



Synthesis Of Gum Tragacanth-CI-Poly (Acrylic Acid) Superabsorbent Hydrogels with Salt, pH and Electrical Responsive Properties

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Abstract

The *Gum tragacanth*-acrylic acid-based hydrogels were prepared using KPS-ascorbic acid as an initiator and glutaraldehyde as crosslinker via free radical graft copolymerization technique. Synthesized polymers were characterized with FTIR, SEM and thermal techniques in order to authenticate the grafting of poly (AA) on to *Gum tragacanth*. The candidate's hydrogel was also evaluated for salt resistant distension studies by means of biological electrolytic system using AC/DC supply. Moreover, the re-swelling ability of the candidate polymer was also studied using different pH media for its utilization in the site specific drug delivery. The results of the study suggested that the candidate polymer shows good salt resistant behavior alongwith pulsatile (swelling/de-swelling) nature. From the results of present study it was concluded that the polymer can be utilized for targeted drug delivery system as carrier.

1 Introduction

Hydrogel formation is also known as the complexation of the polymers^{1,2}. They are utilized in drug delivery^{3,4} system because of their unique capability of swelling under biological conditions alongwith immobilization of proteins, peptides and other therapeutically active compounds⁵. Properties of the swelling medium like pH⁶, ionic strength⁷ and counter ions⁸ primarily affects the swelling characteristic of the hydrogel. Literature suggested that many studies have been carried out regarding the synthesis, characterization, controlled drug delivery and swelling behavior of different polymers in the past using different backbone and monomer^{9,10}.

Kaith et al.¹¹ prepared a hydrogel by the introduction of aryl group in psyllium backbone i.e acrylated psyllium. The salt resistant swelling behavior of the hydrogel was studied along with the pH and temperature sensitivity. Kim et al.¹² studied the poly(vinyl alcohol)/chitosan IPN hydrogels exhibiting electric sensitive behavior. They reported the stepwise bending behavior of IPN hydrogels depending on the electric stimulus. Further they reported that bending angle and bending speed of poly (vinyl alcohol)/chitosan IPN hydrogels increase with applied voltage and concentration of NaCl aqueous solution.

Osada et al.¹³ reported an electro-sensitive artificial muscle system working under isothermal conditions. Singh et al.¹⁴ synthesised psyllium based polymeric network and evaluated for swelling nature by including the parameters like temperature, pH and salt. Vandelli et al.¹⁵, Shu et al.¹⁶ developed a pH responsive chitosan based hydro gels drug release system. Krishnaiah et al.¹⁷ studied the influence of metronidazole and tinidazole on the usefulness of guar gum, a colon-specific drug carrier. Momin et al.¹⁸ carried *in vitro* studies scheduling colon-targeted delivery of sennosides a guar gum based formulation. Rubinstin et al.¹⁹ potentially developed the Chondroitin sulphate based ecological carrier for the colon-specific drug release.

Targeted liberation of the medicaments in colon is achievable only when the drug is secluded from the unreceptive environment of upper GIT. Colon specific drug targeting makes the hydrogel an appropriate carrier for the drug delivery in case of treatment of diseases such as Rheumatoid arthritis, ulcerative colitis, Chron's disease, carcinomas, asthma and inflammation^{20,21}. Moreover, the salt resistant swelling can be utilized in water treatment technology¹¹.

We planned to synthesized *Gum tragacanth*-acrylic acid based hydrogels using KPS-ascorbic acid and glutaraldehydes as an

initiator-cross-linked via free radical graft copolymerization technique. Salt resistant studies on the swelling of candidate polymer using an artificial biological electrolytic system were carried out using AC/DC source. Moreover, the re-swelling ability of the candidate polymer was also studied using different pH media.

2 Materials and Methods

Gum tragacanth (S d Fine Chemicals Pvt. Ltd.) and ascorbic acid-potassium persulphate (S d Fine Chemicals Pvt. Ltd.) were used as backbone and initiator, respectively. Glutaraldehyde (MERCK) and acrylic acid (MERCK) were used as cross-linked and monomer, respectively.

2.1 Instrumental analysis

FTIR analysis of the back bone and cross-linked product was carried out on Perkin Elmer spectrophotometer using KBr pellets. Scanning Electron Micrographs of the polymers were taken on LEO-435VF, LEO Electron Microscopy Ltd. Thermal studies were carried-out on Perkin Elmer thermal analyzer at a heating rate of 10 °C/min in nitrogen atmosphere.

2.2 Synthesis of superabsorbent

1.0 g of *Gum tragacanth* was taken in a reaction flask containing 25 ml of distilled water. 0.5 mol L⁻¹ of acrylic acid was added to the reaction mixture followed by the addition of ascorbic acid-KPS in 1:1.25 molar ratio as an initiating system and 0.42 mol L⁻¹ of glutaraldehyde as a cross-linked. The reaction was carried out at pH 7.0 for 90 min at 40 °C.

At the end of the reaction, the homopolymer was removed on washing with hot water and synthesized gel was allowed to stand for about 10-12 hours undisturbed for gelling process to take place. The product obtained was dried in the oven at 60 °C till a constant weight was obtained. The percentage grafting and percentage swelling were calculated as per the following equations 1:

$$\% G = \frac{F_w - I_w}{I_w} \times 100 \quad (1)$$

I_w

Where

I_w = initial weight of the material taken;

F_w = final weight of the material obtained

2.3 Salt resistant studies using DC / AC source

Apparatus used for the salt resistant sensitive studies is shown in the Fig. 1. The system consists of an inner compartment (20.5 × 15 × 10 cm), two copper electrodes (8 × 5.3 × 0.2 cm), a thermostat, thermometer, and an outer compartment (24.5 × 19 × 12 cm) acting as a closed system. Distance between two copper electrodes was about 15.5 cm. Pre-optimized and dried

hydrogel was immersed in NaCl solution of different concentration (1%, 5%, 10%, 15% and 20%) at 37 °C and 10V AC/DC source.

On the application of electrical stimulus, polymer shows swelling behavior and was weighed after a regular time interval. Percentage swelling (P_s) was calculated by the equation 2:

$$P_s = \frac{F_{sp} - I_{up}}{I_{up}} \times 100 \quad (2)$$

I_{up}

Where

I_{up} = initial weight of unswelled polymer;

F_{sp} = final weight of swelled polymer

2.4 Preparation of solutions of different pH

Alkaline solutions were prepared with NaOH pallets and acidic solutions were prepared by the addition of HCl and pH was determined with Cyberscan 1100, EUTECH INSTRUMENTS, pH meter (Fig 1).

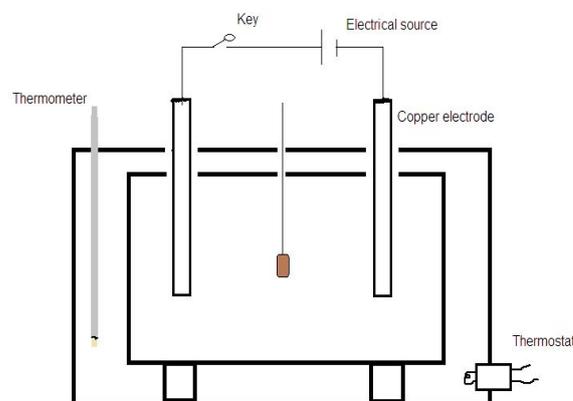


Fig 1: Apparatus for AC/DC stimuli studies

3 Results and Discussions

3.1 Mechanism

For graft copolymerization to occur on the hydroxyl groups of the monomer alongwith the backbone acts as an active site. The steps implicated in the graft copolymerization of acrylic acid on *Gum tragacanth* are represented by the schematic diagram.

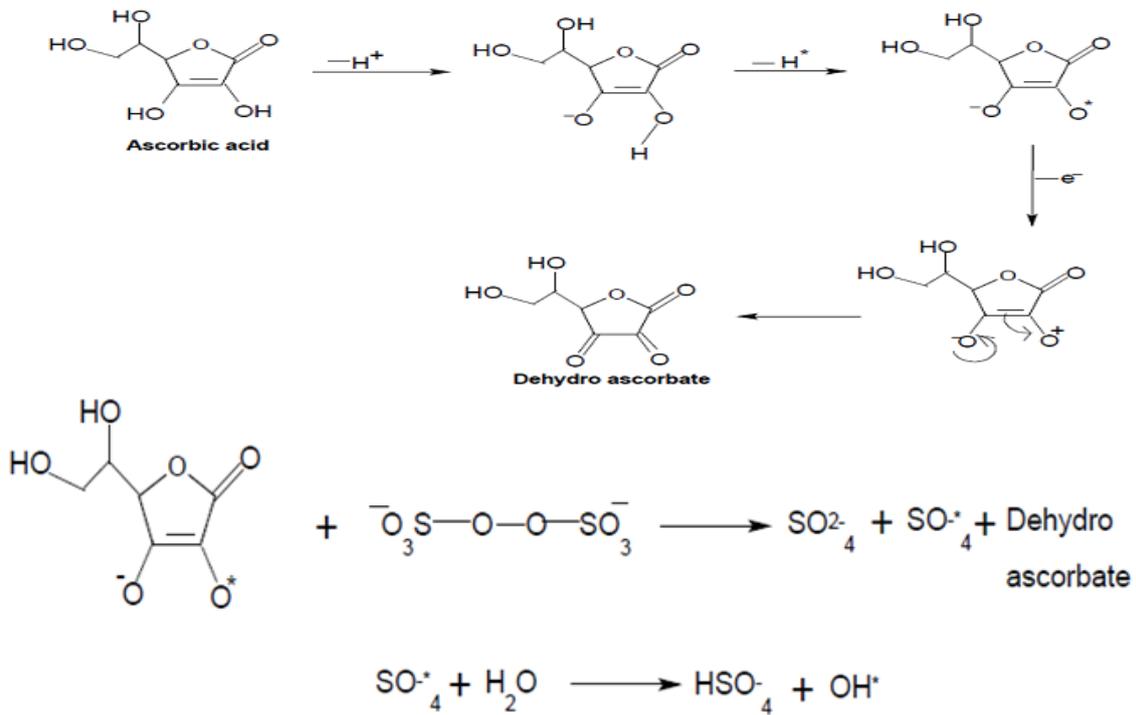
The ionic form of Ascorbic acid reacts with potassium persulphate to produce $SO_4^{\cdot-}$. This on further reaction with H_2O gives out OH^{\cdot} . Both the generated ionic forms (OH^{\cdot} and $SO_4^{\cdot-}$) generate active site for grafting on reaction with backbone and monomer. In the presence of glutaraldehyde the activated monomer and backbone molecules proliferate and give rise to three dimensional cross-linked networks. Reaction between two activated chains or reaction of OH^{\cdot} with live propagating macromolecular chains results in chain termination.

3.2 Characterization

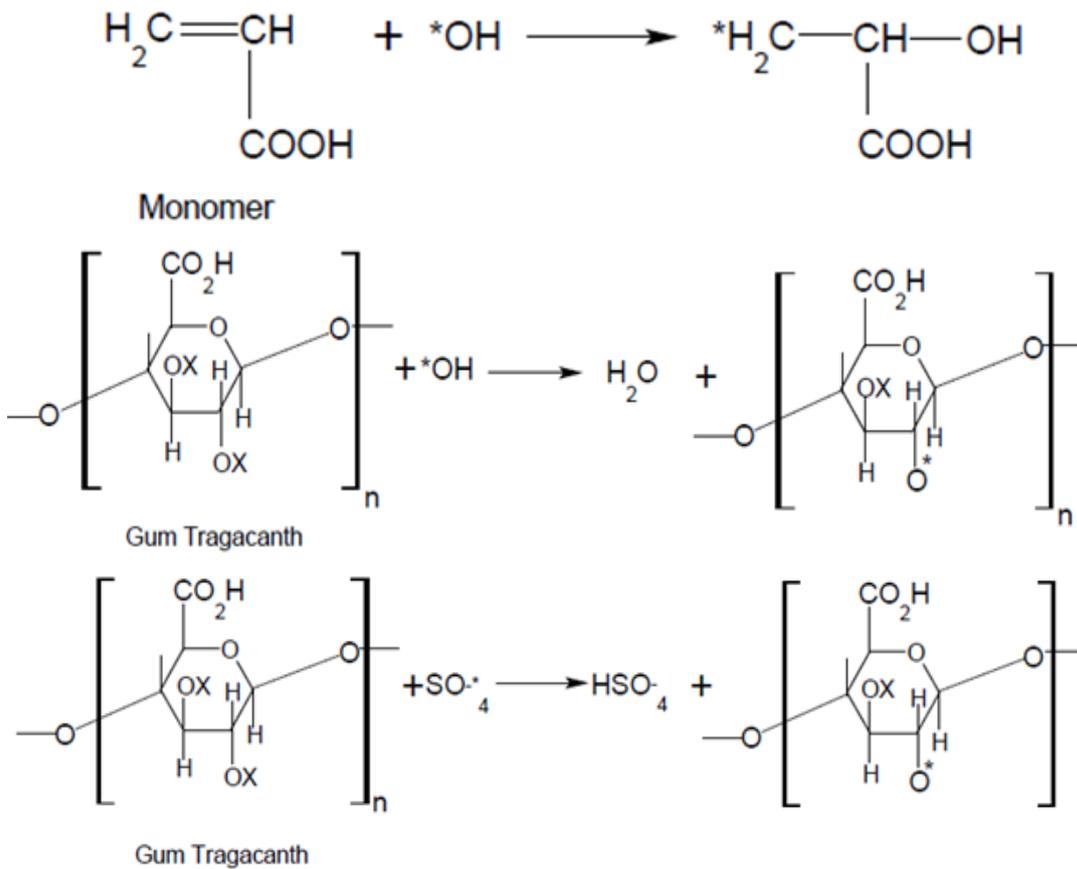
3.2.1 SEM

To demarcate the morphological differences on the surface of both *Gum tragacanth* and Gt-cl-poly(AA) scanning electron micrographs (SEM) was implicated. Morphological changes in

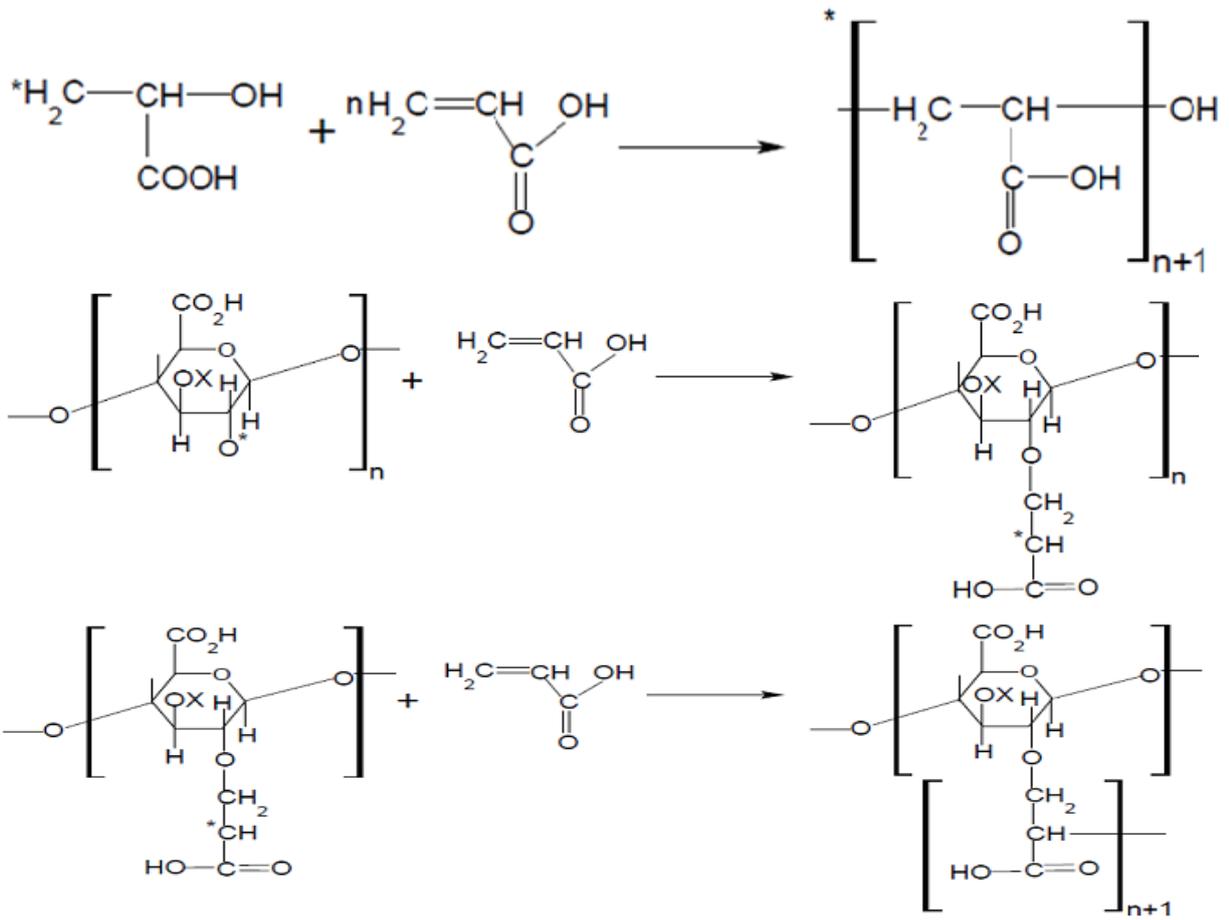
Gum tragacanth are quite evident after grafting and crosslinking. Fig 2b clearly showed that Gt-cl-poly(AA) has some cross-linked networks, whereas *Gum tragacanth* has a smooth and homogenous structure (Fig 2a).



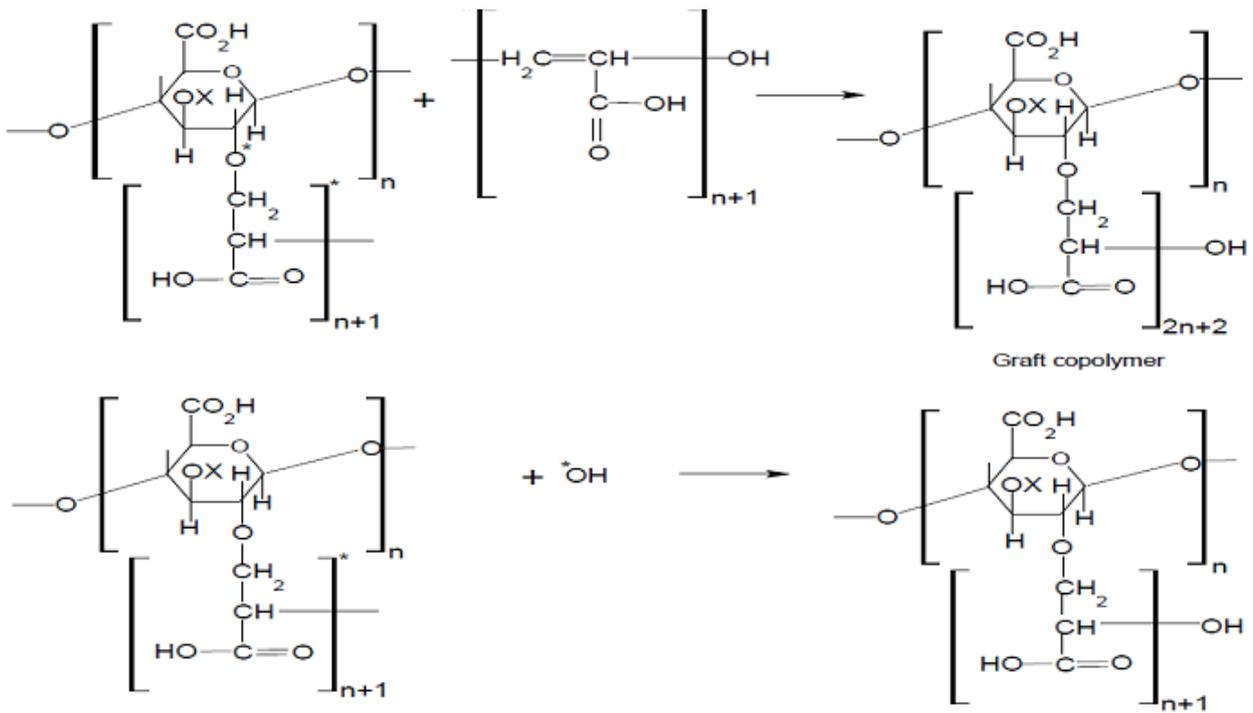
Initiation

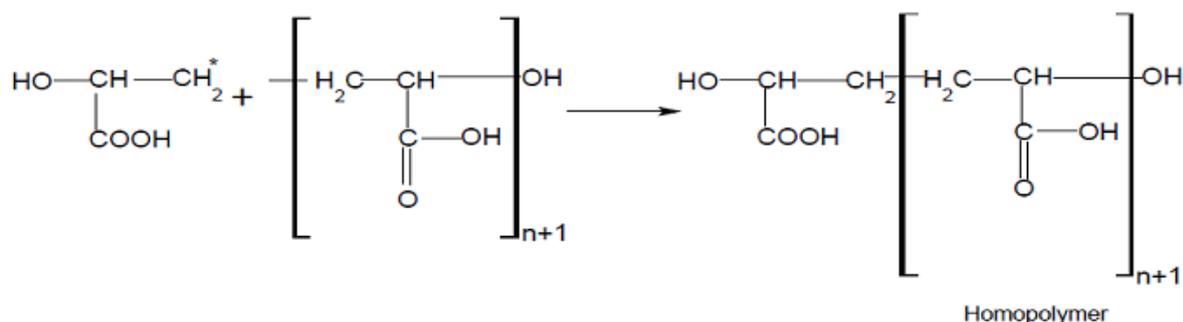


Propagation



Termination





Steps implicated in the graft copolymerization of acrylic acid on *Gum tragacanth*

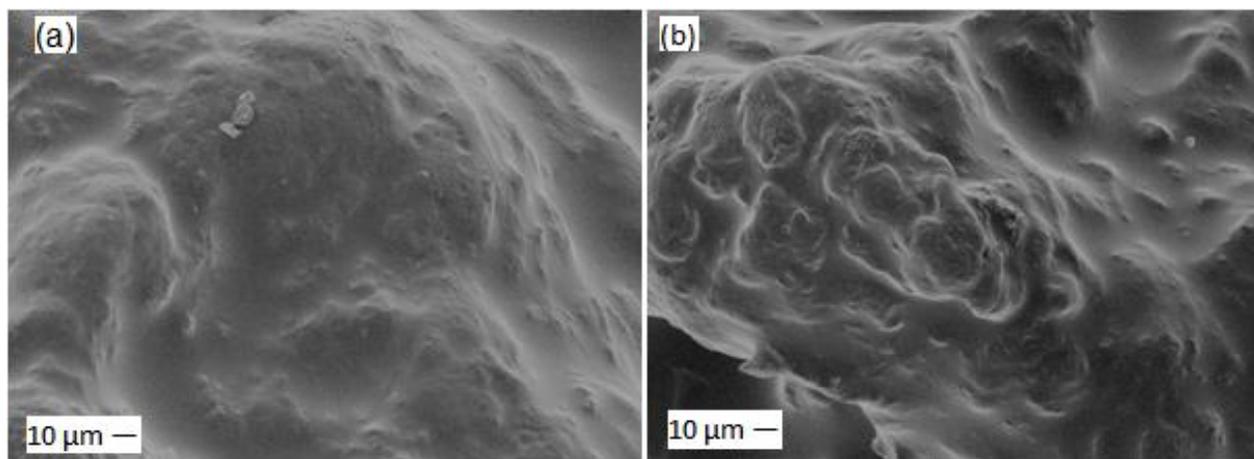


Fig 2: SEM (a) *Gum tragacanth*; (b) Gt-cl-poly(AA)

3.2.2 FT-IR Spectroscopy

Broad peaks are obtained in the FTIR spectrum of Gum tragacanth at 3427.08 cm^{-1} (O-H stretching bonded absorption of carbohydrates), 2934.78 cm^{-1} (CH_2 asymmetric stretching), 1039.07 cm^{-1} (C-O stretching region as complex bands, resulting from C-O and C-O-C stretching vibrations).

On the other hand, FTIR spectrum of Gt-cl-poly(AA) showed peaks at 2854.31 cm^{-1} , 2659.42 cm^{-1} and 2521.73 cm^{-1} (O-H stretching of carboxylic acid). Additional peaks have been observed at 1750.23 cm^{-1} and 1613.40 cm^{-1} due to C=O stretching in carboxylic acid.

3.2.4 Thermal studies

Thermal studies of both the backbone and functionalized polymer were performed as a function of percent weight loss vs. temperature. In case of *Gum tragacanth*, three stage decompositions have observed (Fig 3a). Primary decomposition reactions due to dehydration were observed upto $170\text{ }^\circ\text{C}$. First stage decomposition has been observed from $170\text{ }^\circ\text{C}$ – $473\text{ }^\circ\text{C}$ with 64.1 % weight loss. Second stage decomposition started at $473\text{ }^\circ\text{C}$ and continues upto $577\text{ }^\circ\text{C}$ with 3.3 % weight loss. This is followed by decomposition initialized at $577\text{ }^\circ\text{C}$ and carried upto $644\text{ }^\circ\text{C}$ with 15.5% weight loss in the 3rd stage. The initial decomposition temperature (IDT) and final decomposition temperature (FDT) of *Gum tragacanth* was $170\text{ }^\circ\text{C}$ and $644\text{ }^\circ\text{C}$ respectively.

It has been found that Gt-cl-poly(AA) showed initial decomposition temperature near at $210\text{ }^\circ\text{C}$ and final decomposition temperature at $560\text{ }^\circ\text{C}$ (Fig 3b).

The crystalline structure of grafted poly(AA) with *Gum tragacanth* gets distorted due to morphological changes resulting in low thermal stability of Gt-cl-poly(AA). *Gum tragacanth* showed sharp exothermic peaks at $580\text{ }^\circ\text{C}$ ($143.8\text{ }\mu\text{V}$) and $646\text{ }^\circ\text{C}$ ($87.9\text{ }\mu\text{V}$). On the other hand, Gt-cl-poly(AA) showed exothermic peak at $514\text{ }^\circ\text{C}$ ($136.6\text{ }\mu\text{V}$).

3.3 Effect of NaCl concentration on percentage swelling of biopolymer at $37\text{ }^\circ\text{C}$

It is evident from Fig 4 that the swelling capacity of candidate polymer in NaCl solution decreases with increasing NaCl concentration. Maximum swelling found at 1% NaCl solution is 216%. It is due to reverse osmosis process and in hypertonic solutions (higher concentration), the polymer shows shrinking behavior.

3.4 Effect of NaCl concentration on percentage swelling of biopolymer under the influence of 10V AC-source

It was observed from Fig 5 that the swelling capacity of candidate polymer in NaCl solution decreases with increasing NaCl concentration. Maximum swelling (332%) was found at 1% NaCl, which can be explained based on a reverse osmosis process.

Moreover, under the influence of AC source, ion screening effect (similar ion repulsion) takes place, and the candidate

polymer shows higher percentage swelling in comparison with salt resistant swelling devoid of electric field.

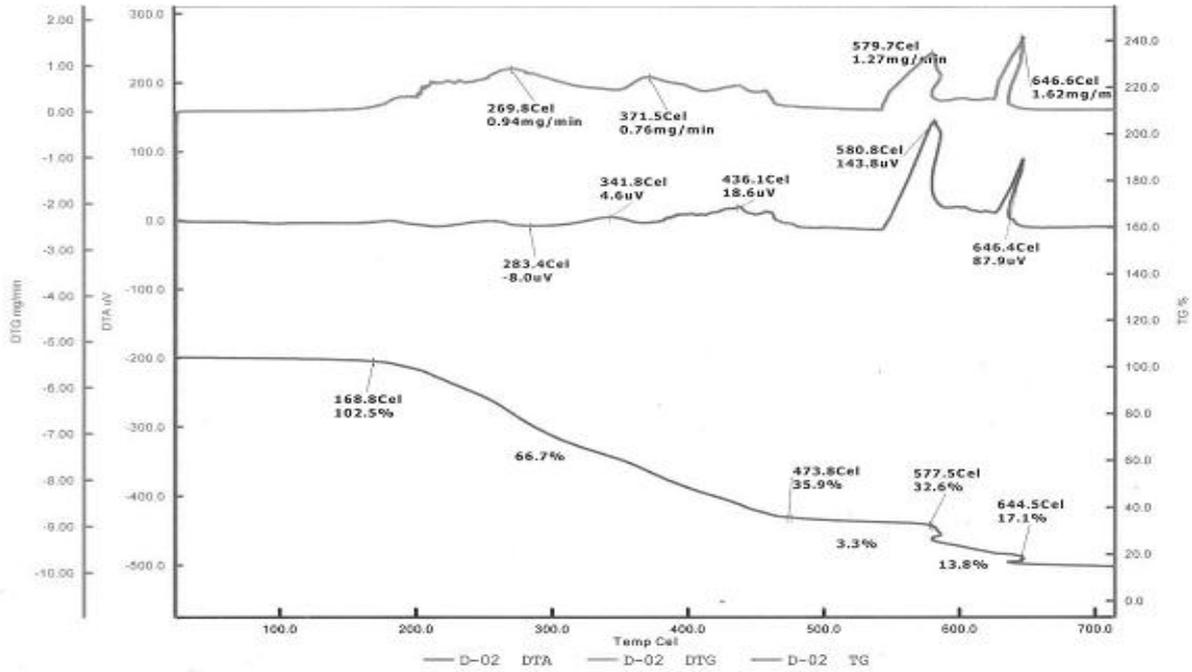


Fig 3a: TGA of Gum tragacanth

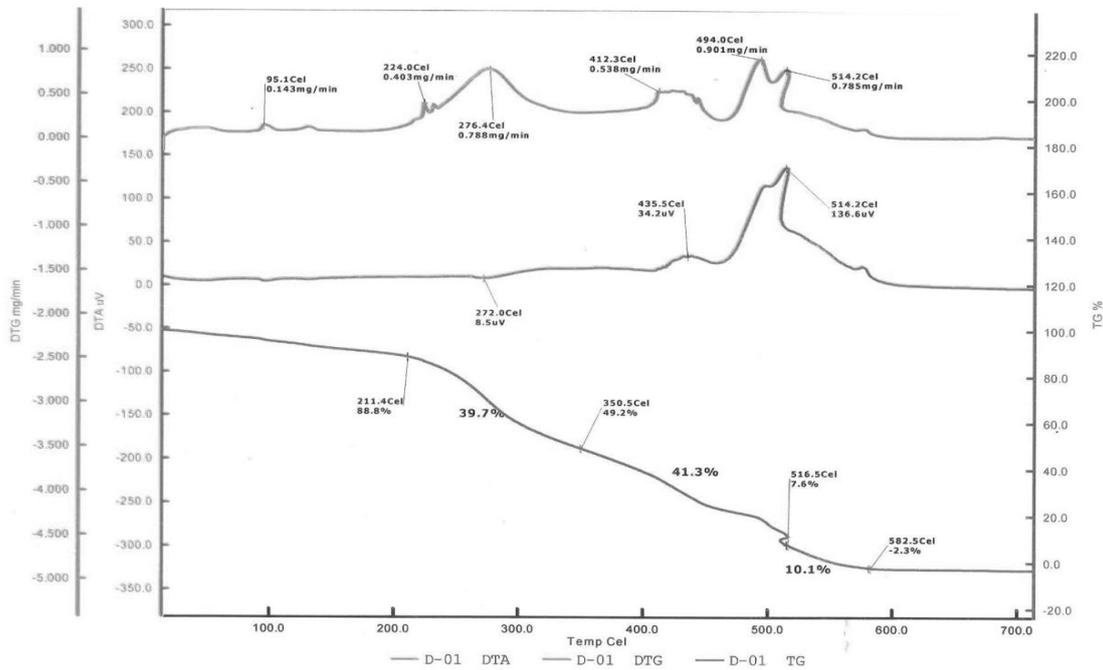


Fig 3b: TGA of Gt-cl-poly(AA)

3.5 Effect of NaCl concentration on percentage swelling of bio-polymer under the influence of 10V DC-source

It has been found from Fig 6 that the swelling capacity of candidate polymer in NaCl solution decreases with increasing NaCl concentration. Maximum swelling found at 1% NaCl solution is 330%. This can be explained based on reverse osmosis process and in hypertonic solutions (higher concentration), the polymer shows shrinking behavior.

Moreover, under the influence of DC source, ion screening effect (similar ion repulsion) takes place, and the candidate polymer shows higher percentage swelling in comparison with salt resistant swelling devoid of electric field.

3.6 Re-swelling ability of bio-polymer

Pulsatile behavior of bio-polymer was analyzed in solutions of different pH and percentage swelling was observed to be significantly affected (Fig 7). When the completely dried

hydrogel sample is placed in the swelling medium of pH 9.2, the solvent diffuses into the outer surface of the candidate polymer through the micro-pores, results in the plasticization of macromolecular chains.

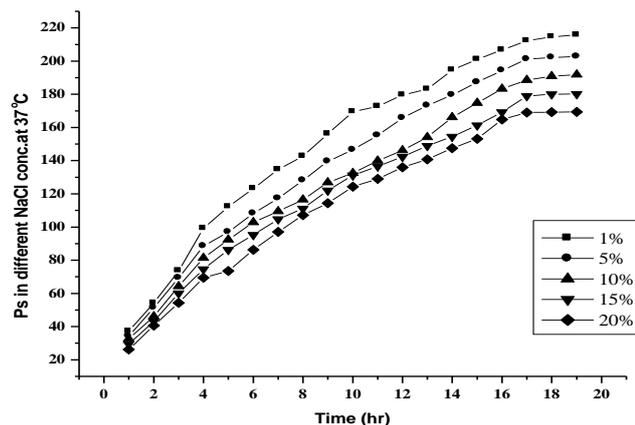


Fig 4: Ps of Gt-cl-poly (AA) in different NaCl concentration

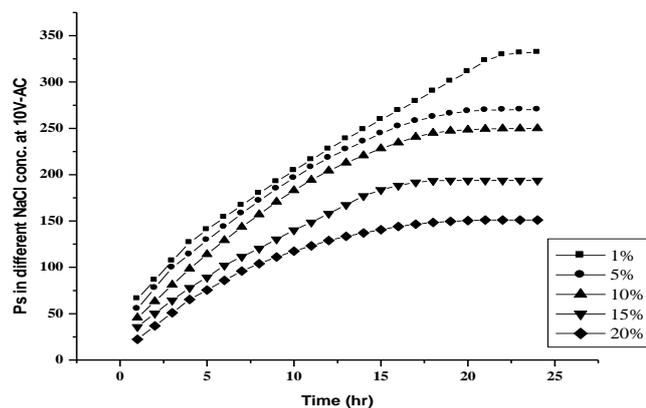


Fig 5: Ps of Gt-cl-poly (AA) in different NaCl concentration under 10V-AC

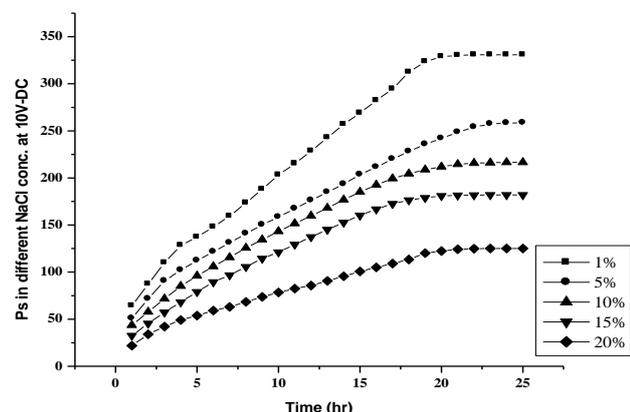


Fig 6: Ps of Gt-cl-poly (AA) in different NaCl concentration under 10V-DC

Simultaneously the ionization of $-\text{COOH}$ results in $-\text{COO}^-$ ions generation resulting in the development of hydrated layer. This hydrated layer causes counter ions moment which cause the gel to swell. The dry core portions of the candidate polymer disappear and the matrix gel shows continuous swelling. The swelling is further enhanced due to relaxation of macromolecular chain. When the fully hydrated gel is placed in the medium of pH 2.0, H^+ ions present in the external solution,

diffuse into the gel matrix through water-filled macrospores that have existed in the fully hydrated gel. The de-swelling of polymer matrix occurs due to the folding of macromolecular chains. This occurs as a result of protonation (H^+ ions) of $-\text{COO}^-$ group to yield uncharged $-\text{COOH}$ groups.

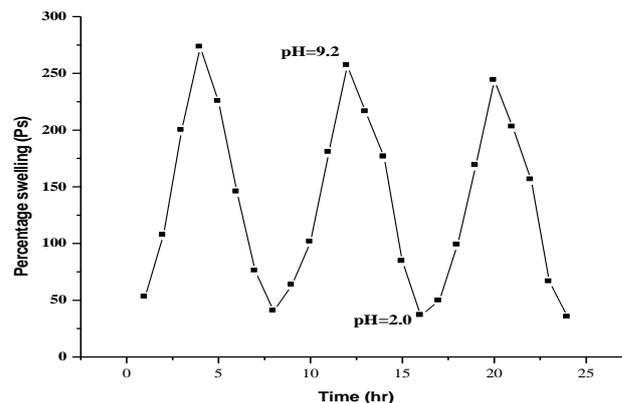


Fig 7: Ps of Gt-cl-poly (AA) at pH 9.2 and 2.0

4 Conclusions

Modification of Gum tragacanth via crosslinking and network formation with acrylic acid improves the property profile and usability of the polymer in various technical fields. Further, the product obtained was found to show salt resistant swelling, which could be of great importance in the purification of portable water, especially in coastal areas. The candidate polymer was found to show pulsatile behavior under acidic and basic conditions, which could be of great significance in the sustained release of colon specific drugs.

5 Conflict of interests

The author declared none

6 Author's contributions

DP has carried out the research work in the laboratory, compiled and analyzed the data.

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