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Research Article

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Preparation, characterization, and water sorption study of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) based hydrogel

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ABSTRACT

A novel biodegradable hydrogel composed of starch, 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and acryl amide(AM) have been prepared by free radical polymerization method using N,N[I]-methylenebisacrylamide(MBA) as cross-linking agent. The structure, morphology, and thermal nature of hydrogel are investigated by FT-IR (Fourier Transform Infrared Spectroscopy) , SEM(Scanning Electron Microscopy), and TGA(Thermo gravimetric Analysis) respectively. The water sorption behaviour of the hydrogel is investigated under different conditions of the swelling medium. The Swelling study shows that the water uptake property of the hydrogel is dependent on composition of polymer, pH and ionic concentration of the medium.

Keywords: Hydrogel, AMPS, Acrylamide, MBA, Water sorption.

INTRODUCTION

Hydrogels are important cross-linking polymers with diverse applications in biomedical and bioengineering fields. Due to unique characteristics, hydrogels have wide applications in drug delivery [1-4], wound dressing [5-7], contact lens [8-10], tissue engineering [11-14]. Many synthetic and naturally derived materials have been reported to form well characterized hydrogels. Since natural polymer possess better biocompatibility, biodegradability, non toxicity and easily modified ability than various synthetic materials, more and more researches have focused on natural polymer based hydrogels using polysaccharides, cellulose derivative and proteins as drug carrier [15, 16]. Among natural polymers, starch is an attractive candidate as starting material for the preparation of hydrogel because of its low cost, large scale production, biodegradability, and biocompatibility, renew ability and no toxicity. But the application of starch is limited due to brittleness and solubility in hot and cold water [17]. However the mechanical properties of the starch can be improved by incorporating the other polysaccharide or vinyl monomer like collagen [18], polyvinyl alcohol [29], gelatine [20, 21], acrylic acid etc through grafted copolymerization [22]. Starch and its derivatives have been utilized in many industrial applications such as food, medicine and cosmetics [23-25]. Another monomer chosen for the preparation of hydrogels is acryl amide (AM) and 2-acrylamide-2-methylpropane sulfonic acid (AMPS). Both AM and AMPS have large applications in medical field as well as other applications [26]. AMPS have attractive application as wound dressing material [27, 28] since it adheres to healthy skin but not to the wound surface and is easily replaceable without any damage to the healing wound.

In this study, a new hydrogel containing starch, AMPS-Na and AM is prepared by free radical polymerization method using MBA as cross-linking agent. The hydrogel is characterized by FT-IR, SEM and TGA techniques. Swelling studies have been performed at different conditions of pH, ionic strength and monomer composition.

EXPERIMENTAL SECTION

2.1 CHEMICALS: Acrylamido-2-methyl-1-propane sulfonic acid (AMPS) was purchased from Merck, India and prepared sodium salt (AMPS-Na) by neutralising with 1 mole of NaOH solution. Acryl amide (AM) (Merck, India) was purified twice by recrystalling with ethanol. Starch, potassium peroxodisulfate (KPS), NaOH, KCl, $CaCl_2$ were purchased from Merck, India. N,N^{l}-methylenebisacrylamide (MBA) was obtained from central drug House (P) Ltd. India.

2.2 Preparation of hydrogel

The hydrogel were prepared by free radical polymerisation method. 0.5 g of starch was dissolved in 5ml of boiled double distilled water and prepared a clear solution. To this solution 14.06 mM AM, 7.02 mM AMPS-Na, 0.073 mM initiator (KPS) and 0.12mM cross linker (MBA) were added and mixed with continuous stirring. The whole mixture was transferred into PVC straw and the polymerization was carried out at 60^0 C for 30 minutes. After complete polymerisation the gel was dried at 50^0 C for 8 h. The polymer was then cut into small pieces and allowed to equilibrate for 10 days by changing the swelling medium every day. After 10 days the hydrogel were taken out from the swelling medium and dried in air.

2.3 Characterisation of hydrogel

IR-spectra of the monomers and the hydrogel were recorded in Shimadzu-8400s Ft-IR spectrophotometer. The morphology of the hydrogel was investigated by using Scanning electron microscope (SEM) (Carlzeissieo Leo 1430VP). The thermal property of the gel was investigated by thermo gravimetric analysis (TGA) (Perkin Elmer 4000).

2.4 Swelling study

The progress of swelling was monitored gravimetrically as described by other workers [29]. 40 mg of dry hydrogel was immersed in 100 ml of double distilled water. After every 30 minutes interval of time the hydrogel was taken out and excess surface adhered water was removed by blotting and the weights of swollen gels were recorded. The swelling ratio was calculated by following equation.

$$\text{Swelling ratio} = \frac{\text{Weight of swellen gel}}{\text{Weight of dry gel}} \quad \text{.....(1)}$$

To understand the effect of monomer composition and external environment on the swelling, the swelling experiment is carried out by varying monomer composition, and pH and electrolyte concentration of the swelling medium.

RESULTS AND DISCUSSION

3.1 IR- Spectra of the hydrogel:

The IR spectra of pure AM, Na-AMPS, starch and prepared hydrogel are depicted in fig 1 (a-d). The IR spectra of the gel in Fig 1(d) clearly shows combined spectral feature of various functional groups of AM, Na-AMPS, and starch. The peak at 3661 cm^{-1} is due to the overlapping peaks of N-H and O-H groups of AM, Na-AMPS, starch. The C-H (symmetric and asymmetric) stretching is observed at 2779 to 3063 cm^{-1}. The N-H bending, N-C and C=O stretching of AM and Na-AMPS are observed at 1527, 1228 and 1693 cm^{-1} respectively. The characteristic peak of Na-AMPS units can be seen at 1049 cm^{-1} due to SO group.

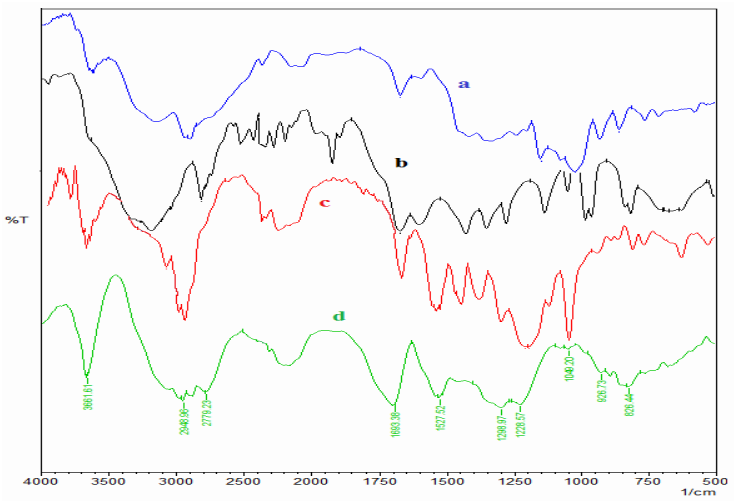

Fig 1: IR spectra of (a) starch (b) AM, (C) AMPS and (d) hydrogel

3.2 SEM study of hydrogel:

The morphological surface of the hydrogel is found to be heterogeneous in nature having some pores as shown by SEM image of the hydrogel in fig 2.

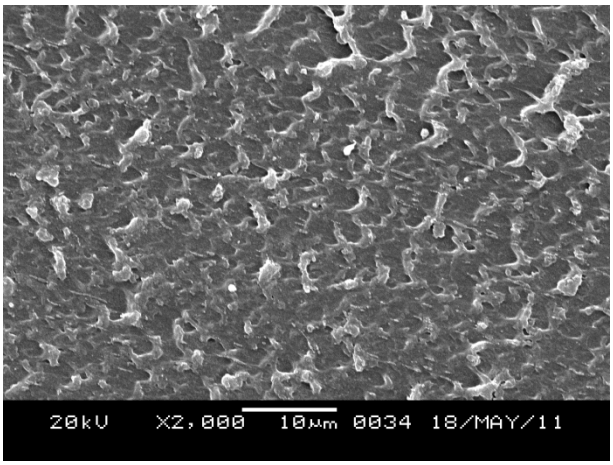

Fig 2: SEM image of hydrogel

3.3 TGA study of hydrogel:

The thermo gravimetric analysis (TGA) of hydrogel is depicted in fig 3. The thermogram shows that the hydrogel is thermally stable and the decomposition takes place in four steps. The first step of degradation due to dehydration is observed up to 237^{0}C with 13.178 % weight loss. Second step of degradation is observed from 237-366^{0}C with 31.17% weight loss and third step from 366-489^0 C with 16.782% weight loss due to degradation of functional groups of hydrogel. The final degradation of hydrogel is observed at 489-810^{0}C with 29.770% weight loss.

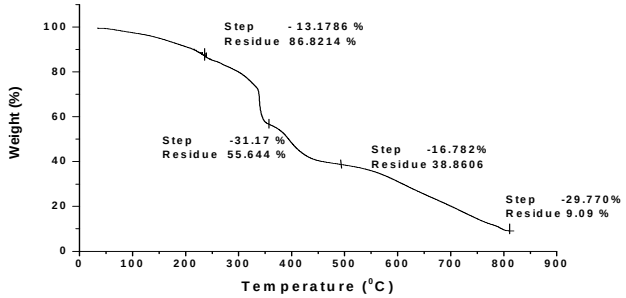

Fig 3: TGA of hydrogel

3.4 Swelling study:

The equilibrium swelling ratio data of hydrogel presented in the table1 indicate that as the amount of AMPS-Na content in the matrix increased from 3.51 mM to 9.36 mM, the equilibrium swelling ratio initially increased from 17.35 to 26.55 and then decreased to 15.675, which is shown in fig 4. Similarly, when AM content increase from 7.03 to 21.1 mM the Swelling Ratio initially increased from 33.45 to 39.05 and then decreased to 21.66, shown in fig 5. The initial rise in equilibrium swelling ratio is due to greater hydration with higher hydrophilic content in the polymer chain, which occurs to a certain limit. However, with further rise in the concentration, formation of dense network structure takes place, which prevents the water molecule penetration inside the network. This leads to decrease in the swelling ratio. The equilibrium swelling ratio decreases as the starch content in the matrix increased as shown in fig 6. The reduction of equilibrium swelling ratio from 38.225 to 26 were due to the formation of tight network structure in the high content of starch respectively, which hinders the mobility of the polymer chains and reduces water penetration into the gel.

Environmental pH value has large effect on the Swelling ratio especially for the hydrogel composed of ionic networks and containing large pendant groups [30] like these hydrogels. The swelling experiment is carried out a pH range of 2-9 by adjusting pH with NaOH and HCl solution. The results in fig 7 indicate that the hydrogel is sensitive to pH and optimum swelling is observed around pH 7. At low pH pendant groups of the polymer ionizes and forms anionic centres along the polymeric chains. Thus, polymer – polymer interaction predominates over the polymer – water interactions. Again, at high pH ionization of sulfonic group and complete deprotonation of amine group take place. This results in formation of new cross linked segments by hydrogen bond. These electrostatic interactions between the functional groups make the macromolecular chain arrangement compact and less chain relaxation and ultimately result in low swelling.

Table 1: Composition of hydrogels, equilibrium swelling ratio at 30^0 C and n values

Samples	AMPS-Na(m)M	AM(mM)	Starch(g)	MBA(mM)	Equilibrium Swelling Ratio	n
S1	3.51	14.06	0.5	0.12	17.35	0.5
S2	4.68	14.06	0.5	0.12	27.225	0.61
S3	5.85	14.06	0.5	0.12	26.98	0.62
S4	7.02	14.06	0.2	0.12	38.225	0.63
S5	9.36	14.06	0.5	0.12	15.675	0.61
S6	7.02	7.03	0.5	0.12	33.45	0.48
S7	7.02	10.55	0.5	0.12	39.05	0.5
S8	7.02	17.6	0.5	0.12	25.25	0.73
S9	7.02	21.1	0.5	0.12	21.66	0.63
S10	7.02	14.06	0.5	0.12	26.55	0.62
S11	7.02	14.06	0.7	0.12	26	0.62

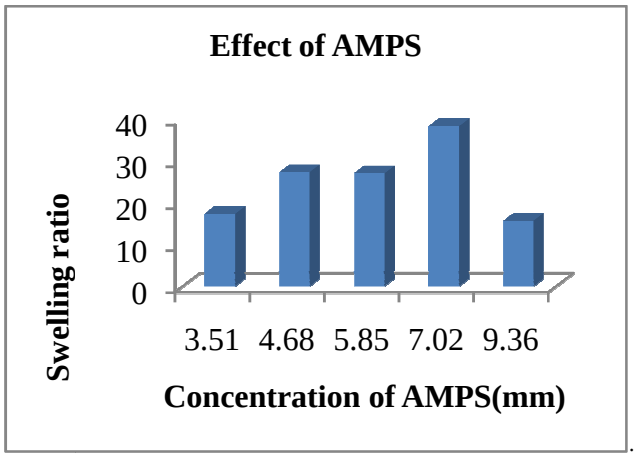

Fig4: Effect of AMPS on swelling ratio

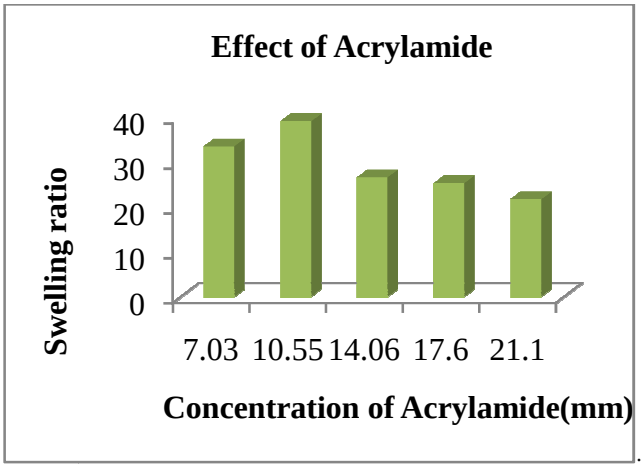

Fig5: Effect of AM on swelling ratio

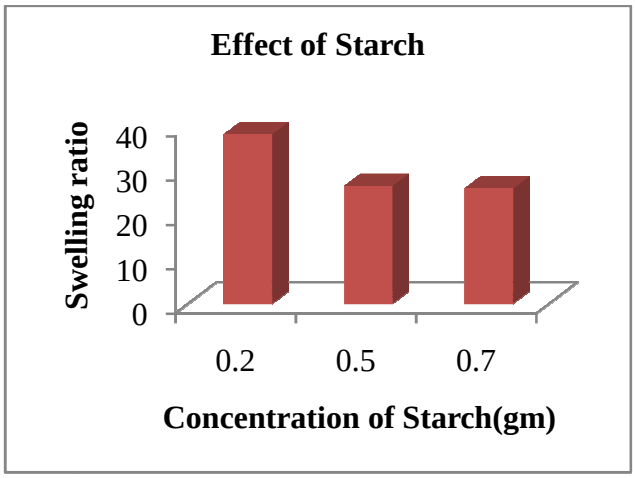

Fig6: Effect of Starch on swelling ratio

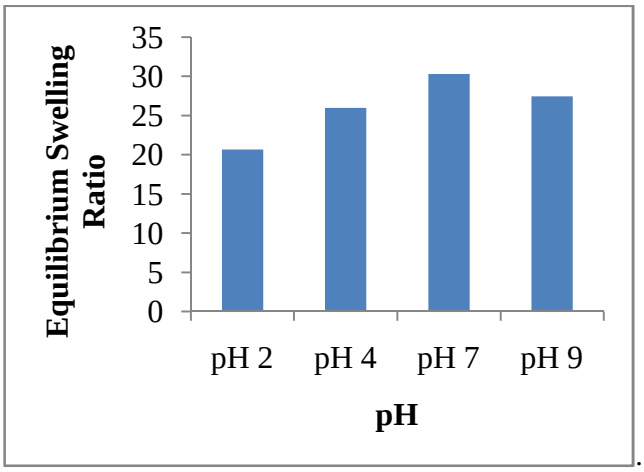

Fig 7: Effect of pH on equilibrium swelling ratio

A remarkable change in the equilibrium swelling ratio is observed at different salts concentration. The reduction in equilibrium Swelling Ratio (Fig 8) from 0.01 M to 1.0 M KCl and $CaCl_2$ solution was due to decrease in the osmotic pressure. Since, there is a balance between the osmotic pressure and the polymer elasticity, which sets the physical dimensions of the hydrogels [31]. The osmotic pressure is results from a net difference in the concentration in the mobile ions between the interior of the gel and the solution. Addition of the ions to the outer medium probably reduces the osmotic pressure and this brings decrease in the swelling ratio at high salt concentration. However,

comparatively lower values of Swelling Ratio in case of $CaCl_2$ than that of KCl is due to greater number of Cl^- ions in the swelling medium.

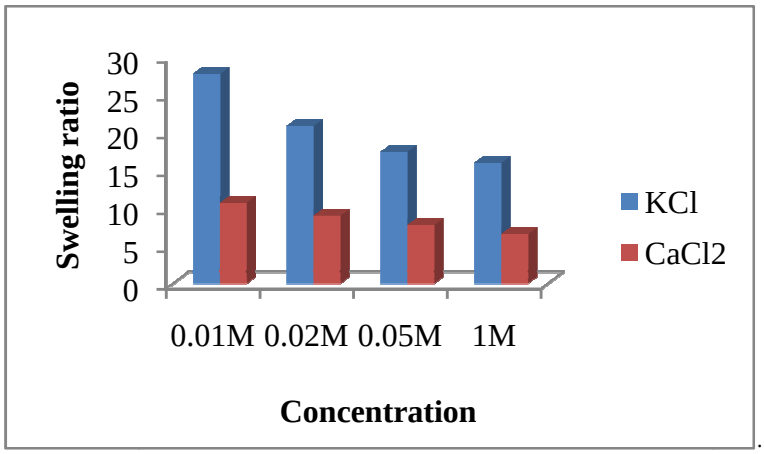

Fig 8: Effect of electrolyte on equilibrium swelling ratio

The water transport mechanism through the hydrogel was determined by several key factors such as the equilibrium water content, chemical architecture of the gel and relative rate of diffusion of water and relaxation of macromolecular chains [32]. Dynamic swelling data of all samples have been fitted to an empirical equation [33, 34] given below.

$$\frac{W_t}{W_\infty} = k\,t^n \quad \text{----------} \quad (2)$$

Where n is the swelling exponent, k is the swelling rate front factor and W_t and W_∞ are the water intakes by the swollen hydrogel at time t and equilibrium time ∞ respectively. A double log plot drown between W_t/ W_∞ and time t provides the value of n, which determined the nature of the solvent diffusion process, that is Fickian (n= 0.5) or non-Fickian (n= 0.5 to 1.0) diffusion. The calculated n values of hydrogels are given in the table 1. It is observed that the swelling exponent (n) values shift from Fickian to non-Fickian when AMPS-Na and AM concentration of hydrogel increased due to the formation of compact arrangement of macromolecular chain, the relaxation rate slowed down and became identical to water diffusion rate. This obviously results in a non-Fickian type of water transport mechanism. Starch does not have any effect on water transport mechanism in the study range.

CONCLUSION

In this work we have synthesized starch containing hydrogel by free radical polymerization using MBA as a crosslinking agent, characterized and studied the swelling behaviour under different conditions. The Swelling study shows that the water uptake property of the hydrogel is dependent on the composition of the polymer, pH and ionic concentration of the medium. The diffusion exponent calculated from empirical equation indicated that the water transport mechanism for all hydrogels followed non-Fickian nature of diffusion.

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