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SYNTHESIS, CHARACTERIZATION AND SWELLING BEHAVIOUR OF SUPER ABSORBENT HYDROGEL FROM SODIUM SALT OF PARTIALLY CARBOXYMETHYLATE GUAR GUM-g-PAN

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ABSTRACT

The graft copolymer of sodium salt of partially carboxymethylated guar gum containing PAN (Na-PCMGG-g-PAN, %G = 301.49) has been synthesized, under the established optimum reaction conditions, using $K_2S_2O_8$/ascorbic acid (AA) as a redox initiator in an aqueous medium at 35°C. The nitrile groups of Na-PCMGG-g-PAN have been completely converted in to a mixture of hydrophilic carboxamide and carboxylate groups by carrying out alkaline hydrolysis of the graft copolymer using 0.7 N KOH solution at 90-95°C to yield the superabsorbent hydrogel, H-Na-PCMGG-g-PAN. The swelling behaviour of the unreported superabsorbent hydrogel, H-Na-PCMGG-g-PAN, has been studied by carrying out its absorbency measurements in low conductivity water, 0.15 M different salt (NaCl, $CaCl_2$ and $AlCl_3$) solutions and simulated urine (SU). The results regarding the swelling behaviour and the salt sensitivity values are discussed. FTIR and SEM techniques have been used to characterize the products.

Keywords: *Sodium salt of partially carboxymethylated guar gum, Polyacrylonitrile, Graft copolymerization, Superabsorbent Hydrogel, Swelling behaviour, Salt sensitivity*

INTRODUCTION

The chemical modification of polymeric materials, based on natural polysaccharides, by grafting has received considerable attention in recent years because of the abundant availability, low cost and eco-friendly nature of the polysaccharides. Recently, the superabsorbent hydrogels based on polysaccharides are widely used since they exhibit potential applications in many fields such as agriculture and horticulture, disposable diapers, pharmaceutics and medical applications [1-3]. Graft copolymerization of vinyl monomers onto polysaccharides followed by crosslinking of their chains is regarded as an efficient method for the synthesis of polysaccharide based superabsorbent hydrogels [4-10].

Guar Gum (GG), an industrially important natural and renewable, nonionic, rigid polymer [11] consists of a linear chain of β-D-mannopyranosyl units linked (1→4) with single membered α-D-galactopyranosyl units (1→6) as side branches. Due to the incomplete hydration of guar gum at ambient temperature and poor solution clarity as well as the desire for products with modified or special properties, earlier we have carried out carboxymethylation of guar gum to obtain sodium salt of partially carboxymethylated guar gum (Na-PCMGG) and as a part of our research programme we have successfully carried out the modification of sodium salt of partially carboxymethylated guar gum (Na-PCMGG, $\overline{DS}$ = 0.497) by graft copolymerization with methyl acrylate (MA) [12], acrylonitrile (AN) [13] methyl methacrylate (MMA) [14], ethyl methacrylate [15] and butyl acrylate (BA) [16] using ceric ammonium nitrate (CAN) as a redox initiator. Recently, we have also compared the reactivity of different vinyl monomers towards grafting [17] and studied the effects of substrate structure and liquor ratio on percentage grafting [18] using the optimum reaction conditions established for affording maximum percentage of grafting of different vinyl monomers onto (Na-PCMGG, $\overline{DS}$ = 0.497). We have also used CAN as a photo-initiator and successfully grafted MMA onto Na-PCMGG ($\overline{DS}$ = 0.291) [19].

However, to the best of the authors' knowledge there is no published report regarding the synthesis of a superabsorbent hydrogel via alkaline hydrolysis of the graft copolymer of Na-PCMGG containing polyacrylonitrile. Therefore, in the present work we have carried out graft copolymerization of acrylonitrile onto Na-PCMGG ($\overline{DS}$ = 0.15) using KPS/AA as a redox initiator and evaluated the optimum reaction conditions for affording maximum percentage of grafting by varying various reaction parameters. The optimally synthesized Na-PCMGG-g-PAN (%G = 301.49 and % GE = 97.77) copolymer has been characterized and finally hydrolyzed in alkaline medium to form a superabsorbent hydrogel, H-Na-PCMGG-g-PAN. The swelling behaviour of the superabsorbent hydrogel has been studied in low conductivity water as well as different saline solutions.

EXPERIMENTAL

Materials

Sodium salt of partially carboxymethylated guar gum (Na-PCMGG, $\overline{DS}$ = 0.15) sample was kindly supplied by Encore Natural Polymers Ltd; Ahmedabad, Gujarat/India. Potassium persulfate (KPS) (Qualigens, Glaxo India Ltd.) and ascorbic acid (AA) (Samir Tech. Chem., Baroda, Gujarat/India) and potassium hydroxide (Samir Tech. Chem., Baroda, Gujarat/India) of analytical

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reagent grade were used as received. Acrylonitrile (Samir Tech. Chem., Baroda, Gujarat/India) was distilled out at an atmospheric pressure and the middle fraction was collected and used. Sodium chloride and urea (Maruti Chemicals Corporation, Anand, Gujarat/India) of analytical reagent grade were used as received. Aluminum chloride (Loba Chemicals, Mumbai, India) as well as Calcium chloride and Magnesium sulfate (Samir Tech. Chem., Baroda, Gujarat/India) of analytical reagent grade were used as received. All other reagents and solvents used in the present work were of reagent grade. Nitrogen gas was purified by passing through fresh pyrogallol solution. Low conductivity water was used for the preparation of solutions as well as for polymerization reactions.

Graft Copolymerization

The graft copolymerization reaction of AN onto Na-PCMGG was carried out using KPS/ascorbic acid as a redox initiator in an aqueous medium under nitrogen atmosphere and the optimum reaction conditions, for affording maximum percentage of grafting, were evaluated by successively varying various reaction conditions such as concentrations of ascorbic acid (10×10^{-3} to 50×10^{-3} mol/L), potassium persulfate (5×10^{-3} to 45×10^{-3} mol/L) and AN (0.037 to 0.665 mol/L) as well as reaction time (0.5 to 10 h), temperature (20^0 to 80^0C) and amount of substrate (0.25 to 3.5 g, dry basis) [20]. In the present work, using the optimum reaction conditions established in the case of grafting of AN onto Na-PCMGG, the graft copolymerization reaction was carried out as per the procedure reported earlier [13]. In a 250 mL three necked flask, equipped with mechanical stirrer, a reflux condenser and a glass inlet system, 0.5 g of Na-PCMGG was dissolved in a low conductivity water (110 mL) with constant stirring and bubbling of a slow stream of nitrogen for 1h at 35^0C. The freshly distilled AN (0.337 M) was then added to the charge. After five minutes, the freshly prepared 10 mL solution of AA (20×10^{-3} M), in low conductivity water was added and stirred for 20 minutes. After 30 minutes, the freshly prepared 10 mL solution of KPS (20×10^{-3} M) in low conductivity water was added and stirred to it. This time was taken as zero time for reaction and the grafting reaction was carried out for 4h. After completion of the reaction, the mixture was immediately poured into excess of methanol. The crude copolymer thus obtained was dried under vacuum at 40^0C. The homopolymer, poly(acrylonitrile) (PAN), was separated from the crude graft copolymer by extraction with dimethyl formamide for 48h. After complete removal of the homopolymer, the pure graft copolymer i.e. Na-PCMGG-g-PAN was dried at 40^0C under vacuum to a constant weight.

Grafting Parameters

Grafting parameters viz. percentage of grafting (%G) and percentage of grafting efficiency (%GE) were calculated by using the following expressions [8]

$$\%\,G \quad \frac{\text{Wt. of Polymer Grafted}}{\text{Initial Wt. of backbone}} \times 100 \qquad (1)$$

$$\%\,GE \quad \frac{\text{Wt. of Polymer Grafted}}{\text{Wt. of Polymer Grafted} + \text{Wt. of Homopolymer}} \times 100 \qquad (2)$$

Saponification or Alkaline Hydrolysis

The graft copolymer, Na-PCMGG-g-PAN (%G = 301.49 and % GE = 97.77) sample synthesized under optimally reaction conditions, was saponified by following the methanol precipitate method [21] for the formation of hydrogel, H-Na-PCMGG-g-PAN. According to this method, in a loosely stoppered 500 mL flask, 10.0 g of the Na-PCMGG-g-PAN was dispersed in 100 mL 0.7N potassium hydroxide solution and gently stirred in the base under atmospheric conditions (5 mins). Then the dispersion was heated at 90-95^0C with occasional stirring. The saponification was continued until the colour of the mixture changed from deep orange-red to light yellow (~2.5 h). The pasty mixture was then allowed to cool to room temperature. Methanol (5 x 10 mL) was added portion-wise to the gelled product while mixing. After 1 h, 200 mL additional methanol was added to the yellow dispersion of the hydrogel (H-Na-PCMGG-g-PAN) to complete the precipitation. The supernatant was decanted after 30 mins; and 300 mL fresh methanol was then further added to completely de-water the particles for 24h. The yellow precipitate of the hydrogel was filtered through sintered glass crucible (no. 3) using suction. Thus, the product of the hydrogel obtained was thoroughly washed with fresh methanol and finally dried at 60^0C and stored in a vacuum desicator.

Swelling or Absorbency Measurements

In order to measure the swelling or absorbency capacity of the hydrogel, 0.1 g of the hydrogel powder, after passing through 100 mesh (150_m) sieve, was put into a weighed tea bag. The tea bag then was immersed in 200 mL low conductivity water and allowed to soak for different timings (4h to 48h) at room temperature. The equilibrated swollen gel was then allowed to drain by removing the tea bag from the water and was hung up until no more drops drained (~10 min). The bag was then weighed to determine the weight of the swollen gel.

By using the swelling or absorbency experimental weights of the hydrogel sample, the values of the Swelling Ratio (S) of the hydrogel sample was calculated using the following equation :

$$S = \frac{W_s - W_d}{W_d} \qquad (3)$$

where W_s and W_d are the weights of the swollen gel and the dry gel, respectively. Thus, the swelling ratio (S) was calculated as grams of water per grams of hydrogel sample (g/g gel). The water absorption capacity was determined three repeats for each case and its average value was reported.

Swelling in Salt Solutions

Absorbency measurements of the hydrogel sample were also carried out in 0.15M solutions of NaCl, $CaCl_2$ and $AlCl_3$ as well as in Simulated Urine (composition: 0.85 g $CaCl_2.2H_20$, 1.14 g $MgSO_4.7H_20$, 8.20 g NaCl, 20g urea and 1000 mL low conductivity water) solution [22] for different timings (4h to 48h) according to the method described above for absorbency measurements in low conductivity water.

Infrared (IR) Spectroscopy

IR spectra of Na-PCMGG, Na-PCMGG-g-PAN (%G = 301.49) and the superabsorbent hydrogel, H-Na-PCMGG-g-PAN were taken in KBr pellets using Nicolet Impact 400D Fourier Transform Infra Red Spectrophotometer.

Scanning Electron Microscopy (SEM)

Model ESEM TMP + EDAX, Philips make has been used to obtain the micrographs of Na-PCMGG, Na-PCMGG-g-PAN (%G = 301.49) and the superabsorbent hydrogel.

RESULTS AND DISCUSSION

Synthesis of Superabsorbent Hydrogel (H-Na-PCMGG-g-PAN)

As discussed above, the saponification of Na-PCMGG-g-PAN (%G = 301.49) sample was carried out by treating it with aqueous 0.7N potassium hydroxide solution at 90-95°C. Scheme 1 represents the mechanism of crosslinking during conversion of nitrile groups of Na-PCMGG-g-PAN into carboxamide and potassium carboxylate groups for the formation of the superabsorbent hydrogel. As shown in the scheme, in the first step the hydroxide ions abstract hydrogen from the –OH group of Na-PCMGG substrate to the formation of the corresponding alkoxide anions. Then, these Na-PCMGG alkoxide anions (i.e. macroalkoxides) initiate crosslinking reaction between some adjacent polyacrylonitrile pendant chains leading to the formation of deep orange-red colour intermediate with naphthyridine cyclic structures, including imine, -C=N-, conjugated bonds with evolution of ammonia [23, 24]. Thus, the intermediate having a conjugated polyimine structure then gets further saponified with residual potassium hydroxide solution to form hydrophilic carboxamide ($-CONH_2$) and carboxylate (CO_2^-) groups. The disappearance of the conjugated system with formation of the hydrophilic groups was indicated when colour of the system got changed from red to light yellow. This sharp change in colour was used as a marker to halt the alkaline treatment. In this way, the starting hydrophobic graft copolymer sample was converted into a hydrophilic gel i.e. superabsorbent hydrogel. The mechanism depicted in Scheme 1 is in accordance with the literature data [8, 25-37].

Swelling Behaviour in Water and Salt solutions

Table 1 represents the results of the swelling ratio values of the superabsorbent hydrogel in low conductivity water, 0.15M different salt (NaCl, $CaCl_2$ and $AlCl_3$) solutions and simulated urine (SU). It is evident from the results that swelling ability of "anionic" hydrogel in different salt solutions is found to be decreased comparing to the swelling values in low conductivity water. It is known that the swelling capacity of superabsorbent hydrogel is mainly related to the characteristics of the external solutions such as its valences (charge number) and salt concentration (ionic strength), as well as the nature of polymer, i.e. the elasticity of the network, the presence of hydrophilic functional groups, and the extent of crosslinking density. The presence of ions in the swelling medium has a profound effect on the absorbency behaviour of the superabsorbent hydrogel. Many theories have been reported in the case of swelling behaviour of ionic hydrogels in saline solutions. The simplest one of the theories is Donnan Equilibrium Theory. This theory attributes the electrostatic interactions (ion swelling pressure) to the difference between the osmotic pressure of freely mobile ions in the gel and in the outer solutions. The osmotic pressure attributable to the polymer network is the driving force for the water absorption and consequently, the swelling of the polymeric network and superabsorbent. Increasing the ionic mobile ion concentration difference between the polymer gel and external medium, which, in turn, reduced the gel volume, i.e. the gel shrinks and swelling capacity decreases. This well known undesired swelling loss is often attributed to a "charge screening effect" of the additional cations causing a non perfect anion-anion electrostatic repulsion leading to decreased osmotic pressure (ionic pressure) difference between hydrogel network and the external solution [3, 26].

Thus, as shown in Table 1, the water absorbency values of the H-Na-PCMGG-g-PAN hydrogel in NaCl, $CaCl_2$ and $AlCl_3$ solutions with same concentration (0.15 mol/L) are found to be lower at different timings than that of low conductivity water which is attributed to the "charge screening effect" of the additional cations [8, 22]. At the swelling equilibrium, the chemical potential of water in the polymer network will be equal to that of the water surrounding to it. Addition of a salt (NaCl or $CaCl_2$ or $AlCl_3$) to the polymer solution leads to network contraction as indicated by the lowering of the viscosity and the chemical potential of the water surrounding a polymer network. Therefore, absorbent polymers can not imbibe as much salt water as pure water alone as it is observed from the results of Table 1.

The influence of different cations with a common anion (Cl^-) on the absorbency of the hydrogel was also investigated and the results are tabulated in Table 1. It can be seen from this table that the swelling capacity decreases with an increase

in the charge of the metal cation ($Na^{+} > Ca^{+2} > Al^{+3}$). This may be explained by complexing ability arising from the coordination of the multivalent cations with carboxylate groups present in the hydrolyzed hydrogel so that the crosslink density increases in the hydrogels and swelling capacity decreases. This "ionic crosslinking" mainly occurs at the surface of particles and makes the hydrogel rubbery and very hard to the touch, when they swell in Ca^{+2} or Al^{+3} solutions, so that it can not swell well. In contrast, H-Na-PCMGG-g-PAN particles swollen in NaCl solution and water exhibits lower gel strength.

Pourjavadi and Zohuriaan – Mehr [9] defined a dimensionless swelling factor, f, in order to achieve a comparative measure of sensitivity of the hydrogels to the type of swelling media as follows (4)

f (Salt Sensitivity) = 1 - (Absorption in a given fluid /Absorption in deionized water)

The f values obtained in the present work are tabulated in Table 2. The influence of increasing cation charge on the ultimate absorption for the superabsorbent hydrogel can be evident upon comparing the average salt sensitivity values (Table 2). It can be seen from this table that due to ionic crosslinking by multivalent cations (Ca^{+2} and Al^{+3}), the average salt sensitivity values of the superabsorbent hydrogel are found to be higher in 0.15M $CaCl_2$ and $AlCl_3$ solutions in comparison with univalent cation Na^{+}, in 0.15M NaCl solution. The average salt sensitivity value for the case of simulated urine solution is also found to be higher compared to 0.15M NaCl solution as the solution contains multivalent cations (Mg^{+2} and Ca^{+2}) in addition to univalent cation (Na^{+}). Thus, lower the cationic charge, the lower will be the average salt sensitivity. In other words, this low average salt sensitivity value is attributed to the low charge screening effect in the hydrogel when the swelling media is 0.15M NaCl solution. Similar results are also reported in literature [8, 27].

Characterization

Infra Red Spectroscopy

Figure 1 is the FT-IR spectrum of Na-PCMGG. The presence of a very strong and broad absorption band appeared at ~3428 cm^{-1} is assigned to –OH stretching. Reasonably sharp absorption band appeared at ~2927 cm^{-1} may be attributed to –CH stretching. The asymmetric and symmetric vibration of –COO- moiety are assigned to ~1640 cm^{-1} and ~1424 cm^{-1} respectively. Thus, the result of the IR spectra provides a substantial evidence of the presence of the carboxymethyl group. The spectra of Na-PCMGG-g-PAN (Figure 2) showed absorption bands of Na-PCMGG (Figure 1) as well as an additional band at ~2245 cm^{-1}, which has been attributed to -C ≡ N stretching mode, characteristic of the spectra of PAN. Thus, the presence of an additional band at ~2245 cm^{-1} in the graft copolymer i.e. Na-PCMGG-g-PAN indicated beyond doubt that grafting of AN onto Na-PCMGG has taken place. After alkaline hydrolysis, the absorption modes at ~1666 and ~1587 cm^{-1} appeared in the spectra (Figure 3) are attributed to C=O stretching in carboxamide functional groups as well as carboxylate groups respectively. As observed in the IR spectra of the alkaline hydrolysed sample (Figure 3) and as shown in the Scheme 1 it is evident that after alkaline hydrolysis, most of the nitrile groups are converted to carboxamide and carboxylate groups.

Scanning Electron Microscopy (SEM)

As the textural characterization of a superabsorbent polymer is important to understand its swelling behavior, the surface appearance and structure of Na-PCMGG, Na-PCMGG-g-PAN and the superabsorbent hydrogel were observed using SEM. These micrographs are shown in Figures 4 (a) to 4 (c). Figure 4 (a) is the SEM of Na-PCMGG. The observed surface morphology showing the clustered granular structure is due to its branched structure and interactions of the hydrophilic or ionic groups present onto it. In Figure 4 (b), after grafting with PAN, a hydrophobic polymer, the surface of the resultant Na-PCMGG-g-PAN exhibits contrastingly different morphology compared to that of the Na-PCMGG [Figure 4 (a)], due to the hydrophobic-hydrophobic interactions taking place between the grafted PAN chains those assemble on the surface of the backbone polymer. Thus, the surface evidence supports the grafting of PAN onto the Na-PCMGG.

The morphology of the graft copolymer, Na-PCMGG-g-PAN [Figure 4 (b)] was converted to a different morphology [Figure 4 (c)] as the graft copolymer was treated in the alkaline medium to yield the superabsorbing hydrogel [Figure 4 (c)]. The hydrogel [Figure 4 (c)] exhibits porous structure. It is supposed that these pores are the regions for the permeation of water into the polymeric network, and ultimately it helps in enhancing the water absorbency of the hydrogel.

CONCLUSIONS

A novel superabsorbent hydrogel, H-Na-PCMGG-g-PAN has been prepared by grafting of AN onto Na-PCMGG ($\overline{DS}$ = 0.15), followed by alkaline hydrolysis of the Na-PCMGG-g-PAN graft copolymer to achieve an in-situ crosslinked hydrogel network, H-Na-PCMGG-g-PAN, with high capability of water absorption (absorbency in water, 119.84 g/g gel; absorbency in 0.15M NaCl, $CaCl_2$ and $AlCl_3$ solutions respectively to be 47.82 g/g gel, 39.19 g/g gel and 34.81 g/g gel). The synthesized hydrogel also exhibited the maximum swelling capacity of the order of 45.14 g/g gel in simulated urine. These promising results make it worth to prepare hydrogel suitable for utilization as diaper as well as adsorbent material. The results regarding the absorbency measurements of the hydrogel in low conductivity water, 0.15M different

salt (NaCl, $CaCl_2$ and $AlCl_3$) solutions and simulated urine have been explained successfully on the basis of "charge screening" effect and "ionic crosslinking" phenomenon. FTIR and SEM techniques have been successfully used to characterize the products.

Table 1

Swelling Ratio (S), (g/g gel) values of the superabsorbent hydrogel, H-Na-PCMGG-g-PAN, in low conductivity water, 0.15M different salt (NaCl, $CaCl_2$ and $AlCl_3$) solutions as well as simulated urine [SU].

Time (h)	Water	NaCl	$CaCl_2$	$AlCl_3$	SU*
4	77.9	37.0	31.5	22.0	35.2
8	94.4	37.9	34.9	23.9	36.9
12	100.4	40.0	37.0	31.3	39.1
16	107.1	41.1	39.2	33.0	39.1
20	114.4	43.3	38.2	34.8	45.0
24	119.8	47.8	39.0	33.9	45.1
36	118.1	45.8	37.5	33.6	43.9
48	117.0	46.9	38.0	34.6	45.0

*Simulated Urine (composition: 0.85g $CaCl_2.2H_2O$, 1.14 g $MgSO_4.7H_2O$, 8.20 g ,NaCl, 20.0 g urea and 1000 mL conductivity water)

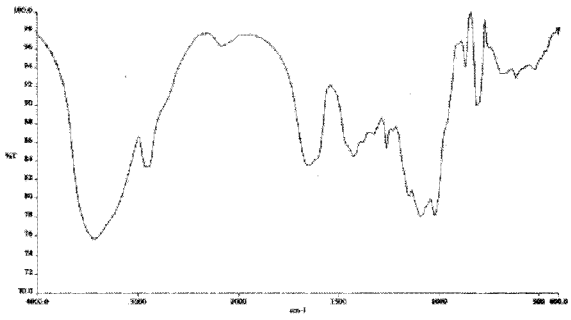


Figure 1. IR spectra of Sodium salt of Partially Carboxymethylated Guar Gum(Na-PCMGG, $\overline{DS}$ = 0.15) sample

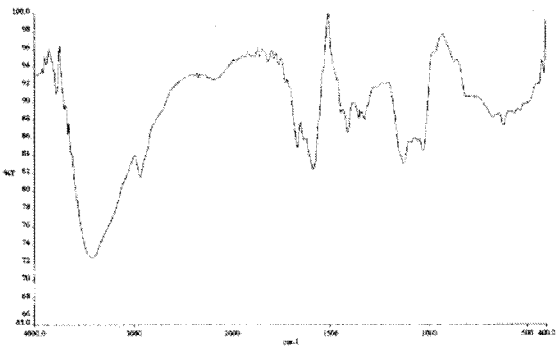


Figure 3. IR spectra of H-Na-PCMGG-g-PAN sample

Table 2

Dependency of the Dimensionless Salt Sensitivity (f) of the Superabsorbent Hydrogel, H-Na-PCMGG-g-PAN) to the type of swelling media at different timings.

Time (h)	f_{NaCl}	f_{CaCl_2}	f_{AlCl_3}	f_{SU}	Average Salt Sensitivity
4	0.535	0.595	0.717	0.548	
8	0.598	0.630	0.746	0.608	f_{NaCl} = 0.595
12	0.601	0.631	0.688	0.610	f_{CaCl_2} = 0.648
16	0.606	0.634	0.692	0.634	f_{AlCl_3} = 0.709
20	0.621	0.666	0.696	0.607	f_{SU} = 0.609
24	0.601	0.674	0.716	0.623	
36	0.612	0.682	0.715	0.628	
48	0.599	0.675	0704	0.615	

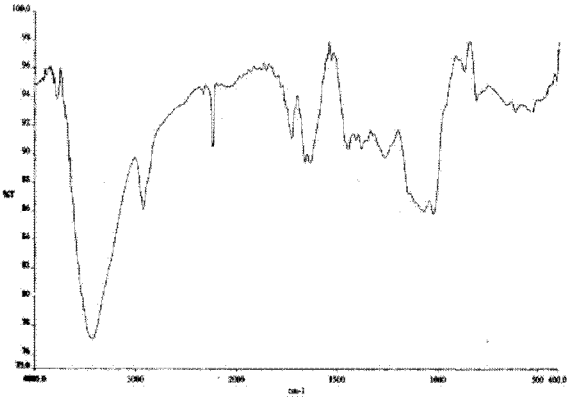


Figure 2. IR Spectra of Na-PCMGG-g-PAN (%G = 301.49) sample

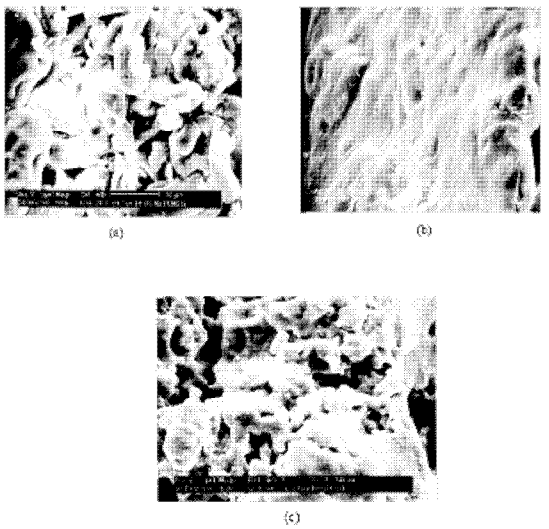
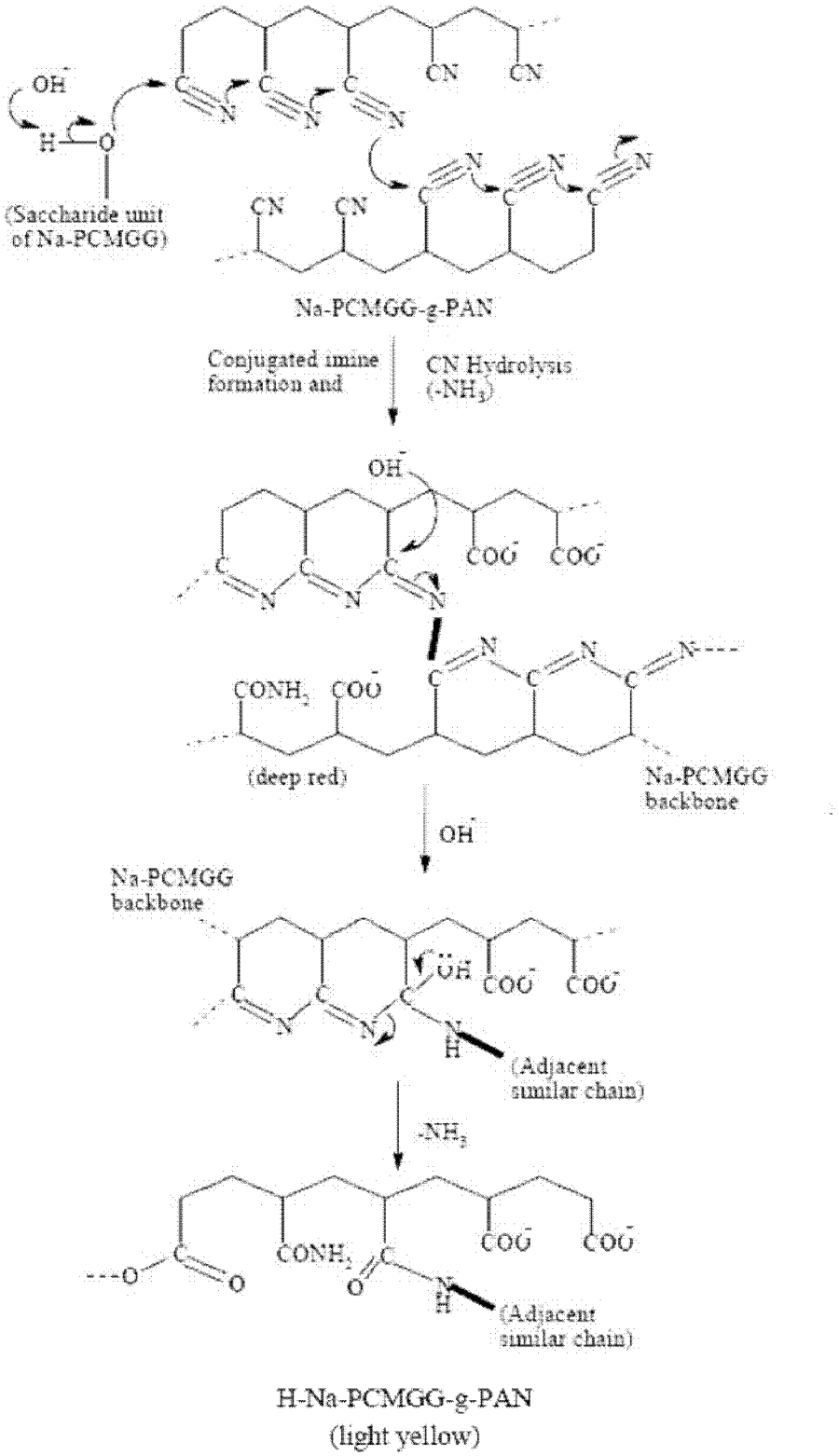


Figure 4. Scanning Electron Micrographs of (a) Na-PCMGG ($\overline{DS}$ = 0.15) (500X), (b) Na-PCMGG-g-PAN (%G = 301.49) (500X) and (c) the superabsorbent hydrogel, H-Na-PCMGG-g-PAN (500X).



Scheme 1. Mechanism of crosslinking during conversion of nitrile groups of Na- PCMGG-g-PAN into carboxamide and potassium carboxylate groups for the formation of superabsorbent hydrogel, H-Na-PCMGG-g- PAN.

REFERENCES

[1] Kost, J. (1999) *"Drug Delivery Systems"* in Encyclopedia of Controlled Drug Delivery, Vol.1, (Ed. Mathiowiz, E.), Wiley, New York, 445.

[2] Hoffman, A. (1996) *"Intelligent Polymers (in Medicine and Biotechnology)"*, in Polymeric Materials Encyclopedia, Vol. 5, (Ed. Salamone, J.), CRC Press Boca Raton, FL., 3282.

[3] Peppas, N. and Mikes, A. (1986) *"Preparation Method and Structure of Hydrogels"*, in Hydrogels in Medicine and Pharmacy, Vol. 1, CRC Press, Boca Raton. FL.

[4] Pourjavadi, A. and Zohuriaan-Mehr, M. (2002) Modification of Carbohydrate Polymers via Grafting in Air. 1. Ceric-Induced Synthesis of Starch-g-Polyacrylonitrile in Presence and Absence of Oxygen. *Strach/Strake*, **54**: 140-147.

[5] Zohuriaan-Mehr, M. and Pourjavadi, A. (2003) Superaborbent Hydrogels from Starch-g-PAN : Effect of Some Reaction Variables on Swelling Behaviour. *Journal of Polymer Materials*, **20**: 113-120.

[6] Sinha, V., Patel, C. and Trivedi, H. (1993) Grafting of Acrylonitrile onto Sodium salt of Partially Carboxymethylated Starch: Hydrolysis of Graft Copolymers and its Water Absorbency. *Journal of Polymer Materials*, **10**: 209-212.

[7] Shah, S., Patel, B., Patel, C. and Trivedi, H. (1992) Saponification of Graft Copolymers of Sodium salt of Partially Carboxymethylated Amylose and its Water Absorbency. *Starch/Strake*, **44**: 108-110.

[8] Trivedi, J. (2013) Synthesis, Characterization and Swelling Behaviour of Superabsorbent Hydrogel from Sodium salt of Partially Carboxymethylated Tamarind Kernel Powder-g-PAN. *Journal of Applied Polymer Science*, **129**: 1992-2003.

[9] Pourjavadi, A., Zohuriaan-Mehr, M. and Ghasempoori, S. (2007) Modified CMC. V. Synthesis and Super-Swelling Behaviour of Hydrolyzed CMC-g-PAN hydrogel. *Journal of Applied Polymer Science*, **103**: 877-883.

[10] Mohamadnia, Z., Zohuriaan-Mehr, M., Kabiri, K. and Razavi-Nouri, M. (2008) Tragacanth gum-graft-polyacrylonitrile: Synthesis, Characterization and Hydrolysis. *Journal of Polymer Research*, **15**: 173-180.

[11] Goldstein, A., Alter, E. and Seaman, J. (1973) *"In Industrial Gums"*, 2nd ed, Academic Press, New York, Ch 14, p.303.

[12] Trivedi, J., Kalia, K., Patel, N. and Trivedi, H. (2005) Modification of Sodium salt of Partially Carboxymethylated Guar Gum by Graft Copolymerization with Methyl Acrylate. *Polymers and Polymer Composites*, **13**: 301-312.

[13] Trivedi, J., Kalia K., Patel, N. and Trivedi, H. (2005) Ceric-Induced Grafting of Acrylonitrile onto Sodium salt of Partially Carboxymethylated Guar Gum. *Carbohydrate Polymers*, **60**: 117-125.

[14] Trivedi, J., Kalia, K., Patel, N. and Trivedi, H. (2005) Graft Copolymerization of Sodium salt of Partially Carboxymethylated Guar Gum with Methyl Methacrylate : An Examination of Reaction Variables. *Journal of Applied Polymer Science*, **96**: 1855-1864.

[15] Trivedi, J., Bhatt, T., Kalia, K., Patel, N. and Trivedi, H. (2008) Grafting of Ethyl Methacrylate into Sodium Salt of Partially Carboxymethylated Guar Gum by Tetravalent Cerium Ion. *Journal of Polymer Materials*, **25**: 541-555.

[16] Trivedi, J., Bhatt, T., Kalia, K., Patel, N. and Trivedi, H. C. (2011) Grafting of Butyl Acrylate onto Sodium salt of Partially Carboxymethylated Guar Gum Using Ceric Ions. *Journal of Pure & Applied Sciences - "PRAJNA" (Sardar Patel University)*, **19**: 25-31.

[17] Trivedi, J., Kalia, K., Patel, N. and Trivedi, H. (2005) Grafting of Vinyl monomers onto Sodium salt of Partially Carboxymethylated Guar Gum :Comparison of their Reactivity. *Polymer Plastics Technology & Engineering*, **44**: 407-425.

[18] Trivedi, J., Kalia, K., Patel, N. and Trivedi, H. (2005) Ceric-induced Grafting of Vinyl monomers onto Sodium salt of Partially Carboxymethylated Guar Gum : Effects of Substrate structure and Liquor Ratio. *Journal of Pure & Applied Sciences - "PRAJNA" (Sardar Patel University)*, **13**: 44-55.

[19] Thakar, M. and Trivedi, H. (2005) Ultraviolet- radiation-induced graft copolymerization of methyl acrylate onto the sodium salt of partially carboxymethylated guar gum. *Journal of Applied Polymer Science*, **97**: 1977-1986.

[20] Shah, U. (2008) Studies in Potential Graft Copolymers, Ph.D. Thesis, Sardar Patel University, Vallabh Vidyanagar, Gujarat State, India.

[21] Fanta, G., Burr, R., Doane, W. and Russel, C. (1978) Absorbent Polymers from Starch and Flour Through Graft Polymerization of Acrylonitrile and Comonomer Mixtures. *Starch/Stake*, **30**: 237-242.

[22] Ziderman, I. and Bleayche, J. (1986) Role of polyacrylate starch copolymer in water sorption. *Journal of Applied Polymer Science*, **32**: 5791-5798.

[23] Athawale, V. and Rathi, S. (1999) Graft Polymerization: Starch as a Model. Substrate. *Journal of Macromolecular Science - Reviews* in *Macromolecular Chemistry & Physics*, **C39**: 445-480.

[24] Fanta, G. and Doane, W. (1986) *In : Modifed Starches : Properties and Uses*. Wurzburg, O.B., Ed., CRC Press, Boca Raton, FL, pp 149-178.

[25] Pourjavadi, A., Harzandi, A. and Hosseinzadeh, H. (2004) Modified carrageenan 3. Synthesis of a novel polysaccharide-based superabsorbent hydrogel via graft copolymerization of acrylic acid onto kappa-carrageenan in air. *European Polymer Journal*, **40**: 1363-1370.

[26] Castel, D., Ricard, A. and Audebert, R. (1990) Swelling of Anionic and Cationic Starch- Based Superabsorbents in Water and Saline Solution. *Journal of Applied Polymer Science*, **39**: 11-29.

[27] Mahdavinia, G., Zohuriaan-Mehr, M. and Pourjavadi, A. (2004) Modified chitosan III, superabsorbency, salt- and pH-sensitivity of smart ampholytic hydrogels from chitosan-g-PAN. *Polymers for Advanced Technologies*, **15**: 173-180.

[28] Savoji, M. T. and Pourjavadi, A. (2006) Partially hydrolyzed kappa carrageenan polyacrylonitrile as a novel biopolymer-based superabsorbent hydrogel: Synthesis, characterization, and swelling behaviors. *Polymer Engineering & Science*, **46**: 1778-1786.

[29] Flory, P. (1953) *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY.

[30] Xu, S., Cao, L., Wu, R. and Wang, J. (2006) Salt and p^H responsive property of a starch-based amphoteric superabsorbent hydrogel with quaternary ammonium and carboxyl groups (II). *Journal of Applied Polymer Science*, **101**: 1995-1999.

[31] Gugliemelli, L., Weaver, M., Russell, C. and Rist, C. (1969) Base-hydrolyzed starch-polyacrylonitrile (S-PAN) graft copolymer. S-PAN-1:1, PAN M.W. 794,000. *Journal of Applied Polymer Science*, **13**: 2007-2017.

[32] Pourjavadi, A., Barzegar, Sh. and Mahdavinia, G. (2006) MBA-crosslinked Na-Alg/CMC as a smart full-polysaccharide superabsorbent hydrogels. *Carbohydrate Polymers*, **66**: 386-395.

[33] Farag, S. and Al-Afaleq, E. (2002) Preparation and characterization of saponified delignified cellulose

polyacrylonitrile-graft copolymer. *Carbohydrate Polymers,* **48**: 1-5.

[34] Saraydin, D., Karadag, E. and Guven, O. (1998) The Releases of Agrochemicals from Radiation Induced Acrylamide Crotonic acid hydrogels. *Polymer Bulletin*, **41**: 577-584.

[35] Peniche, C., Cohen, M., Vazquez, B. and Roman, J. (1997) Water-sorption of flexible networks based on 2-hydroxyethyl methacrylate-triethylenglycol dimethacrylate copopymers. *Polymer,* **38**: 5977-5982.

[36] Saraydin, D., Oztop, H. Z., Karadag, E., Caldiran, Y. and Guven, O. (1999) Influence of some amino acids on the dynamic swelling behavior of radiation-induced acrylamide hydrogel. *Applied Biochemistry & Biotechnology*, **82**: 115-125.

[37] Karadag, E. and Saraydin, D. (2002) *Swelling studies of super water retainer acrylamide/crotonic acid hydrogels crosslinked by trimethylolpropane triacrylate and 1,4–butanediol dimethacrylate. Polymer Bulletin,* **48**: 299-307.

Legends to the Figures/Scheme

Scheme 1. Mechanism of crosslinking during conversion of nitrile groups of Na- PCMGG-g-PAN into carboxamide and potassium carboxylate groups for the formation of superabsorbent hydrogel, H-Na-PCMGG-g- PAN.

Figure 1. IR spectra of Sodium salt of Partially Carboxymethylated Guar Gum (Na- PCMGG, $\overline{DS}$ = 0.15) sample

Figure 2. IR Spectra of Na-PCMGG-g-PAN (%G = 301.49) sample

Figure 3. IR spectra of H-Na-PCMGG-g-PAN sample

Figure 4. Scanning Electron Micrographs of (a) Na-PCMGG ($\overline{DS}$ = 0.15) (500X), (b) Na-PCMGG-g-PAN (%G = 301.49) (500X) and (c) the superabsorbent hydrogel, H-Na-PCMGG-g- PAN (500X).