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Synthesis, characterization and swelling behaviour of poly(acrylamide-co-methacrylic acid) grafted *Gum ghatti* based superabsorbent hydrogels

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ABSTRACT

A mixture of acrylamide (AAm) and methacrylic acid (MAA) was crosslinked onto Gum ghatti (Gg) using N, N'-methylene-bis-acrylamide (MBA) as a crosslinker and ascorbic acid (ABC) and potassium persulphate (KPS) redox pair as an initiator. Optimized reaction parameters for the graft copolymerization of Gum ghatti with AAm were time (min)=90; temperature (^{0}C)=50; pH=7.0; deionized water (ml)=10; molar ratio of initiators (ABC:KPS mol:mol)=1:1; [AAm] (molL^{-1})=0.7746; [MBA] (molL^{-1})=0.0974. After that molar ratio of AAm-co-MAA keeping AAm as the principle monomer was optimized and was found to be 0.77+5.85 molL^{-1}. Synthesized superabsorbent hydrogel was characterized by FTIR, SEM, TGA/DTA and XRD. Water absorption capacity of Gg-cl-poly(AAm-co-MAA) was investigated in deionized water and the polymer was found to show maximum swelling of 1312%. Effect of the ionic strength of various cations (Na^+, Ba^{+2}, Fe^{+3} and Sn^{+4}) on P_s in different choride salt solutions (NaCl, $BaCl_2$, $FeCl_3$ and $SnCl_4$) was studied. The hydrogel exhibited salt-sensitivity and cation exchange properties. pH responsive and on-off switching properties of the superabsorbing hydrogel was studied as well.

Keywords: Hydrogel, swelling, crosslinking, graft copolymerization.

INTRODUCTION

Hydrogels are three-dimensional high-molecular weight networks composed of a polymer backbone, water and a crosslinking agent. These are polymeric materials that do not dissolve in water at physiological temperature and pH. They swell considerably in an aqueous medium [1] and demonstrate extraordinary capacity (>20%) for imbibing water into the network structure. Hydrogels form the class of most biocompatible materials as they resemble natural tissue more than any other class of biomaterials because of their high water content, soft and rubbery consistency and low interfacial tension with water or biological fluids [2]. They form another important class of smart materials that are stimuli responsive as they exhibit a phase transition in response to change in external conditions such as pH, ionic strength, temperature and electric

currents [3]. Smart hydrogels are very different from inert hydrogels in that they can 'sense' changes in environmental properties and respond by increasing or decreasing their degree of swelling. Being insoluble, these three-dimensional hydrophilic networks can retain a large amount of water that not only contributes to their good blood compatibility but also maintains a certain degree of structural integrity and elasticity [4]. It is because of the hydrophilic functional groups such as –OH, –COOH, $–CONH_2$ and $–SO_3H$ present in the hydrogels that they are capable of absorbing water without undergoing dissolution. Hydrogels can be prepared from natural or synthetic polymers [5]. Although hydrogels made from natural polymers may not provide sufficient mechanical strength and may contain pathogens or evoke immune/inflammatory responses and also pose difficulty in processing, they do offer several advantageous properties such as inherent biocompatibility, biodegradability and biologically recognizable moieties that support cellular activities. Synthetic hydrogels, on the other hand, do not possess these inherent bioactive properties. Fortunately, synthetic polymers usually have well-defined structures that can be modified to yield tailored degradability and functionality [6]. Since, natural polymers face many drawbacks including less stability and difficulty in processing, therefore, they have been successfully modified through graft copolymerization so as to meet out the end usage.

This new class of materials has better mechanical strength, biocompatibility and flexibility than those of the single components. Grafting and network formation of the natural polymers with different vinyl monomers and crosslinkers improve their properties and make them potential candidate materials in various fields ranging from food additives to pharmaceuticals and biomedical implants [7-9]. In addition to this, the sensitivity of these polymeric materials to a large number of physical factors like pH, temperature, ionic strength, electric field, magnetic field or ultra violet light [10-14] have broaden the versatility of their applications. They are gaining tremendous importance in many tissue engineering scaffolds, biosensors, bioMEMS devices and drug delivery systems [15-21].

In this research paper, synthesis of crosslinked graft copolymer of AAm-co-MAA onto *Gum ghatti* using MBA as a crosslinking agent and ascorbic acid-potassium persulphate redox pair as an initiator via free radical initiation was reported. Swelling properties of the synthesized polymer in deionized water and different salt solutions were also investigated.

MATERIALS AND METHODS

Gum ghatti, potassium persulphate and ascorbic acid procured from Sd-Fine Chemicals Pvt. Ltd. and N, N'-methylene-bis-acrylamide, methacrylic acid and acrylamide purchased from MERCK were used as received.

Synthesis of Gg-cl-poly(AAm-co-MAA)

Gum ghatti (1.0g) was immersed in 10ml of deionized water for 24h prior to graft copolymerization. A definite ratio of potassium persulphate and ascorbic acid followed by a known amount of acrylamide-co-methacrylic acid and N,N'-methylene-bis-acrylamide were added to the reaction mixture with continuous stirring. For the removal of polyacrylamide graft copolymer was soxhlet extracted with acetone for about 3-4h. Further the traces of polyacrylamide were separated by immersing it in acetone for about 24h. Whereas, polymethacrylic acid was removed by washings with distilled water. Synthesized polymers were dried in hot air oven at 50˚C till a constant weight was obtained. Optimization of various reaction parameters was carried-out as a function of percent grafting (P_g) and percent swelling(P_s) which were calculated as [22, 23]:

$$P_g = \frac{W_f - W_b}{W_b} \times 100 \quad (1)$$

where W_f and W_b are the weights of the functionalized and backbone polymers, respectively.

$$P_s = \frac{W_s - W_d}{W_d} \times 100 \quad (2)$$

where W_s and W_d are the weights of the swelled and dry polymers, respectively.

Instrumental Analysis

FTIR spectra of the samples were taken on PERKIN ELMER RXI Spectrophotometer using KBr pellets. Scanning Electron Micrographs of the dried samples were taken on LEO, 435VF, LEO Electron Microscopy Ltd. In order to have the conducting impact, the samples were gold plated and the scanning was synchronized with microscopic beam so as to maintain the small size over a large distance relative to the specimen. The resulting images had a great depth of the field. A remarkable three dimensional appearance with high resolution was obtained in case of crosslinked graft copolymerized superabsorbent. TGA/DTA/DTG studies of the synthesized samples were done on TG/DTA 6300, SII EXSTAR 6000 in air at a heating rate of 10°C/min. X-ray diffraction studies of the samples were done on X-ray diffractometer (BRUKER AXS D8 ADVANCE). X-ray diffractions were performed under ambient conditions on Bruker-D_8 advance model using Cu Kα (1.5418 ºA) radiation, Ni-filter and scintillation counter as detector at 40 KV and 40 mA on rotation between 0.5 º or 1.0 mm of divergent and anti-scattering slit.

Swelling studies at different pH

To investigate the swelling behavior of Gg-cl-poly(AAm-co-MAA) at various pHs, solutions of various pH ranging from pH 1.0 to 13.0 were prepared. The pH values were precisely checked with Cyberscan 1100, EUTECH INSTRUMENTS, pH meter. A known amount of the dried hydrogel was immersed in solutions of different pH and P_s was calculated as per the Eq. (2).

Swelling studies in different salt solutions

Effect of ionic strength and cationic charges of different cations on the P_s of the hydrogel was investigated in NaCl, $BaCl_2$, $FeCl_3$ and $SnCl_4$ salt solutions at preoptimized time, temperature and pH in deionized water. Salt solutions of different ionic strength (0.01, 0.02, 0.03, 0.04 and 0.05 $molL^{-1}$) of cations were prepared. A known amount of the dried hydrogel was immersed in different salt solutions and P_s was calculated as per the Eq. (2).

RESULTS AND DISCUSSION

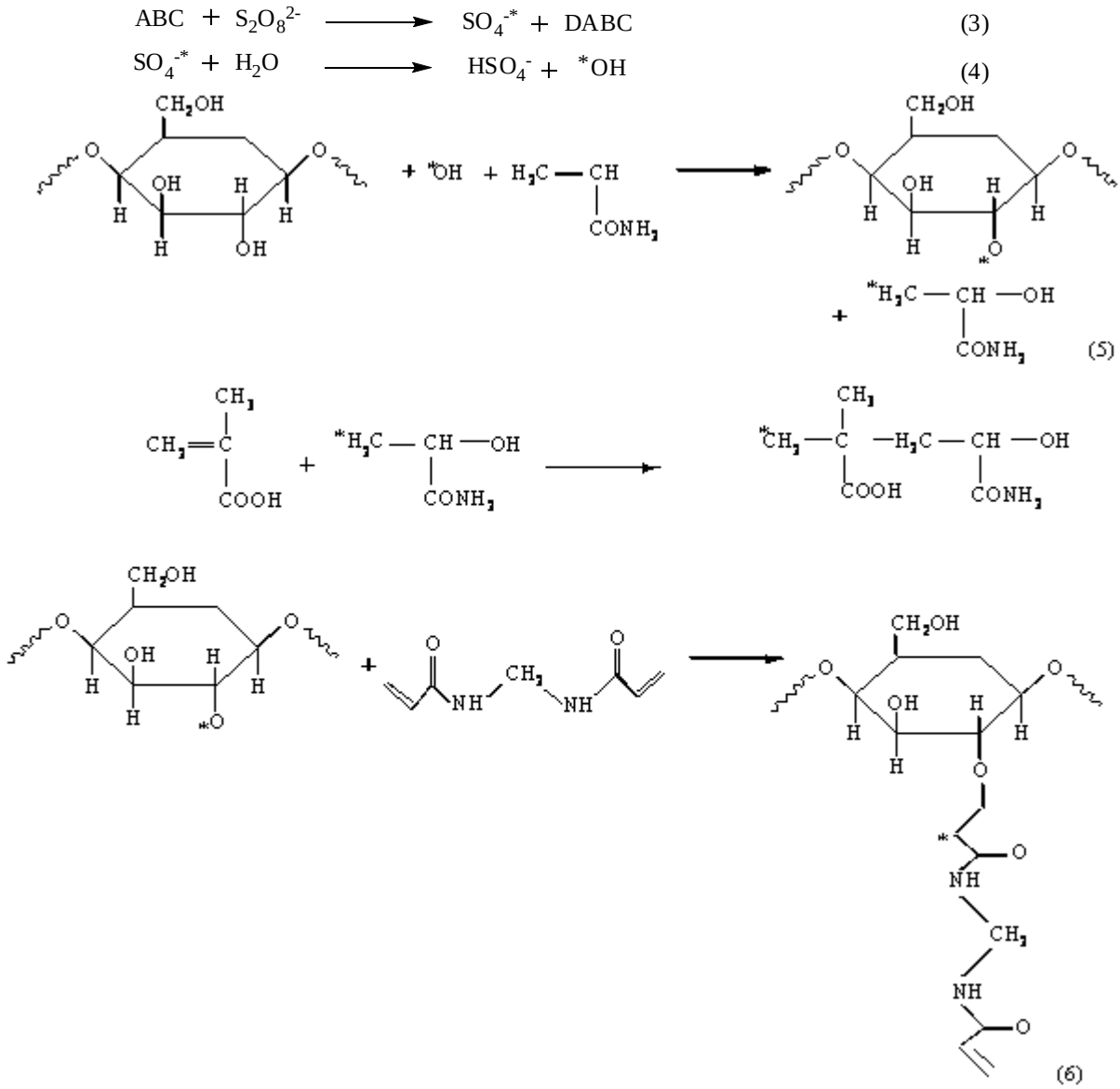
Mechanism

Hydroxyl groups present on the backbone and monomers are the active sites for graft copolymerization to take place. Various steps involved in the graft copolymerization of *Gum ghatti* with AAm-co-MAA are depicted in Scheme-I:

Initially, ascorbic acid ion reacts with the potassium persulphate to generate SO_4^{-*} which on further reaction with water molecule generates OH^* followed by the interaction of OH^* and SO_4^{-*} with backbone and monomer resulting in generation of active sites. Activated monomer and backbone molecules propagate further and give rise to three dimensional crosslinked network in the presence of N,N'-methylene-bis-acrylamide. However, chain termination reactions take place either by the reaction of OH^* with the live propagating macromolecular chains or reaction between two activated chains.

Optimization of various reaction conditions

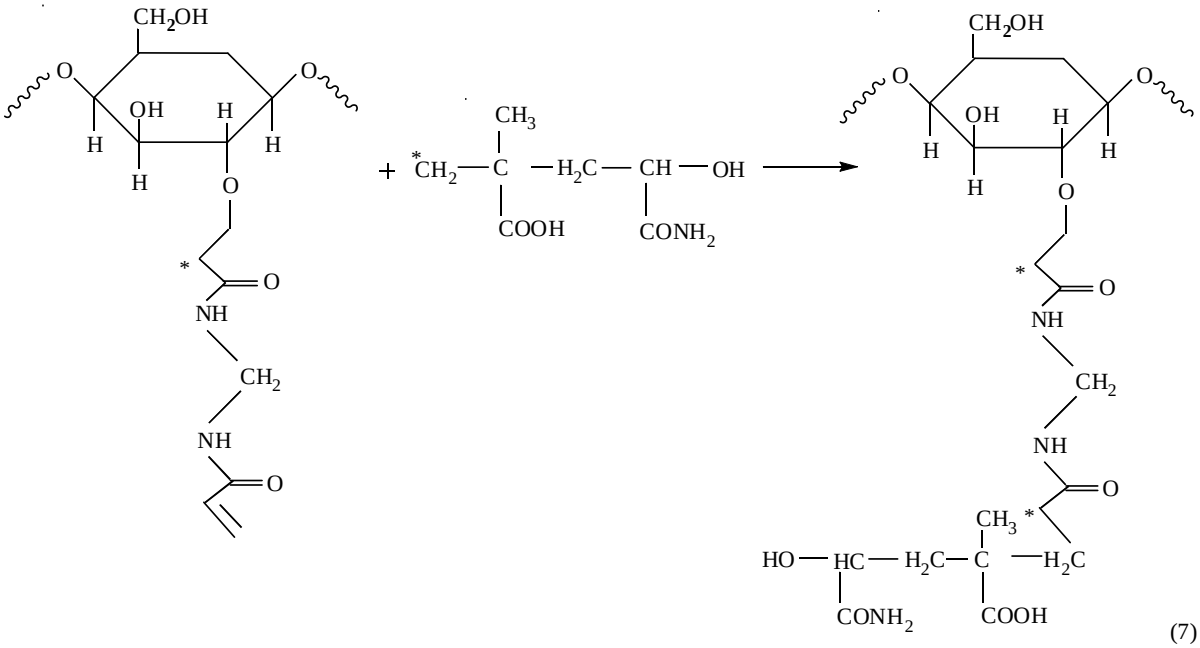
In case of principal monomer, the different optimized reaction parameters were reaction time (min)=90; temperature(^{0}C)=50; amount of solvent(ml)=10; pH=7.0; initiator ratio(KPS:ABC, mol:mol)=1:1, [AAm] (molL^{-1})=0.7042 and [MBA] (molL^{-1})=0.0974 [24].



Optimization of co-monomer concentration in binary mixture

After the optimization of various reaction parameters with principal monomer (AAm), concentration of MAA in combination with AAm was optimized and was found to be 5.85 molL^{-1} with maximum P_s of 1285% (Table 1). Initially, P_s increased with increase in concentration of MAA but after getting maximum a decline in P_s was observed with further increase in MAA concentration.

Initial increase in P_s was due to the formation of more porous and flexible structure which can accommodate more water molecules but further increase in MAA concentration beyond optimum level resulted in a rigid and compact crosslinked entity, thereby exhibiting lesser swelling.



(7)

Characterization

FTIR

IR spectrum of *Gum ghatti* showed broad peaks at 3408.4 cm^{-1} (O-H stretching of carbohydrates), 2936.6 cm^{-1} (-CH_2 asymmetric stretching) , 1445.35 cm^{-1} (-CH and -CH_2 in-plane bending in carbohydrates), 1089.51cm^{-1} (-CO stretching region as complex bands resulting from C-O and C-O-C stretching vibrations) and 643.71 cm^{-1} (pyranose ring).

Table 1: Effect of acrylamide-co-methacrylic acid concentration on percent swelling during grafting

Sample	[AAm+MAA] x molL^{-1}	P_s	±SD	±SE
1.	0.77+3.51	875	7.00	4.04
2.	0.77+4.68	1043	6.24	3.60
3.	0.77+5.85	1285	3.60	2.08
4.	0.77+7.02	1072	3.00	1.73
5.	0.77+8.20	965	3.60	2.08

where, no. of replications=03, weight of *Gum ghatti*=1.0g

In addition to the peaks obtained in IR of *Gum ghatti*, Gg-cl-poly(AAm-co-MAA) showed peaks at 1743.18 cm^{-1} (-CO stretching of acid), 1679 cm^{-1} (-CO stretching of amide-I), 1384.09 cm^{-1}(-NH in plane bending of amide-II) and 1113.50 cm^{-1} (CN stretching of amide-III) (Figs. 1a-b).

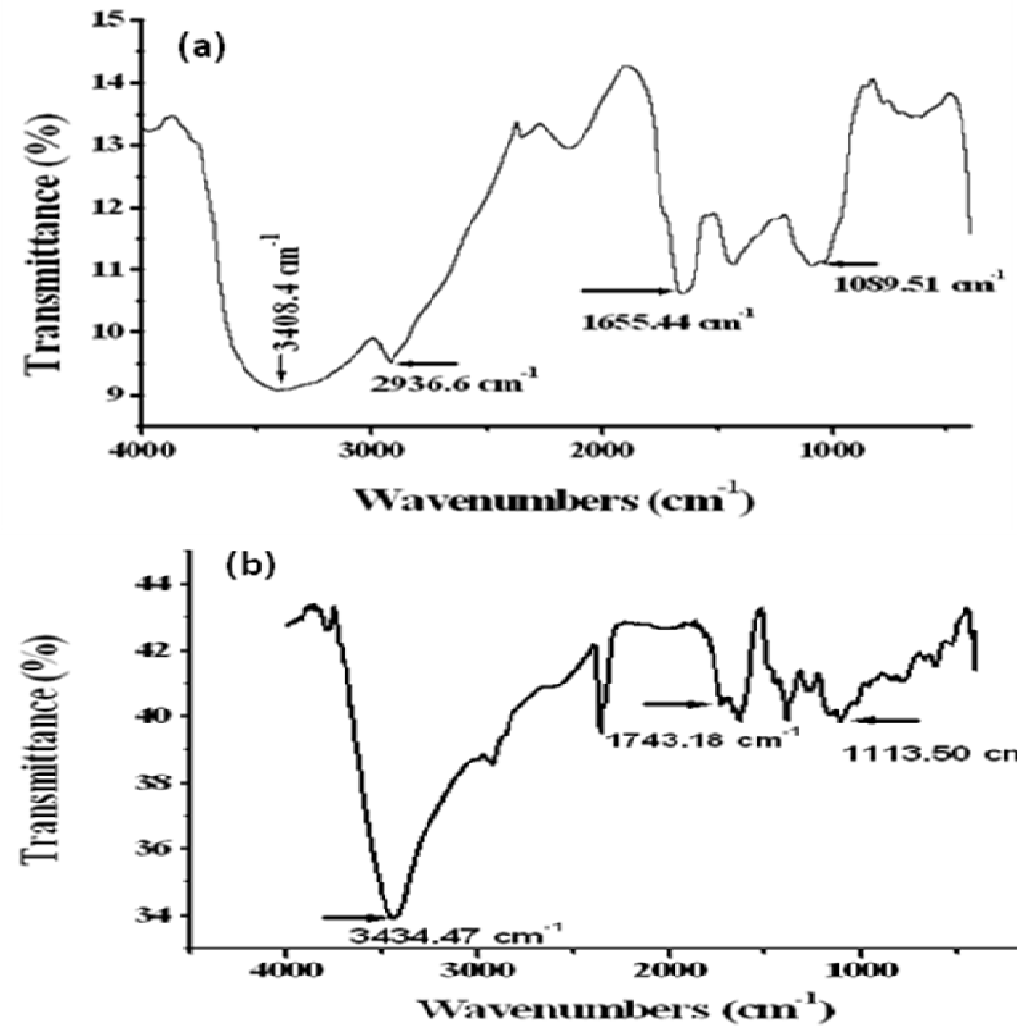
Scanning electron microscopy

The morphological changes brought about by the grafting and crosslinking were studied with the help of SEM. It was observed that the surface of the Gg-cl-poly(AAM-co-MAA) was highly rough as compared to *Gum ghatti* which was due to the incorporation of covalent bonds between different polymeric chains on crosslinking with MBA (Figs. 2a-b).

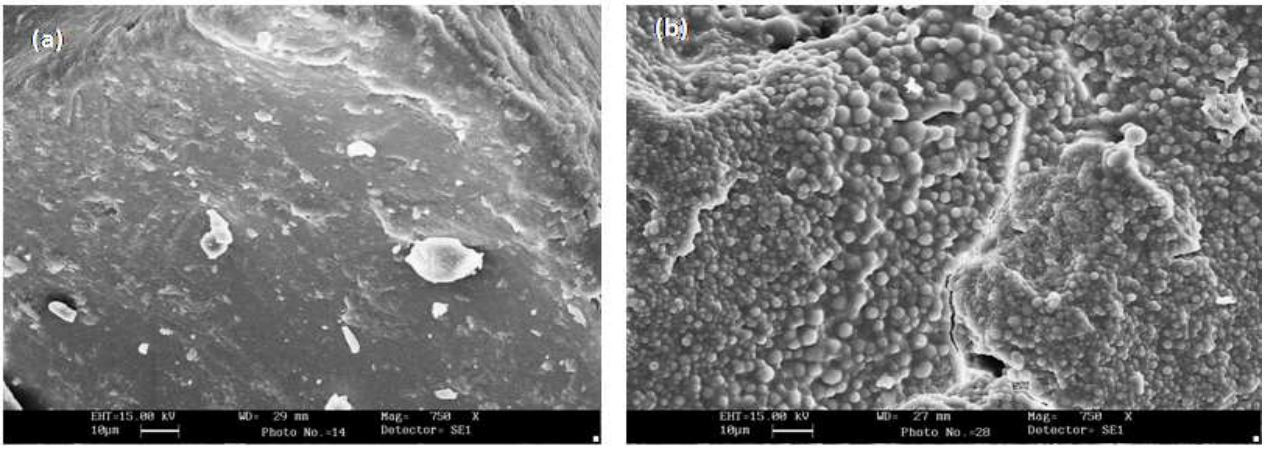
Thermal analysis

In case of TGA of *Gum ghatti* two stage decomposition was observed. First stage decomposition was due to initial dehydration and loss of volatile molecules whereas second stage decomposition was due to depolymerization reactions. First stage decomposition was observed in

the temperature range from 206.9°C-331.4°C with 46.6% weight loss and second stage decomposition was observed in the temperature range from 331.4°C-521.6°C with 31.2% weight loss. *Gum ghatti* exhibited initial decomposition temperature (IDT) at 206.9°C and final decomposition temperature (FDT) at 521.6°C. Two exothermic peaks at 483.2°C (203µV) and 492.7°C (154µV) were obtained in case of DTA of *Gum ghatti*.



Figs. 1a-b: FTIR of (a) *Gum ghatti*; (b) Gg-cl-poly(AAm-co-MAA)



Figs. 2a-b: SEM of (a) *Gum ghatti*; (b) Gg-cl-poly(AAm-co-MAA)

Table 2: Thermal behavior of *Gum ghatti* and Gg-cl-poly(AAm-co-MAA)

Sample Code	[AAm+MAA] (mol/L)	d-Spacing	Angle of Diffraction at 2Θ-scale	FWHM at 2Θ- scale	Coherence length (Å)
Gg	-	4.76151	20.908°	6.74^0	1.057
Gg-cl-poly (AAm-co-MAA)-I	0.77+3.51	4.82840	22.317^0	5.3843^0	2.474
Gg-cl-poly(AAm-co-MAA)-II	0.77+4.68	5.03755	20.621^0	4.9178^0	2.777
Gg-cl-poly (AAm-co-MAA)-III	0.77+5.85	4.88049	19.857^0	4.7623^0	2.870
Gg-cl-poly (AAm-co-MAA)-IV	0.77+7.02	5.10228	17.591^0	4.5568^0	2.962
Gg-cl-poly (AAm-co-MAA)-V	0.77+8.20	5.02089	16.217^0	4.5568	2.997

It has been observed that IDT of Gg-cl-poly(AAm-co-MAA) (174.4^0C) is lower than that of *Gum ghatti* (206.9°C). However, FDT of Gg-cl-poly(AAm-co-MAA) is higher than that of *Gum ghatti*.

Two stage decomposition ranging from 174.4°C-427.4°C and 427.4°C-531.3°C has been observed. In case of DTA, two endothermic peaks at 528.2°C (97.1µV) and 538.7°C (110.1µV) were observed, which shows that exothermic combustion of Gg-cl-poly(AAm-co-MAA) persists at higher temperature as compared to *Gum ghatti* (Table 2) [25-28].

X-Ray Diffraction studies

Coherence length of the samples was calculated by using Scherrer equation [29, 30]:

$$L = 0.9\lambda / \beta_{½} \times \cos\theta$$

where, λ=wavelength, ɵ=diffraction angle, L=coherence length and $\beta_{½}$=full width half maximum

Table 3: X-ray diffraction studies of *Gum ghatti* and Gg-cl-poly(AAm-co-MAA)

Sample Code	TGA				DTA	
	IDT (^{0}C)	1st stage Decomposition, ^{0}C (% wt. loss)	2st stage Decomposition, ^{0}C (% wt. loss)	FDT, ^{0}C (residue left)	Exothermic peaks at different decomposition Temp.,˚C (µV)	
					1st	2nd
Gum Ghatti	206.9	206.9-331.4 (46.6%)	331.4-521.6 (31.2%)	521.6	483.2 (203)	492.7 (154)
Gg-cl-poly(AAm-co-MAA)	174.4	174.4-427.4 (64.8%)	427.8-531.3 (24.2%)	531.3	528.2 (97.1)	538.7 (110.1)

Gum ghatti was found to be least crystalline among its crosslinked products with least value of coherence length. It is evident from Table 3 that in case of Gg-cl-poly(AAm-co-MAA), the crosslinked networks with AAm+MAA concentration 0.77+3.51, 0.77+4.68, 0.77+5.85, 0.77+7.02and 0.77+8.20 $molL^{-1}$ maximum intensity peak correspond to 2θ= 22.317^0 (L=2.474 Å), 20.621^0 (L=2.777 Å), 19.857^0 (L=2.870 Å), 17.591^0 (L=2.962 Å) and 16.217^0 (L=2.997 Å) with 0.7042+3.51, 0.7042+4.68, 0.7042+5.85, 0.7042+7.02 and 0.7042+8.20 $molL^{-1}$, respectively. Whereas, in case of *Gum ghatti* maximum intensity peak correspond to 2θ=20.908° (L=1.057 Å). Thus coherence length was found to increase with increased crosslinker concentration and resulted in increased anisotropy. Hence the polymer became more crystalline in nature. This might be due to the fact that with increase in crosslinker concentration,

crosslinker density between polymeric chains got enhanced leading to more aligned crystalline structure [30].

Swelling studies in deionized water

Effect of time

Effect on swelling time on P_s was studied at different time intervals (4, 8, 12, 16, 20, 24h). It was observed that initially P_s increased with increased in time and showed maximum P_s (946%) after 16h, whereas further increase in swelling time beyond optimum value resulted in no further increase in P_s. This might be because of the fact that with increase in swelling time beyond optimum level, porous network of polymer became fully saturated with no more accommodation of water molecules (Fig. 3a).

Effect of temperature of swelling medium

Effect of temperature on P_s of Gg-cl-poly(AAm-co-MAA) was investigated at different temperatures (30, 40, 50, 60 and 70 ^{0}C) and at preoptimized time (16h). It was observed that initially P_s increases with the increased in temperature and attained maxima at 60^{0}C. Further increase in temperature resulted in a decrease in P_s (Fig. 3b). This might be because of the fact that initially with increase in temperature the pore size of hydrogels goes on increasing because of breaking of crosslinks between different polymeric chains. Also the kinetic energy of water molecules increases. At optimum temperature equilibrium is maintained between the rate of penetration of water inside the polymeric network and the rate of oozing out of water from polymer network. After optimum temperature due to further increase in pore size the rate of oozing out of water molecules dominates, thereby leading to desorption with further increase in temperature. Furthermore, water molecules form hydrogen bonds with the hydrophilic groups of the candidate polymer leading to the stable shell of hydration around these hydrophilic groups and resulting in the greater absorption of water and a larger P_s, However, at higher temperatures the associated interactions among the hydrophilic groups release the entrapped water molecules from the hydrogel network [31].

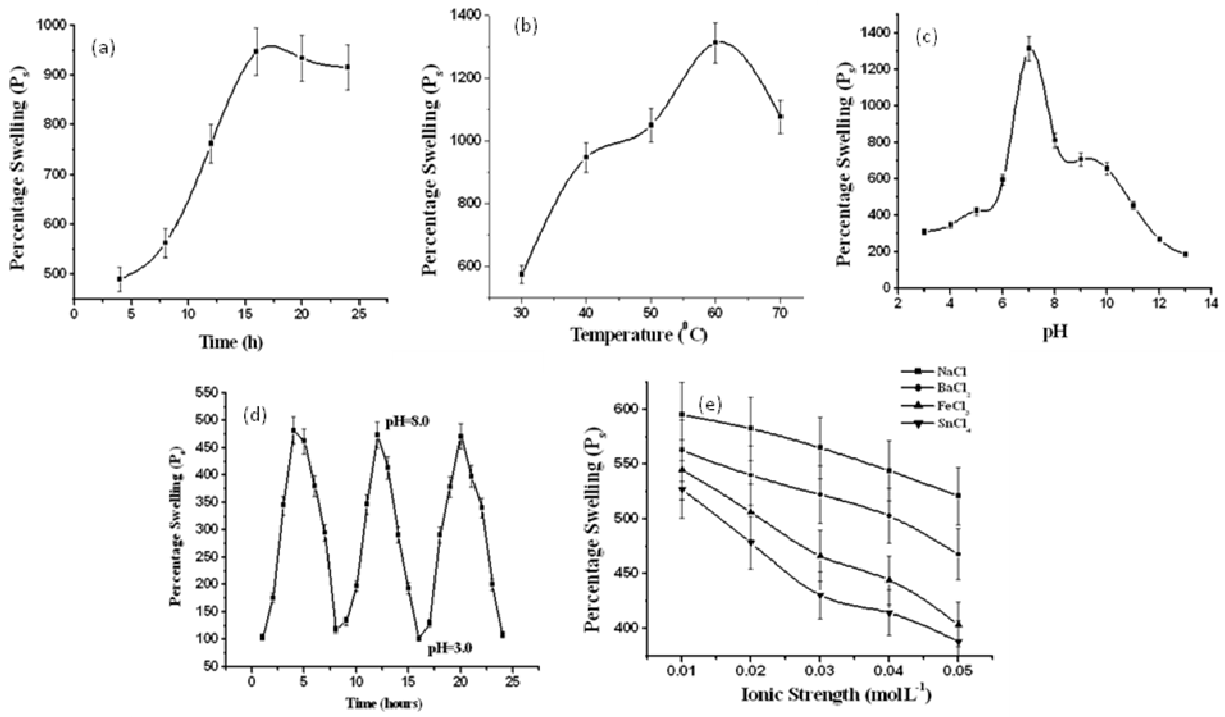
Effect of pH

Swelling studies of Gg-cl-poly(AAm-co-MAA) were carried-out at different pHs (1.0 to 13.0) and at preoptimized time (16h) and temperature (60^{0}C) (Fig. 3c). Maximum P_s (1312%) was observed in neutral medium whereas, a lesser P_s was observed in acidic as well as in alkaline media. This type of behavior could be explained on the basis of osmotic swelling pressure (π_{ion}) theory [32]. For a weakly charged hydrogel network, osmotic swelling pressure is given as:

$$\pi_{ion} = RT\sum (C_i^g - C_i^s)$$

where, C_i^g and C_i^s are the molar concentrations of mobile ions in the swelled gel and external solution, respectively. R is the gas constant and T is the absolute temperature.

As glucoronic acid is one of the components of *Gum ghatti* [33] so it comprises of carboxylate groups (COO^-) along the polymer chain. In neutral medium concentration of mobile ions in external solution (C_i^s) is almost negligible therefore π_{ion} becomes very large leading to the larger P_s. Moreover, the electrostatic repulsion between carboxylate ions adds to the P_s in neutral medium. Whereas, in acidic medium π_{ion} becomes very small because the carboxylate ions within the swelled gel get protonated resulting in a low value of C_i^s [34].



Figs. 3a-e: (a) Effect of time on P_s in deionized water; (b) Effect of temperature on P_s in deionized water; (c) Effect of pH on P_s in deionized water; (d) Pulsatile behaviour of Gg-cl-poly(AAm-co-MAA); (e) effect of ionic strength of various cations on P_s in different chloride salt solutions

Also in acidic medium carboxylate ion-carboxylate ion repulsion is screened by H^+ ions which did not allow the network to expand and resulted in decreased P_s. On the other hand, in alkaline solution, dissociation of –COOH group is almost complete but very high concentration of Na^+ and ^-OH ions leads to the reduction in π_{ion} and P_s. Also higher concentration of Na^+ ions acted as a screening bar, thereby reducing the repulsion between different carboxylate groups, hence a lesser P_s was observed.

Swelling-deswelling-reswelling behavior

Fig. 3d revealed the effect of change in pH of the swelling medium on the swelling-deswelling-reswelling behavior of hydrogel. The ability of the candidate polymer to exhibit reversibility in swelling behavior was examined in the solutions of pH 3.0 and 8.0. It was observed that when hydrogel was immersed in the solution of pH 8.0 swelling occurred because of anion-anion repulsion, however, on placing the swelled hydrogel in the solution of pH 3.0 it deswells due to protonation of carboxylate groups. Now, again on placing the deswelled hydrogel in the solution of pH 8.0 it swells again, thereby exhibiting the pulsatile behavior.

Effect of ionic strength of different cations on percent swelling

Fig. 3e showed the swelling data obtained from the chloride salt solutions of various cations of different ionic strength. From the figure it is clear that P_s decreased with an increase in charge of the metal cation ($Na^+ > Ba^{2+} > Fe^{3+} > Sn^{4+}$). Though initially candidate polymer showed swelling behavior in each salt solution but after certain time interval a definite difference in swelling behavior of candidate polymer in different salts was observed. It could be due to the fact that as the ionic charge increased, there is proportionate increase in cation-cation repulsion which did not allow more entry of solution containing cations inside the crosslinked network thereby resulted in desorption of ions. This ultimately lead to decreasing trend in swelling behavior of the candidate polymer. It is further observed that P_s of the candidate polymer decreased with

increase in ionic strength of the cation in the respective salt solutions. Decrease in P_s with increasing ionic strength of the cations was due to reverse osmosis process.

CONCLUSION

Modification of *Gum ghatti* via graft copolymerization and network formation with acrylamide-co-methacrylic acid improves the property profile and usability of the polymer in various technical fields. Crosslinked product was found to be thermally more stable than the initial backbone polymer. The polymer behaved as a smart polymer as it showed temperature and pH dependent absorptions. Thus, the functionalized polymer is important from technological view point.

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