Investigation on itaconic acid based pH and salt-responsive biopolymeric hydrogels

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Abstract — Hydrogels are water entrapping polymer network with responding to external stimuli (pH, temperature, electric field, chemical environments, etc.) are often denoted to as "intelligent" hydrogels. In this work, an unique pH and salt-responsive polymeric hydrogel was synthesised based on itaconic acid (IA) via condensation followed by free radical polymerization with ethylene glycol with acrylic acid (AA) using ammonium persulfate (APS) as an initiator sequentially. The formation of the synthesized hydrogels was studied using FT-IR spectroscopy. Swelling equilibrium studies in the pH range of 4.0 to 10.0 revealed that the extent of swelling increased with increasing pH due to deprotonation occurred in the hydrogels network. SEM analysis supported the surface morphology and tuning behaviour of pH in different buffer solutions. In addition, salt sensitive behaviour was performed with various chloride salt solutions viz., NaCl, $CaCl_2$, $AlCl_3$. There has been a reciprocal relationship was monitored while increasing charge of ion from monovalent to trivalent, decrease in the swelling behaviour. This could be related to the complexing ability of the hydrogels encouraging the increase in the crosslinking density. Swelling in salt solutions is of chief implication in many practical applications like personal hygiene products and release systems in agriculture.

Keywords: Itaconic acid, swelling, hydrogels, salt responsive etc.,

I. INTRODUCTION

Hydrogels are weakly crosslinked tri-dimensional hydrophilic polymer which retains large quantities of water without dissolution. Networks can be built from homo- or copolymers and crosslinking points can be chemical or physical bonds. Environmentally sensitive hydrogels exhibit marked volume changes with changing external conditions, such as temperature, pH, solvent, ionic strength, etc. Itaconic acid is renewable resource based monomer, such as carbohydrate materials as molasses and hydrolyzed starch, by fermentation. Itaconic acid is very hydrophilic and is expected to show high biocompatibility because of its natural source The main advantage of IA application compared to the others carboxylic acids is the fact that it can be obtained from renewable resources, i.e. from carbohydrate materials such as molasses and hydrolysed starch, by fermentation. IA easily undergoes polymerization and provides polymer chains with carboxylic side groups, which are highly hydrophilic and able to form hydrogen bonds with corresponding groups or ionize in aqueous solutions of appropriate pH. Acrylic acid (AA) is the mostly used functional monomer to prepare the hydrogels. Due to its versatile nature, pH sensitive hydrogels has showed lot application, Viz., Food industry (as thickening agent, etc.), pharmaceutical (as controlled release preparations, etc.), agriculture and related fields (in controlled release of moisture, fertilizer, pesticide etc.), as technical and electronic instruments (as protector from corrosion, and short circuit etc.) biomedicine (as artificial organs etc.), bioengineering (in biomolecule immobilization), veterinary, photographic technology and adsorbent on removal of some unwanted agent in environmental applications [1]. Ethylene glycol (EG) was chosen as a difunctional monomer to improve the properties of hydrogels because of its flexibility and biocompatibility [2]. Tomic et al. demonstrated a pH-sensitive swelling behavior itaconic acid based hydrogels and their applications [3]. pH sensitive hydrogels are normally produced by adding pendant acidic or basic functional groups to the polymer backbone; these either accept or release protons in response to appropriate pH and ionic strength changes in aqueous media

The present investigation is focused on synthesis and characterization of itaconic acid based polymeric hydrogels and characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM). In addition to this the swelling and salt responsive studies were also investigated.

II. EXPERIMENTAL

Materials and methods

Itaconic acid (IA) was procure from sigma-Aldrich Company (Bangalore, India) ethylene glycol (EG) and acrylic acid (AA) were obtained from Merck. AA was vacuum distilled at 54˚C/ 25 mm Hg to extract inhibitor hydroquinone. Demineralized water was used for polymerizations and the preparation of the buffer solutions.

Infrared spectra were recorded using an Alpha Bruker Fourier-transform infrared spectrometer (FTIR), with a resolution of 2 cm^{-1}. Samples were prepared by adding a drop of a polymer solution (HFIP (1 g/L)) on a pressed KBr pellet, and the measurements were carried out at room temperature. Spectra were recorded between 4000 and 400 cm^{-1} at 2 cm^{-1} resolution.

The swelling experiment is an essential property of polymeric hydrogel. The dried hydrogel were immersed in an excess of carbonate buffer solutions (CBS) of desire pH values ranging from 4.0 to 10.0 at ambient temperature. Swelling process was monitored by gravimetrically. Swollen hydrogel were removed from the aqueous medium, blotted with filter paper, weighed at regular intervals and replaced in the same flask. The pH of aqueous medium was adjusted with dil. HCl and dil. NaOH, checked by pH meter (citizen 3000). The degree of swelling (S %) was calculated through following equation (1)

$$S_{eq}\% = \frac{W_{eq} - W_d}{W_d} \times 100 \qquad (1)$$

Here W_d is the initial weight of the dried IEA based hydrogel, W_t weight of the swollen sample at time t and W_{eq} weight of the swollen sample at equilibrium, respectively. Salt response were carried out according to the following procedure, air dried hydrogel sample was immersed in 50mL of saline solution **(NaCl, $CaCl_2$ and $AlCl_3$)** at varying concentration at room temperature until the swelling equilibrium was attained for 24 hours.

Synthesis of itaconic acid hydrogels

The IEA polymeric hydrogels were prepared through free radical polymerization. The monomers were itaconic acid (0.025 mol) and acrylic acid (0.025 mol). Initially itaconic acid was dissolve in acid medium (5.0 ml of HCl), added with ethylene glycol to form pre-polyester at 130^{0}C with constant stirring for 1 h in a silicon oil bath. The initiator ammonium persulfate (APS) (1%) was added in pre poly ester, then it stirred for 5 min followed by acrylic acid (0.025 mol) was added and stirring was continued for another 1 hr till the formation of glassy hydrogel, it implies the completion of the reaction. After the completion the reaction, the hydrogel were immersed in distilled water for a week to remove the nonreactive itaconic acid. The distilled water was changed daily. The disc was dried at favourable condition for 24 hrs. The synthetic procedure was repeated with varies moles of itaconic acid and ethylene glycol respectively. The polymeric hydrogel of itaconic acid, ethylene glycol and acrylic acid were named IEA, I_1E_4A and I_2E_3A respectively.

III. RESULTS AND DISCUSSION

FT-IR spectral analysis was used to describe the chemical structure of IEA based hydrogel and nature of the bond formed (Fig 1). A broad IR band in the region around 3250 cm^{-1} which corresponded to the O-H stretching vibration of the carboxylic group of IA and AA, the C=O stretching vibration of ester group also observed at 1687 cm^{-1}, the spectrum of weak shoulder around 2950 cm^{-1}, which implied aliphatic -CH_2 , C-H groups, the C-O stretching appeared around 1000-1260 cm^{-1}. The increased peak intensity of C=O functional group at 1698 cm^{-1}, which confirmed that formation of ester group in IEA based hydrogel. Several absorption band are appeared at finger print region. The peak at 690 cm^{-1} indicates the presence of C-H bending in ethylene glycol. The other characteristic bands represented C-C, C-H and CH_2 groups [4,5].

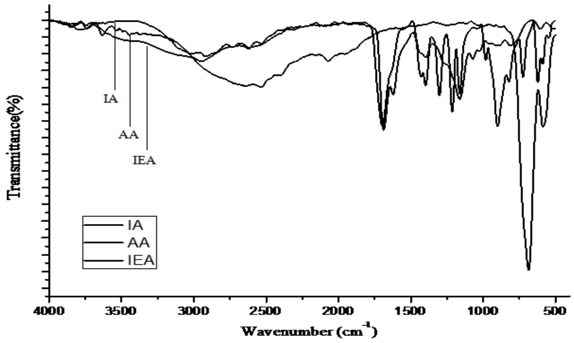

Figure.1: Comparison of IEA biopolymeric hydrogel

Equilibrium swelling studies of IEA hydrogel.

The equilibrium swelling studies were examined for IEA based hydrogel equilibrated in a carbonate buffer (CBS) with definite pH value ranging from 4.0 to 10.0 at ambient temperature (Fig. 2). The S_{eq}% value of IEA hydrogel were found out 260.00, 460.00, 600.00, 720.00 and 900.00%, I_1E_4A hydrogels S_{eq}% values were 280.00, 480.00, 660.00, 780.00 and 1010.00 % respectively [6].

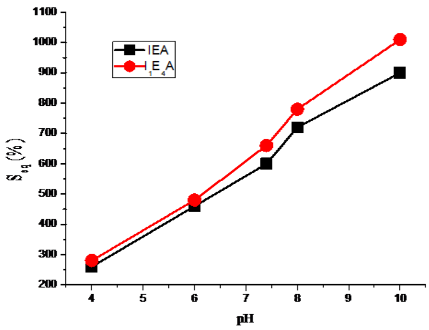

Figure 2: pH sensitive equilibrium swelling of IEA hydrogel and I_1E_4A hydrogel.

It is clearly indicated that S_{eq}% of IEA hydrogels increases with respect to pH. It was purely indicated that swelling % of synthesized biopolymeric hydrogels were significantly higher at higher pH, when compared to the lower pH value. Due to the presence of electrostatic repulsion among the charges present in polymeric hydrogels of IEA which improved the swelling behavior [7]. This type of pH sensitive IEA hydrogels could be a potential candidate in Metal ion, Dye removal and drug delivery applications.

Salt responsive behaviour of IEA biopolymeric hydrogel

Swelling capacity in various salt solutions is of prime significance in analytical applications such as hygiene products and waste water, agriculture and environmental applications. The swelling ability of IEA polymeric hydrogels in various salt solutions is appreciably decreased compared to the swelling values. This well-known desired swelling-loss is often attributed to a "charge screening effect" of the additional cations, causing anion–anion electrostatic repulsion. Moreover, in salt solution the osmotic pressure resulting from the difference in the mobile ion concentration between hydrogel and the aqueous phases is decreased. In addition, in the case of salt solutions with different cations, "ionic crosslinking" within the hydrogel causes an appreciable decrease in swelling capacity. In this series of experiments, the swelling capacity was measured in various salt solutions. With increasing charge of cation, the degree of crosslinking is increased and swelling is consequently decreased. Therefore, the swelling equilibrium were observed in various salt solution of the synthesized polymeric hydrogel is in the order NaCl >$CaCl_2$> $AlCl_3$ [8].

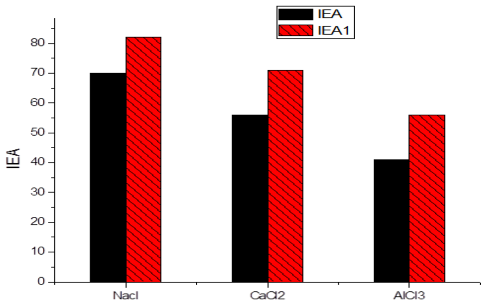

Figure 3: Surface morphology of IEA biopolymeric hydrogel

Scanning electron microscopy (SEM) technique is useful to expose the surface morphology of hydrogels. Fig. 4 shows the SEM image of dried SEA hydrogels. Synthesized hydrogels showed uneven-porous and elliptical nature on its surface structure, which permits water and interaction sites of external stimuli with the hydrophilic groups of the polymers

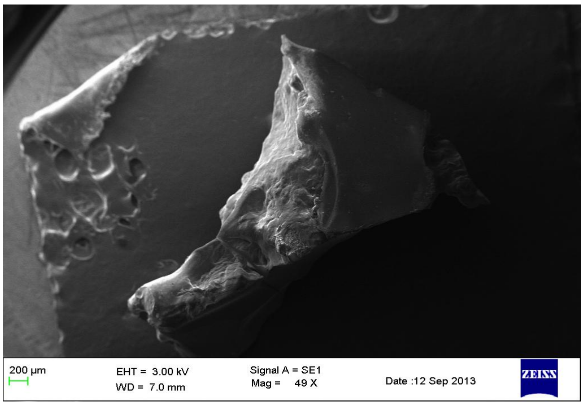

Figure 4: Surface morphology of SEA based polymeric hydrogels

IV. CONCLUSIONS

Itaconic acid based polymeric hydrogels have been synthesized via condensation followed by free radical polymerization. The enhanced swelling behavior was well supported by SEM studies. The results clearly indicated that the hydrogels could also be an excellent candidate for drug delivery system, opening for industrial and biological applications (metal ion removal, cationic dye removal).

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