanical properties have been studied. Different types of crosslinked sodium polyacrylate polymers have been prepared by variation of reaction parameters. Initiator, activator and cross-linking agents are ammonium peroxodisulfate [$(NH_4)_2S_2O_8$], sodium bisulphite ($NaHSO_3$) and N,N'-Methylene bisacrylamide ($C_7H_{10}N_2O_2$) respectively.

Synthesis of Cross-linked Sodium Polyacrylate:-
Cross-linked sodium polyacrylate was prepared by solution polymerization method. The first step of the reaction was to prepare sodium acrylate monomer by the reaction of acrylic acid with sodium hydroxide in an ice bath, as illustrated in Scheme [1] (First step). The polymerization reaction of sodium acrylate with initiator ammonium peroxodisulfate, activator sodium bisulphate and cross-linking agent N,N'-Methylene bisacrylamide (MBA) at 50^0C yielded the product cross-linked sodium polyacrylate as illustrated in Scheme [1] (Second step). Reaction parameters time, temperature, concentration of initiator, activator and concentration of cross-linking agent were selected by observing the results of these parameters variation effect on fixed concentration of monomer. And it was found that increasing the value of these parameters above the selected parameters had no effect on the quality of the products.

First Step:-

Acrylic acid + NaOH ⟶ Sodium Acrylate

Second Step:-

Sodium Acrylate —(Initiator, Activator / Crosslinking agent)⟶ Cross-linked Sodium Polyacrylate

Scheme [1]

FT-IR Spectroscopic Characterization of Cross-linked Sodium Polyacrylate:-
The synthesized product cross-linked sodium polyacrylate has been characterized by infrared spectroscopic analysis. The IR spectrum of cross-linked sodium polyacrylate has been described in the Table [2]. The IR spectrum of cross-linked sodium polyacrylate is presented in Fig. [1].

The IR spectrum shows characteristic bands of carbonyl stretching at the region of 1725.5 cm^{-1}. The characteristic bands at 1557 cm^{-1} and 1402 cm^{-1} are due to the antisymmetric and symmetric vibration mode of the -COO group of sodium polyacrylate . And at the region of near 1456 cm^{-1} and 848 cm^{-1} peak are due to $-CH_2$ bending and wagging.

Table 2:- FT-IR spectral data of Cross-linked Sodium Polyacrylate

Peak Position (cm^-)	Assignment
3263	OH broad, strong band from the moisture content of polymer
2925	Methyl -CH
1725	C=O group
1557	-C00 group

1456	$-CH_2$
1402	-C00 group
1167	C-O
848	$-CH_2$ group

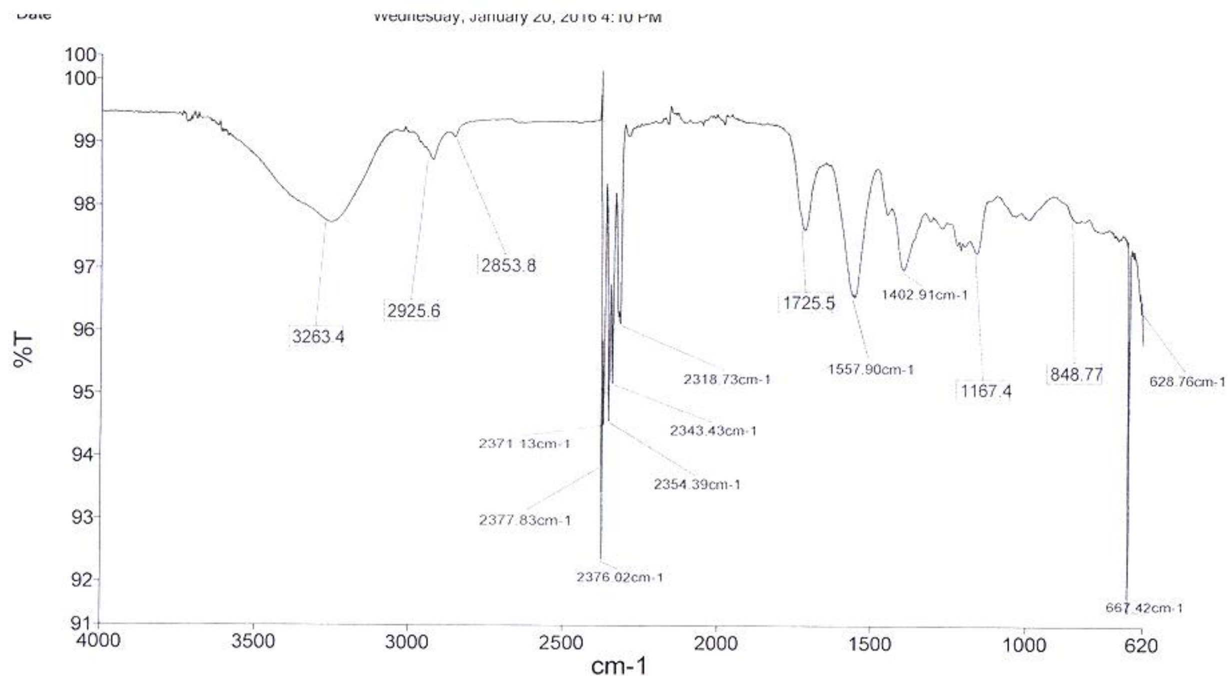

Fig.1:- Infrared spectrum of Cross-linked Sodium Polyacrylate

Physical properties of synthesized cross-linked sodium polyacrylate polymers:-
Some physical properties of crosslinked sodium polyacrylate polymers have been measured and presented in Table [3]. It is found from this table that the solid material (nearly equal polymer content) in the synthesized polymer solution is higher for product no 3.

Table 3:- Physical Properties of Crosslinked Sodium Polyacrylate Polymers

Cross-linked Sodium Polyacrylatae product no.	Solid content at 105^0C (%)	Solubility in water	pH at 24^0C.	Density of 1% dilute solution (g/ml) at 24^0C	Viscosity at 24^0C (Poise)	Melting Point
1	22.63	Insoluble	7.36	0.99	Couldn't measure for insolubility in water	Decomposed at 380^0C
2	22.64	Insoluble	7.27	0.99	Couldn't measure for insolubility in water	Decomposed at 380^0C
3	23.40	Insoluble	7.15	1.0	Couldn't measure for insolubility in water	Decomposed at 380^0C

Mechanical properties of cross-linked sodium polyacrylate polymers:-
Tesile strength, tensile modulus and elongation at break of the cross-linked sodium polyacrylate polymers have been determined following the ASTM method described in the experimental sections. The results obtained in this study are presented below.

Tensile strength, modulus and elongation at break:-

The tensile strengths of the cross-linked sodium polyacrylate polymers are presented in Fig. [2]. It is found that the tensile strength of the wet cross-linked sodium polyacrylate polymer is less than that of its dry polymer. Increasing the concentration of crosslinking agent in cross-linked sodium polyacrylate polymer increases its tensile strength, elongation at break and decreases its tensile modulus Fig. [2, 3 and 4]. This may be due to the hydrogel properties of cross-linked sodium polyacrylate polymer. So Stiffness of the cross-linked sodium polyacrylate polymer decreases with decreasing tensile modulus but toughness or ductility of the cross-linked sodium polyacrylate polymer increases with increasing elongation at break.

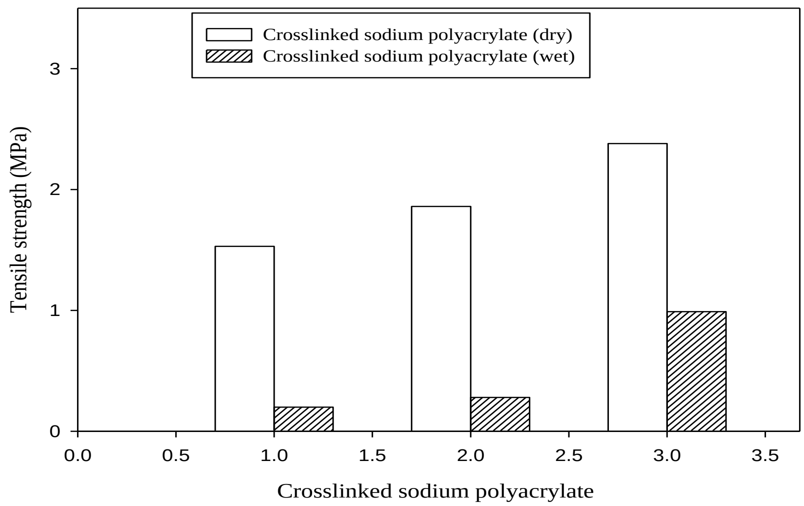

Fig 2:- Tensile strength vs crosslinked sodium polyacrylate polymers

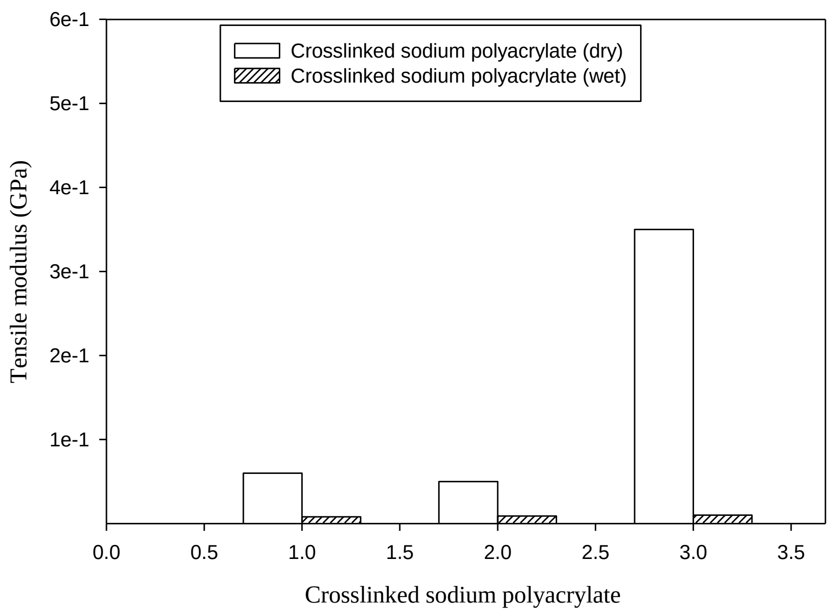

Fig 3:- Tensile modulus vs crosslinked sodium polyacrylate polymers

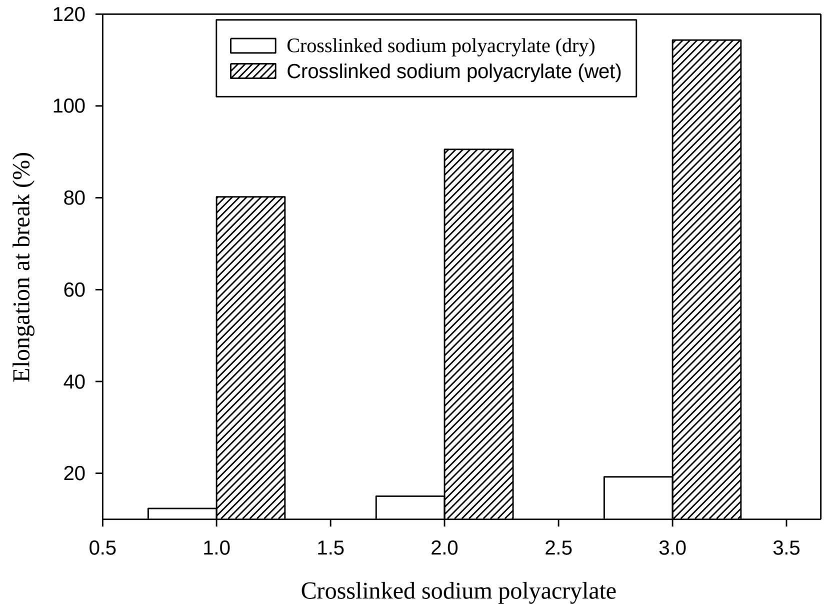

Fig 4:- Elongation at break (%) vs crosslinked sodium polyacrylate polymers

It is also found that dry cross-linked sodium polyacrylate polymer shows higher tensile modulus than that of wet cross-linked sodium polyacrylate polymer. It is also found that elongation at break of wet cross-linked sodium polyacrylate polymer higher than dry cross-linked sodium polyacrylate polymers Fig. [3, 4]. This result indicates that wet sodium polyacrylate polymers have rubber properties and they are not hard and brittle like other acrylic polymers. This property is similar to hydrogel properties.

Swelling properties:-

Swelling properties of cross-linked sodium polyacrylate polymers (product no. 3) were measured in distilled water, tap water and aqueous sodium chloride solution respectively. Results of water absorbency obtained in our study are shown in Fig. [5, 6]. It is observed from the figure that water absorbency of the cross-linked sodium polyacrylate polymer increases with increasing swelling time/hr. It is also found that water absorbency of the cross-linked sodium polyacrylate polymers are most in distilled water, less in tap water and considerably less in 0.9% sodium chloride solution. This may be due to the ionic strength of swelling solution. As swelling of hydrogel is induced by the electrostatic repulsion of the ionic charges of its network. This ionic strength of swelling solution decreases the electrostatic repulsion between the carboxylic groups of polymers. As a result hydrogel swelling decreased in aqueous sodium chloride solution. Highly swelling polymers, i.e. superabsorbent hydrogel can absorb water in the amount from 10% up to thousands of times their dry weight as they are hydrophilic and contain three dimensional networks. It is observed from fig. [5 and 6] that water absorbencies of cross-linked sodium polyacrylate polymers are more than thousands of times their dry weight. From fig. [6], it is also observed that swelling of cross-linked sodium polyacrylate polymer in aqueous sodium chloride solution decreases with increasing concentration of sodium chloride in solution. This is due to the more ionic strength of swelling solution decreases the electrostatic repulsion more between the carboxylic groups of cross-linked sodium polyacrylate polymer.

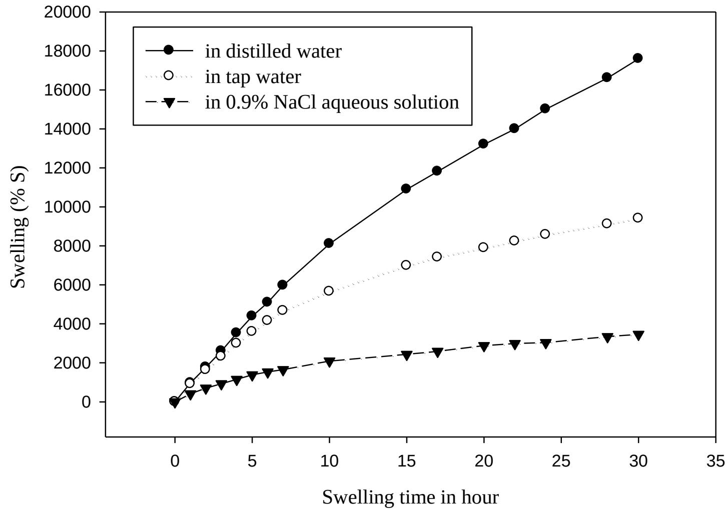

Fig 5:- Swelling behavior of crosslinked sodium polyacrylate in different fluids: distilled water, tap water and 0.9% NaCl aqueous solution

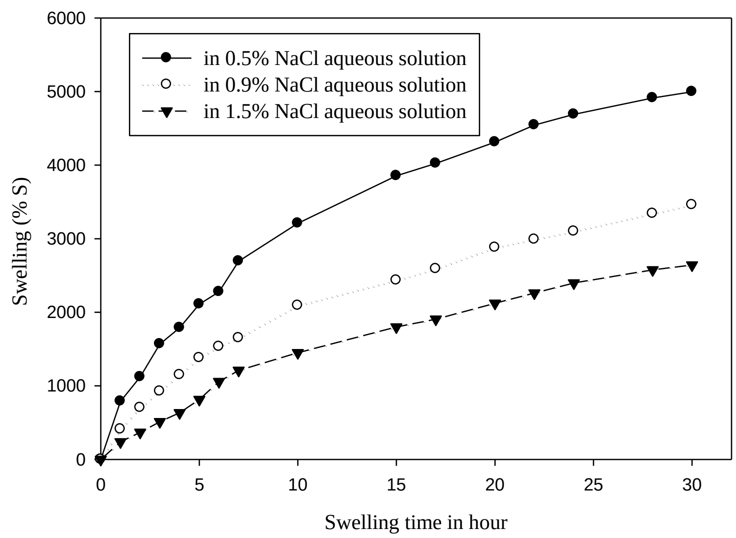

Fig 6:- Swelling behavior of crosslinked sodium polyacrylate in different fluids: 0.5%, 0.9% and 1.5% NaCl aqueous solution

Conclusion:-

Cross-linked sodium polyacrylate can be prepared by solution polymerization method and it can be used as a super absorbent polymer in diaper, pharmaceutical, agricultural, environmental and biomedical applications. Cross-linked sodium polyacrylate can be prepared from sodium acrylate mononmer by reacting with initiator, activator and cross-linking agent. FT-IR spectroscopic analyses indicate that positive polymerization has occurred to prepare crosslinked sodium polyacrylate polymer from sodium acrylate monomer. Physico-mechanical properties of cross-linked sodium polyacrylate polymers show the evidence of crosslinked hydrogel polymers. It is found from tensile properties that tensile strength and elongation at break increase with increasing concentration of crosslinking agent in crosslinked sodium polyacrylate due to its hydrogel property. Elongation at break higher for wet crosslinked sodium polyacrylate polymers than that of dry crosslinked sodium polyacrylate but tensile strength and tensile modulus are very low for wet crosslinked sodium polyacrylate polymers than that of dry crosslinked sodium polyacrylate due to its rubber like property. Swelling properties of cross-linked sodium polyacrylate polymer show better result to be used as a super absorbent polymer. Swelling behavior of cross-linked sodium polyacrylate polymer was observed in distilled water, tap water and aquous sodium chloride solution respectively. Percentage of swelling of cross-linked sodium polyacrylate polymers are more than thousands of times of their dry weight in distilled water. Percentages of swelling of cross-linked sodium polyacrylate decreases in tap water and aquous sodium chloride solution due to increase of ionic strength of swelling solution. Swelling of cross-linked sodium polyacrylate increases when electrostatic repulsion between the carboxylic groups of cross-linked sodium polyacrylate polymer increases.

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