Superabsorbent hydrogels from poly(acrylamide-co-acrylonitrile) grafted *Gum ghatti* with salt, pH and temperature responsive properties

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ABSTRACT

This research paper deals with the graft copolymerization of mixtures of acrylamide (AAm) and acrylonitrile (AN) with Gum ghatti (Gg) using ascorbic acid (ABC) and potassium persulphate (KPS) redox pair as an initiator and N,N'-methylene-bis-acrylamide (MBA) as an initiator via free radical graft copolymerization technique. Initially, effect of the various reaction parameters on graft copolymerization of Gum ghatti with AAm was studied and the effect of molar concentration of AAm-co-AN on water absorption capacity been investigated. Synthesized polymer was characterized by using different techniques like FTIR, SEM, XRD and TGA/DTA/DTG. Gg-cl-poly(AAm-co-AN) was found to be more crystalline and thermally more stable than Gum ghatti. Water absorption capacity of the candidate polymer was investigated in deionized water as a function of percentage swelling (P_s). Gg-cl-poly(AAm-co-AN) was found to show the maximum P_s of 921%. Effect of ionic strength and ionic charge of various cations on the P_s of candidate polymer in different chloride salt solutions (NaCl, BaCl$_2$, FeCl$_3$ and SnCl$_4$) were investigated. It was observed that P_s decreased with increase in ionic strength and cationic charge.

Keywords: *Gum ghatti*, hydrogel, graft copolymerization, swelling, crosslinking

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INTRODUCTION

Superabsorbent hydrogels are the three dimensional crosslinked polymer networks with hydrophilic polymer chains. They can absorb water up to thousand folds of their dry volume while maintaining the three dimensional network structure. This ability to absorb water is mainly due to the presence of ionic functional groups [1]. Hydrogels which swell and contract in response to external conditions like salt, pH, temperature and electric stimulus have been studied

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[2-4]. In case of ionic hydrogels many structural factors like charge, crosslinking density, hydrophilicity and degree of ionization, pKa value of the ionisable groups affect the degree of swelling. Also, properties of swelling medium like pH, ionic strength of counter ion and its valency influences the swelling properties [5-8]. Workers from all over the world are working on the synthesis of superabsorbents based on natural polysaccharides as backbone because of their exceptional properties like biodegradability, biocompatibility, renewability and non-toxicity [9, 10].

Ionic hydrogels based on N,N-dimethylacrylamide, acrylamide and itaconic acid were synthesized by free radical crosslinking polymerization in aqueous medium using APS-N,N'-methylene-bis-acrylamide as an initiator-crosslinker system [11]. The same initiator-crosslinker system was used by Pourjavadi *et al.* [12] to synthesize crosslinked hydrogel of chitosan and AAm under inert atmosphere and investigated the effect of monomer and crosslinker concentrations on swelling behaviour. Ghosh *et al.* [13] used potassium persulphate as an initiator for the graft copolymerization of AAm onto cotton fibers in a limited aqueous system. The mechanism of copolymerization was discussed alongwith the determination of grafting parameters. Sanghi *et al.* [14] grafted acrylamide onto *Cassia javahikai* seed gum in the presence of KPS-ascorbic acid as an initiator. The same redox pair (KPS - ascorbic acid) was used as an initiator by Singh *et al.* [15] to graft copolymerize methyl methacrylate onto guar seed Galactomannan. Garcia *et al.* [16] synthesized polymeric hydrogels based on biocompatible materials and MAA in which KPS-N,N'-methylene-bis-acrylamide was used as an initiator-crosslinker redox system. Further the characterization was done using FTIR, ^{1}H NMR and DSC techniques and the synthesized gel was used to study the release behaviour of metoclopramide which was found to be non-Fickian.

In our recent research work we have synthesized superabsorbent from the mixture of acrylamide and acrylonitrile with *Gum ghatti* using ascorbic acid and potassium persulphate redox pair as an initiator and N,N'-methylene-bis-acrylamide as a crosslinker via free radical graft copolymerization technique. Swelling studies of the candidate polymer in deionized water were also done.

MATERIAL AND METHODS

Gum ghatti (sd Fine Chemicals Pvt. Ltd.), ascorbic acid-potassium persulphate (sd Fine Chemicals Pvt. Ltd.), N,N'-methylene-bis-acrylamide (MERCK), acrylamide (MERCK) and acrylonitrile (MERCK) were used as received.

Synthesis of superabsorbent
Gum ghatti (1g) was added to the known volume of deionized water in a reaction flask. A known molar ratio of ascorbic acid-KPS was added to the reaction mixture and mixed thoroughly to attain the homogeneity. Different reaction parameters like reaction time, amount of solvent, pH of medium and initiator ratio were optimized as a function of percentage grafting (P_g) as per the equation:
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$$P_g = \frac{W_f - W_b}{W_b} \times 100 \qquad (1)$$

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

Monomer and crosslinker concentrations were optimized with respect to percent swelling so as to get maximum water absorption capacity as per the equation [9]:

$$P_s = \frac{W_s - W_d}{W_d} \text{ X } 100 \tag{2}$$

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

Instrumental Analysis
FTIR spectra of the samples were taken on PERKIN ELMER RXI Spectrophotometer using KBr pellets. Scanning Electron Micrographs of the samples were taken on LEO, 435VF scanning electron microscope (LEO Electron Microscopy Ltd). 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 candidate polymer were done on BRUKER AXS 08 ADVANCE.

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.

Swelling studies in deionized water
Swelling capacity of the candidate polymer in deionized water as a function of swelling time, temperature and pH of the swelling medium was investigated. 100mg of the sample was immersed in 100ml of deionized water. After a definite time interval sample was taken out, wiped and weighed. P_s was calculated as per Eq. 2. After the optimization of swelling time temperature and pH of swelling medium were optimized.
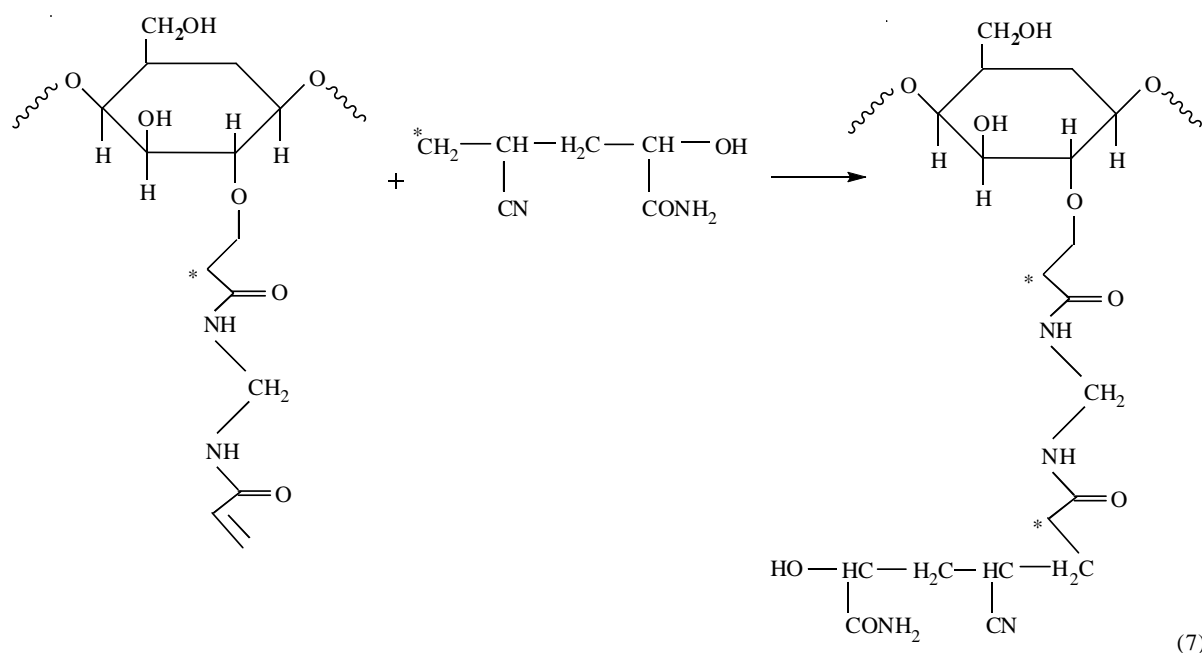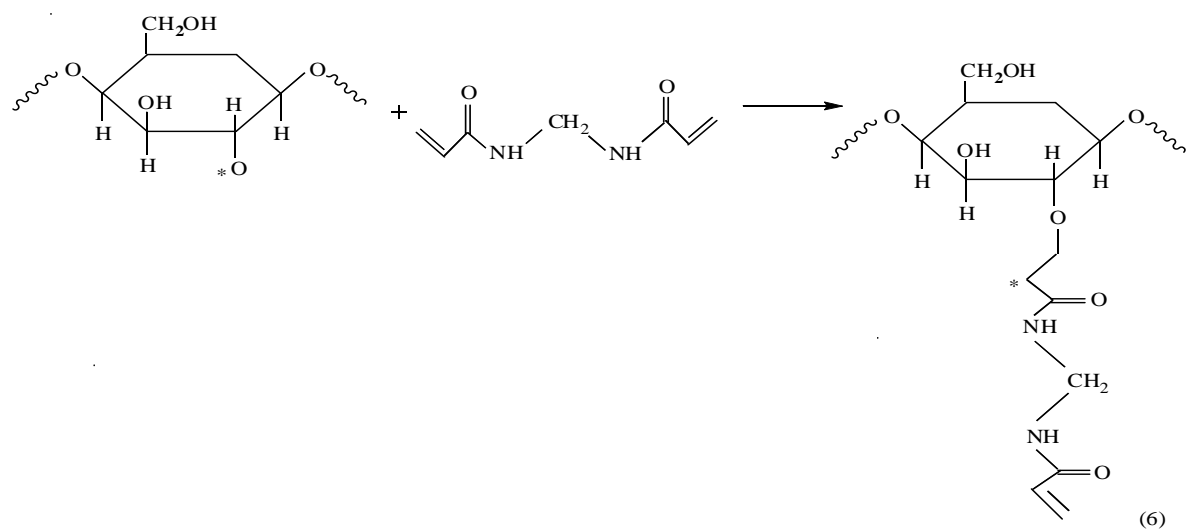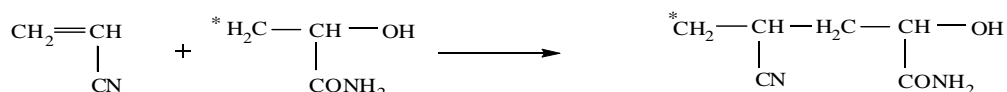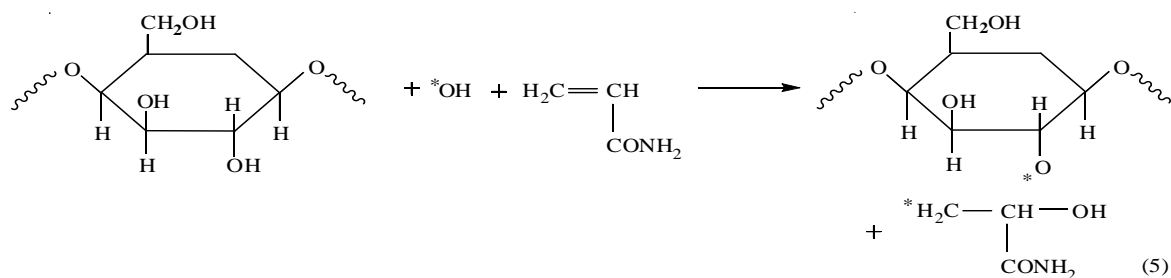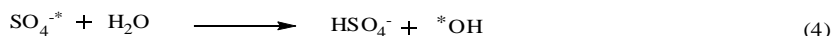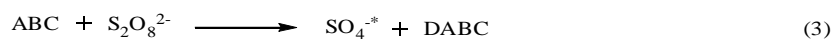
Swelling studies in different salt solutions
Effect of ionic strength and ionic charges of different cations on the percentage swelling of the hydrogel was investigated in NaCl, $BaCl_2$, $FeCl_3$ and $SnCl_4$ salt solutions at preoptimized time, temperature and pH in deionized water. Salt solutions of different ionic strength (0.01, 0.02, 0.03, 0.04 and 0.05 $molL^{-1}$) 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 different vinyl monomer mixtures are depicted in Scheme-I:

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$$ABC + S_2O_8^{2-} \longrightarrow SO_4^{-*} + DABC \qquad (3)$$

$$SO_4^{-*} + H_2O \longrightarrow HSO_4^{-} + {}^*OH \qquad (4)$$

(5)

(6)

(7)

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^{-*}

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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 takes 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 = 90 min, reaction temperature = 50°C, amount of solvent = 10 ml, pH = 7.0 and initiator molar ratio = 1:1, AAm=0.7042 $molL^{-1}$ and MBA=0.0974 $molL^{-1}$ [17].

Optimization of co-monomer concentration in binary mixture
After the optimization of various reaction parameters with primary monomer mixtures (AAm), concentration of AN in combination with AAm was optimized and was found to be 9.136 $molL^{-1}$ with maximum P_s of 965% (Table 1). Initially, P_s increased with increase in AN concentration but after getting maximum a decline in P_s with further increase in AN concentration was observed. Initially increase in P_s was due to the formation of more porous

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

Sample	[AAm+AN] x $molL^{-1}$	P_s	±SD	±SE
1.	0.77+4.56	564	4.35	2.51
2.	0.77+6.09	684	3.00	1.73
3.	0.77+7.6	825	4.35	2.51
4.	0.77+9.1	965	3.46	2.00
5.	0.77+10.06	750	3.60	2.08

where, no. of replications=03

and flexible structure which can accommodate more water molecules but further increase in AN concentration beyond optimum level resulted in a rigid and compact crosslinked entity, thereby exhibiting lesser swelling.

Characterization
FT-IR
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} (-C-O stretching region as complex bands resulting from C-O and C-O-C stretching vibrations) and 643.71 cm^{-1} (pyranose ring).
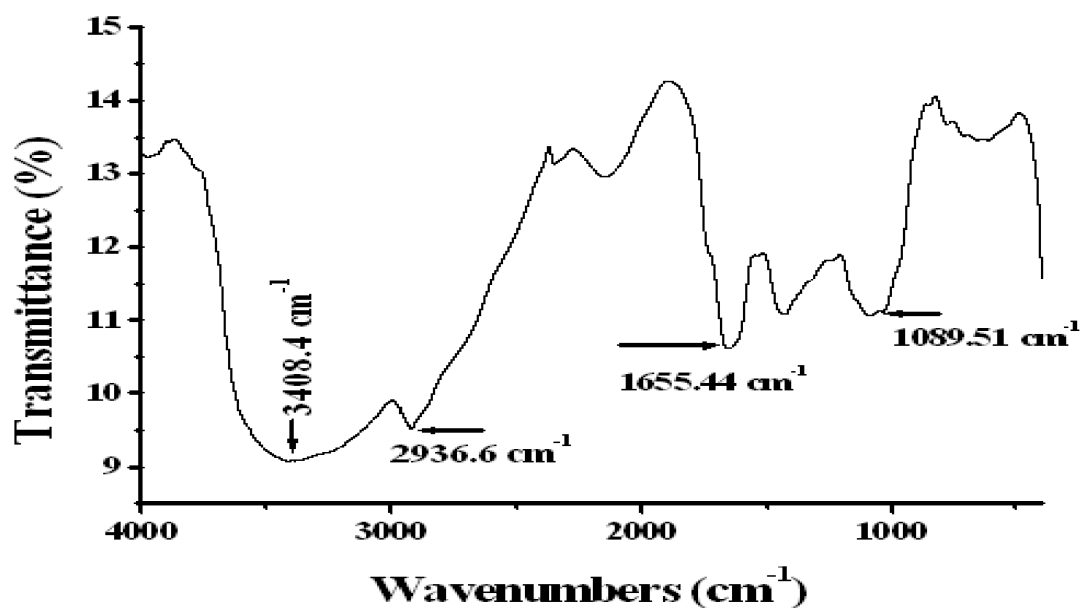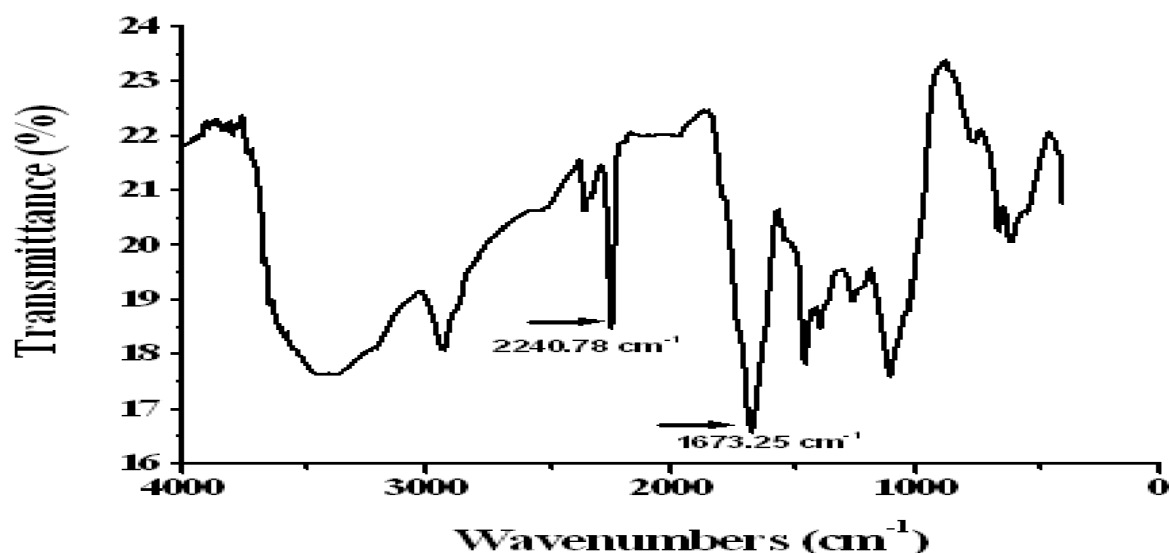
Fig. 1(a)

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

Whereas, in case of Gg-cl-poly(AAm+AN) one peaks at 2240.78 cm-1 (C≡N stretching of nitrile), 1673.25 cm-1 (C=O stretching of amide-I), 1456.56 cm-1 (N-H in plane bending of amide-II) and 1248.48 cm-1 (C-N stretching of amide-III) were observed in addition to the peaks observed with IR of *Gum ghatti* (Figs. 1a-b).

SEM
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. A remarkable three dimensional appearance with high resolution was obtained in case of crosslinked product. SEM images clearly exhibited the differences in the surface morphology of the *Gum ghatti* and Gg-cl-poly(AAm_AN) which were brought about through graft copolymerization and crosslinking (Figs. 2a-b).
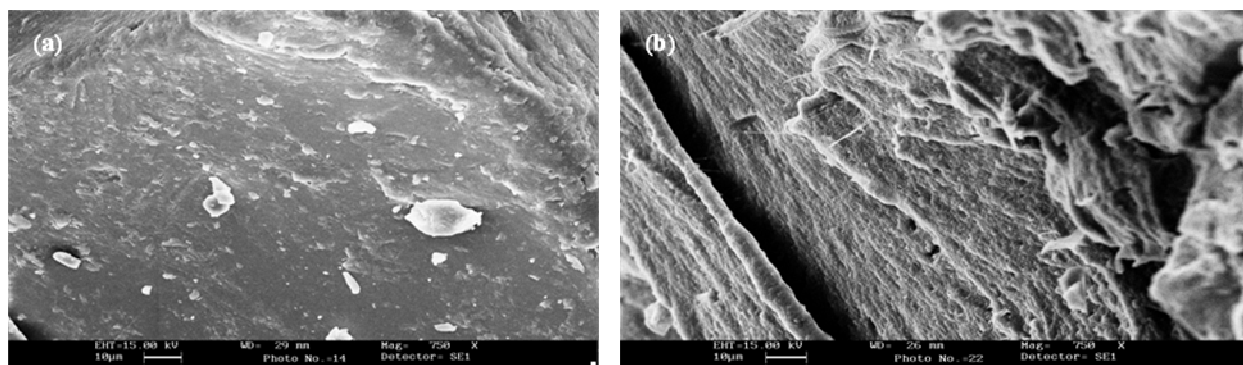
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Fig. 2: SEM of (a) *Gum ghatti***; (b) Gg-cl-poly(AAm-co-AN)**

TGA/DTA/DTG

TGA of *Gum ghatti* and Gg-cl-poly(AAm) was studied as a function of %wt loss versus temperature. 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 206.9^0C-331.4^0C with 46.6% weight loss and second stage decomposition was observed in the temperature range from 331.4^0C-521.6^0C with 31.2% weight loss. *Gum ghatti* exhibited initial decomposition temperature (IDT) at 206.9^0C and final decomposition temperature (FDT) at 521.6^0C. Two exothermic peaks at 483.2^0C (203μV) and 492.7^0C (154μV) were obtained in case of DTA of *Gum ghatti*. DTG of *Gum ghatti* showed decompositions at 299.1^0C and 479.0^0C with 1.463 and 2.230 mg/min weight loss, respectively.

It has been observed that in case of Gg-cl-poly(AAm+AN), IDT was observed at 133.6^0C, which is less than *Gum ghatti* (206.9^0C), whereas FDT of Gg-cl-poly(AAm+AN) has been found to be higher (681.8^0C) than *Gum ghatti* (521.6^0C). It shows that rate of decomposition of crosslinked polymer with respect to temperature is less than that of *Gum ghatti*. Hence, grafting and crosslinking of *Gum ghatti* with (AAm+AN)-MBA increases the stability towards the thermal decomposition. Two stage decomposition ranging from 133.6^0C-436.2^0C and 436.2^0C-681.8^0C was observed in case of TGA of Gg-cl-poly(AAm+AN). The results were further supported by DTA studies. In Gg-cl-poly(AAm+AN), exothermic peaks at 280.8^0C (102.2 μV) corresponding to TGA temperature range of 133.6^0C-436.2^0C and at 669.9^0C (136.2 μV) corresponding to the TGA temperature range of 436.2^0C-681.8^0C were observed. In DTG curve, weight loss rate 2.223 mg/min at 280.8^0C corresponding to first stage decomposition of TGA and 1.01 mg/min at 669.4^0C corresponding to second stage decomposition of TGA was observed [18, 19].

X-ray diffraction studies

Coherence length (L)of the samples were calculated using Scherrer Equation:

$$L = 0.9\lambda \,/\, \beta_{1/2} \text{ x cos} \theta$$

where, λ=wavelength, ө=diffraction angle, L=coherence length and $\beta_{1/2}$=full width half maximum.
Gum ghatti was found to be least crystalline among its crosslinked products with least value

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

Sample Code	TGA				DTA		DTG	
	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., $^{\bullet}$C (µV)		Decomposition Temp., $^{\bullet}$C (Rate of wt. loss in mg/min)	
					1st	2nd	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)	299.2 (1.463)	479.0 (2.230)
Gg-cl-poly(AAm-co-AN)	133.6	133.6-436.2 (35.6%)	436.2-681.8 (61.3%)	681.8	280.8 (102.2)	669.4 (136.2)	280.8 (2.223)	669.4 (1.01)

where IDT=Initial decomposition temperature, FDT=Final decomposition temperature, TGA=Thermo gravimetric analysis, DTA=Differential thermal analysis and DTG=Differential thermo gravimetric

of coherence length. It has been observed that anisotropy increases with increase in coherence length [20, 21]. In case of Gg-cl-poly(AAm+AN) hydrogels maximum intensity peak correspond to $2\theta=24.696^0$ (L=1.6175 Å), 24.165^0 (L=1.8649 Å), 23.553^0 (L=2.0034 Å), 21.296^0 (L=2.0734 Å) and 21.215^0 (L=2.2517 Å) with crosslinker concentration 0.77+ 4.56, 0.77+ 6.09, 0.77+ 7.614, 0.77+ 9.136 and 0.77+ 10.065, respectively (Table 3). Whereas, incase of *Gum ghatti* maximum intensity peak corresponds to $2\theta=20.908^0$ (L=1.057). It is clear from Table 3 that with the increase in acrylamide-co-acrylonitrile concentration value of coherence length increased 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.

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

Sample Code	[AAm+AN] mollL^{-1}	d-Spacing	Angle of Diffraction at 2θ-scale	FWHM at 2θ-scale	Coherence length (Å)
Gg	-	4.24532	20.908^0	13.17^0	1.057
Gg-cl-poly (AAm+AN)-I	0.77+ 4.56	3.60204	24.696^0	8.5444^0	1.6175
Gg-cl-poly(AAm+AN)-II	0.77+ 6.09	3.67995	24.165^0	7.4031^0	1.8649
Gg-cl-poly (AAm+AN)-III	0.77+ 7.614	3.7742	23.553^0	6.8838^0	2.0034
Gg-cl-poly(AAm+AN)-IV	0.77+ 9.136	4.16850	21.296^0	6.6255^0	2.0734
Gg-cl-poly (AAm+AN)-V	0.77+ 10.065	4.18453	21.215^0	6.0590^0	2.2517

Swelling studies in deionized water
Effect of time
Effect on time on P_s was studied at different time intervals (4, 8, 12, 16, 20, 24h). It was found that candidate polymer showed maximum P_s (669%) after 16h, whereas further Effect of temperature on swelling capacity of the candidate polymer was investigated at different temperature (30, 40, 50, 60 and 70 ^{0}C) and at preoptimized time (16h) (Fig. 3b). 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 [22-24].
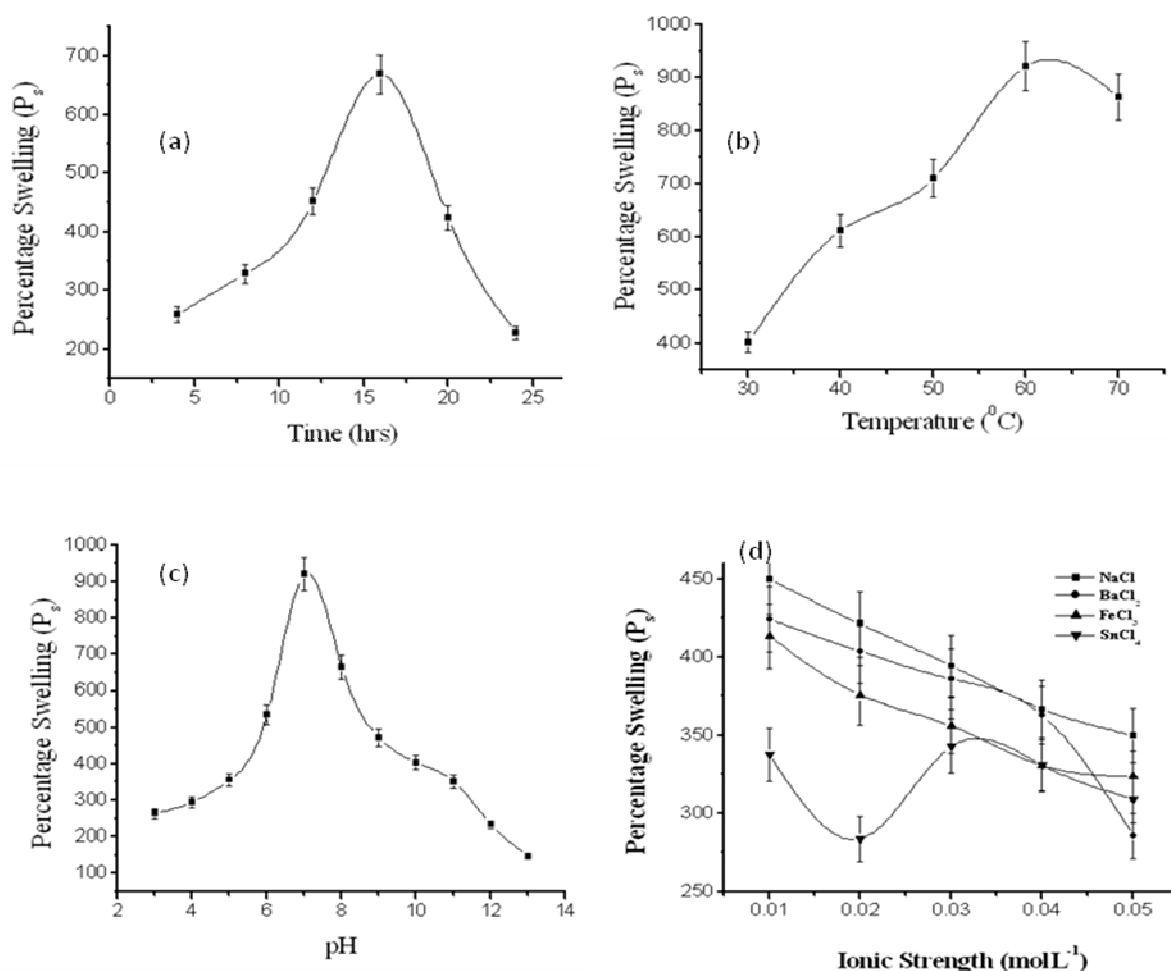
Effect of Temperature
Effect of temperature on Ps of Gg-cl-poly(AAm-co-AN) was investigated at different temperatures (30, 40, 50, 60 and 70 ^{0}C) and at preoptimized time (16h). It was observed that initially P_s increases with the increase in temperature and attained a maxima at 60^0C. Further increase in temperature resulted in a decrease in P_s. 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 [25-27].

Effect of pH
Swelling studies of the candidate polymers were carried-out at different pH values (1.0 to 13.0) and at preoptimized time and temperature (Fig. 3c). Maximum P_s was observed at 7.0 pH whereas, a lesser P_s was observed in acidic as well as in alkaline medium. This type of behavior could be explained on the basis of osmotic swelling pressure (π_{ion}) [28]. 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 swollen gel and external solution, respectively. R is the gas constant and T is the absolute temperature.

Figs. 3a-b: (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 Ps in deionized water; (d) effect of ionic strength of various cations on Ps in different chloride salt solutions

As glucoronic acid is one of the components of *Gum ghatti* [29] so it contains 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 almost very large leading to the larger P_s. Moreover, the electrostatic repulsion between carboxylate ions increases 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 [30]. Also in acidic medium

carboxylate ion repulsion is screened by H^+ ions which did not allowed 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.

Effect of ionic strength of different cations on percent swelling
Effect of ionic strength of various cations cation (Na^+, Ba^{2+}, Fe^{3+}, Sn^{4+}) on the on Ps of the Gg-cl-poly(AAm+AN) in different chloride salt solutions was investigated. It was observed that as the ionic strength of cations increased, a sharp decline in Ps was observed in respective salt solutions. Decrease in Ps with increase in ionic strength of the cations may be due to the reverse osmosis process [19]. Also with the increase in ionic strength of cations concentration of mobile ions in solution increased resulting in the decreased value of osmotic swelling pressure (π_{ion}) hence lesser Ps was observed. It was further observed that with the increase in cationic charge Ps decreased. It could be due to fact that with the increase in ionic charge, there is proportionate increase in cationic-cationic repulsion which did not allow more entry of solution containing cations inside the crosslinked network thereby resulted in desorption of cations.

CONCLUSION

Modification of *Gum ghatti* via graft copolymerization and network formation with acrylamide-co-acrylonitrile 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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