

Photo-induced Sodium salt of Partially Carboxymethylated Psyllium-g-Polyacrylonitrile: II. Synthesis, Characterization and Swelling Behaviour of its Superabsorbent Hydrogel

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Abstract- Polyacrylonitrile (PAN) grafted sodium salt of partially carboxymethylated psyllium (Na-PCMPsy-g-PAN, %G = 219.62 and %GE = 99.85) was prepared using the established optimized reaction conditions in the case of ultraviolet-radiation induced grafting of acrylonitrile (AN) onto Na-PCMPsy ($DS = 0.13$) using uranyl nitrate (UN) as a photo-initiator. The saponification of the graft copolymer, Na-PCMPsy-g-PAN (%G = 219.62), was then performed in 0.7N NaOH solution at 90-95°C to yield a superabsorbent hydrogel, H-Na-PCMPsy-g-PAN. The swelling behaviour of the hydrogel was studied by carrying out its absorbency measurements in low conductivity water, 0.15M salt (NaCl, CaCl₂, AlCl₃) solutions and simulated urine (SU) at different timings. The average salt sensitivity values of the superabsorbent hydrogel were also calculated and compared. The tendency of the absorbency for the hydrogel in salt solutions is found to be in the order $Na^+ > Ca^{2+} > Al^{3+}$ for NaCl, CaCl₂ and AlCl₃ aqueous salt solutions. The swelling kinetics of the hydrogel in different swelling media was found to obey second order kinetics. The values of the various swelling characteristics of the hydrogel were also reported. FTIR, TGA and SEM techniques were used to characterize the products.

Index Terms- Na-PCMPsy-g-PAN, saponification, superabsorbent hydrogel, swelling kinetics, water absorbency

I. INTRODUCTION

In recent years, increasing interest in natural based and especially polysaccharides based superabsorbent hydrogels has been developed mainly due to high hydrophilicity, biocompatibility, non-toxicity and biodegradability of biopolymers. Superabsorbent hydrogels are hydrophilic, three-dimensional networks and exhibit the ability to highly swell in water, saline, or biological fluids and retain a significant fraction of them within their structure, but they do not dissolve in water (Buchholz and Graham, 1997). Superabsorbent hydrogels are widely used in sanitary goods such as disposable diapers and hygienic napkins. They are also used in soil conditioning and improving water retention capacity of soil in agriculture and horticulture (Po, 1194). Graft copolymerization of vinyl monomers onto polysaccharide backbones followed by crosslinking of their chains is regarded as an efficient method for the synthesis of polysaccharide-based superabsorbent hydrogels (Pourjavadi and Zohuriaan-Mehr, 2002; Shah et al., 1992; Pourjavadi et al., 2007; Wang and Wang, 2010; Mohamadnia et al., 2008; Sadeghi, 2010; Tian et al., 2012; Trivedi et al., 2013).

Psyllium (PSy) is mucilage forming natural polysaccharide, mainly known for its medicinal value (Fischer et al., 2004). The easy availability, low cost and widespread usage makes it a popular and attracted further to explore it for diverse applications. It consists of combination of highly substituted arabinoxylan polysaccharides (Kaith and Kumar, 2007; Izydorczyk and Biliaderis, 1995). These polysaccharides are linear chains of xylose units [β -(1→4)-xylan] to which single units of arabinose and additional xylose are attached. Rhamnose, galactose, glucose and rhamnosyluronic acid residues are present as minor constituents. The physiologically active component of PSy is known to be a highly branched, neutral arabinoxylan.

Literature survey reveals that the psyllium based hydrogels have been used as the drug delivery device (Singh et al., 2006; Singh et al., 2008) for metal ion sorption (Singh et al., 2006) as well as for the absorption of water from different water-oil emulsions (Kaith and Kumar, 2007). Recently, swelling properties of the Psy-g-poly(AA) superabsorbent hydrogels (Kumari et al., 2010; An et al., 2010) have also been reported.

However, due to low solubility of PSy in cold water, poor solution clarity as well as the desire for products with modified or special properties, we have carried out carboxymethylation of PSy to obtain Sodium salt of Partially Carboxymethylated Psyllium (Na-PCMPsy) and reported first time in the literature ultraviolet-radiation induced grafting of various vinyl monomers (Trivedi et al.,

2009; Dholakia et al., 2011; Dholakia et al., 2011; Dholakia et al. 2012) onto it using ceric ammonium nitrate (CAN) as a photo-initiator in an aqueous medium.

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-PCMPSy containing polyacrylonitrile (PAN). Therefore, in the present work, using the established optimized reaction conditions in the case of the ultraviolet-radiation induced graft copolymerization of AN onto Na-PCMPSy ($\overline{DS} = 0.13$) using UN as a photo-initiator, we have synthesized the graft copolymer Na-PCMPSy-g-PAN (%G = 219.62 and %GE = 99.85) and it has been saponified in an alkaline medium to form a superabsorbent hydrogel, H-Na-PCMPSy-g-PAN. The swelling behaviour of the superabsorbent hydrogel, H-PCMPSy-g-PAN, has also been studied in different salt solutions and the swelling kinetics of the hydrogel has been investigated.

I. EXPERIMENTAL

2.1. Materials

Psyllium (PSy) was obtained from Sat-Isabgol Factory (Unjha, Gujarat, India). The methods of preparation and purification, as well as the measurement of degree of substitution (\overline{DS}) of sodium salt of partially carboxymethylated psyllium (Na-PCMPSy) were followed as described and reported earlier (Dholakia et al., 2012). The \overline{DS} of Na-PCMPSy was found to be 0.13. AN (Fluka) was distilled out at an atmospheric pressure and the middle fraction was collected and used. Uranyl nitrate (UN) (Chiti Chem., Baroda, Gujarat, India) was used as received. Analar grade nitric acid was used. Fresh solution of the photo-initiator (UN) was prepared by dissolving the required amount of UN in nitric acid. Sodium hydroxide, Calcium chloride and Magnesium sulphate (all Samir Tech. Chem. Baroda, Gujarat, India) were used as received. Sodium chloride as well as Urea (both Maruti Chemicals Corporation, Anand, Gujarat, India) and Aluminium chloride (Loba Chemicals, Mumbai, 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 photo-graft copolymerization reactions.

2.2 Methods

2.2.1. Photo-graft copolymerization

The photo-graft copolymerization reaction was carried out in a photochemical reactor supplied by Scientific Aids and Instrument Corp. (SAIC, Madras, India) as per the procedure described earlier (Thaker and Trivedi, 2005). A weighed amount of Na-PCMPSy ($\overline{DS} = 0.13$, 0.5g, dry basis) was dissolved in 144.28 mL of low conductivity water in the reaction flask and the solution was stirred with continuous bubbling of a slow stream of nitrogen gas for one hour at 55°C and thereafter for twenty minutes at room temperature. 2.5 mL of freshly prepared UN solution (4.15×10^{-3} mol/L) in nitric acid (0.10 mol/L) was added to the reaction flask, and the contents were then flushed with purified nitrogen gas which was followed by the addition of freshly distilled AN (0.222 mol/L). The reaction flask was then assembled with an immersion well containing a 125W medium pressure mercury lamp. The whole assembly (photochemical reactor) was placed in a dark cabinet after covering it completely with aluminum foil. The lamp was then illuminated. Water from a constant-temperature water circulation bath was circulated over the immersion well and the reaction flask. The solution then was irradiated with continuous stirring for 2h at 35°C. After the completion of the grafting reaction, the irradiated sample solution was removed carefully, and the crude graft copolymer was isolated by centrifugation. It was then purified by washing with dilute nitric acid and repeated washings with 95% methanol and finally with pure methanol. The crude copolymer sample of Na-PCMPSy-g-PAN thus obtained was dried in vacuum at 40°C. The homopolymer, polyacrylonitrile (PAN), was separated from the crude graft copolymer by carrying out soxhlet extraction with dimethyl formamide for 48h. After the complete removal of the homopolymer, the pure graft copolymer was dried at 40°C in vacuum until a constant weight was obtained.

2.2.2. Grafting Parameters

Grafting parameters viz. percentage of grafting (%G) and percentage of grafting efficiency (%GE) were calculated by using the following expressions (Vora et al., 1995).

$$\%G = \frac{\text{Weight of grafted polymer}}{\text{Initial weight of backbone}} \times 10^2 \quad \dots(1)$$

$$\%GE = \frac{\text{Weight of grafted polymer}}{\text{Weight of grafted polymer} + \text{Weight of homopolymer}} \times 10^2 \quad \dots(2)$$

2.2.3. Isolation of grafted chains

The graft copolymer of Na-PCMPSy ($\overline{DS} = 0.13$) containing PAN was hydrolyzed by refluxing it for 12h in 1NHCl as described elsewhere (Brockway and Seaberg, 1967) for the isolation of the grafted PAN chains.

2.2.4. Saponification or alkaline hydrolysis

The graft copolymer, Na-PCMPSy-g-PAN (%G = 219.62 and %GE = 99.85) synthesized under optimally reaction conditions was saponified by following the methanol precipitate method (Fanta et al., 1978) for the formulation of the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN. According to this method, in a loosely stoppered 500 mL flask, 10.0 g of the Na-PCMPSy-g-PAN was dispersed in 100 mL 0.7N sodium hydroxide solution and gently stirred in the base under atmospheric conditions (5 mins). Then the dispersion was heated at 90-95°C 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-PCMPSy-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 (H-Na-PCMPSy-g-PAN) was filtered through sintered glass crucible (no. 3) using suction. Thus, the product of the hydrogel, H-Na-PCMPSy-g-PAN obtained was thoroughly washed with fresh methanol and finally dried at 60°C and stored in a vacuum desiccator.

2.2.5. Swelling or absorbency measurements

In order to measure the swelling or absorbency capacity of the hydrogel, 0.1 g of the saponified Na-PCMPSy-g-PAN (i.e. H-Na-PCMPSy-g-PAN) powder, after passing through 100 mesh (150 μm) 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 (0.5 to 24 h) 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) and the Equilibrium Water Content (EWC%) of the hydrogel sample were calculated using the following equations :

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

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.

$$EWC(\%) = \frac{W_{eq} - W_d}{W_s} \times 100 \quad \dots(4)$$

where W_{eq} is the weight of swollen gel at equilibrium.

2.2.6. Swelling in salt solutions

Absorbency measurements of the H-Na-PCMPSy-g-PAN hydrogel sample were also carried out in 0.15M solutions of NaCl, CaCl₂ and AlCl₃ as well as in Simulated Urine (composition: 0.85 g CaCl₂.2H₂O, 1.14 g MgSO₄.7H₂O, 8.20 g NaCl, 20g urea and 1000 mL low conductivity water) solution (Ziderman and Bleayche, 1986) for different timings (0.5h to 24h) according to the method described above for absorbency measurements in low conductivity water.

2.2.7. Swelling kinetics

The swelling kinetics of the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN, was studied by measuring the equilibrium swelling capacity of the hydrogel in low conductivity water, different salt (NaCl, CaCl₂ and AlCl₃) solutions (0.15M) and simulated urine solution at different time intervals according to the above mentioned method.

2.3. Characterization

2.3.1. Viscosity measurements

The molecular weight of the isolated PAN-side chains was determined from the measurements of intrinsic viscosity, $[\eta]$. The measurements were carried out at 25°C in dimethyl formamide using an Ubbelohde Viscometer.

2.3.2. Infrared (IR) spectroscopy

IR spectra of the Na-PCMPSy ($DS = 0.13$), Na-PCMPSy-g-PAN (%G = 219.62) and the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN were taken in KBr pellets using Excalibur 3100 (varian) spectrophotometer.

2.3.3. Thermogravimetric analysis (TGA)

The thermal behaviour of PSy, Na-PCMPSy ($\overline{DS} = 0.13$), Na-PCMPSy-g-PAN (%G = 219.62), PAN and the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN was examined in an inert atmosphere at a heating rate of 10°C/min with the help of Q-600 (TA) thermogravimetric analyzer.

2.3.4. Scanning electron microscopy (SEM)

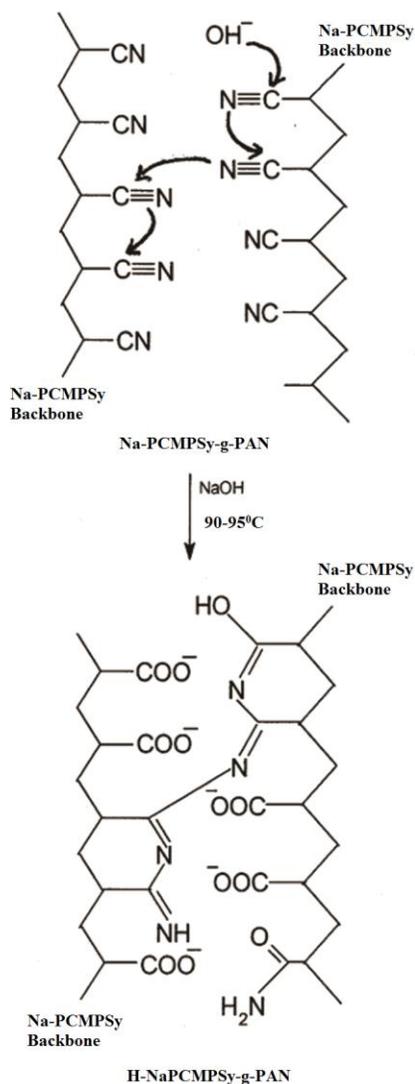
Model S-4300 (Hitachi) was used to obtain the micrographs Na-PCMPSy ($\overline{DS} = 0.13$), Na-PCMPSy-g-PAN (%G = 219.62) and the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN.

III. RESULTS AND DISCUSSIONS

3.1. Superabsorbent hydrogel, H-Na-PCMPSy-g-PAN

3.1.1. Mechanism of hydrogel formation

As discussed above in the experimental section, the saponification of Na-PCMPSy-g-PAN (%G = 219.62) sample was carried out by treating it with aqueous 0.7N sodium hydroxide solution at 90-95°C. Scheme 1 represents the concise mechanism of crosslinking during conversion of nitrile groups of Na-PCMPSy-g-PAN into carboxamide and sodium carboxylate groups for the



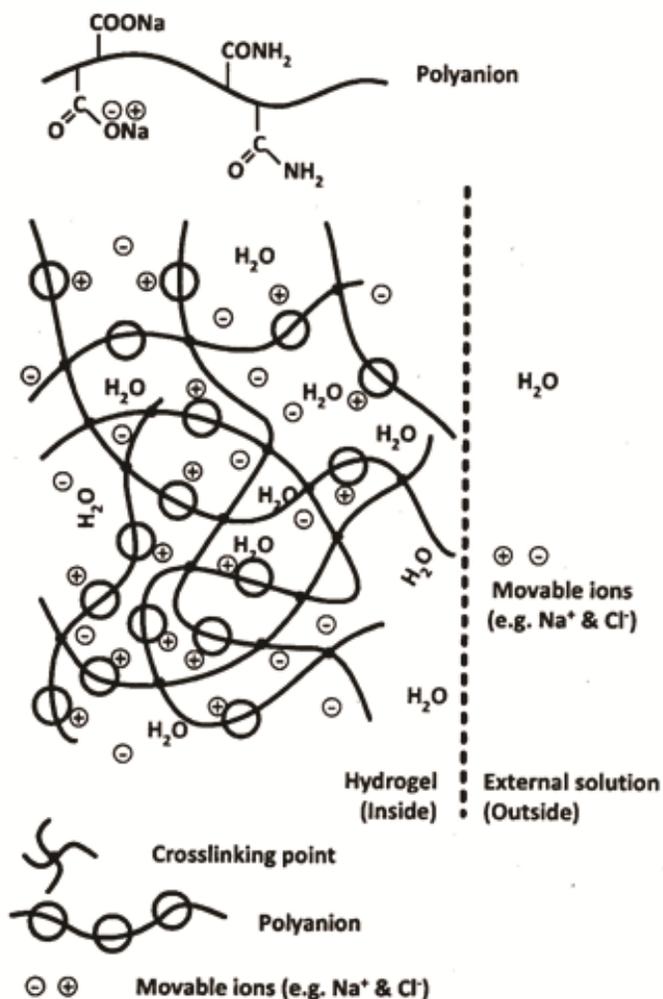
Scheme 1. A concise mechanism for the synthesis of the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN.

formation of the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN. As per the mechanism of the saponification reaction, in the first step the hydroxide ions abstract hydrogen from the -OH group of Na-PCMPSy substrate to the formation of the corresponding

alkoxide anions. Then, these Na-PCMPsy alkoxide anions (i.e. macroradicals) initiate cross-linking reaction between some adjacent polyacrylonitrile pendant chains which leads to the formation of deep red colour intermediate with naphthyridine cyclic structures, including imine, with evolution of ammonia. This intermediate, then further gets saponified with residual sodium hydroxide solution to produce hydrophilic carboxamide and carboxylate groups. The disappearance of the conjugated system with the formation of the hydrophilic groups was indicated when colour of the system changed from red to light yellow. This sharp change in colour was used as a marker to halt the alkaline or saponification treatment. In this way, the starting hydrophobic graft copolymer sample i.e. Na-PCMPsy-g-PAN was converted into a hydrophilic gel i.e. superabsorbent hydrogel, H-Na-PCMPsy-g-PAN. The mechanism depicted in Scheme 1 is in accordance with the literature data (Castel et al., 1990; Savoji and Pourjavadi, 2006)

3.1.2. Swelling behaviour in water and salt solutions

In view of the great impact of external saline solutions on water absorbency of superabsorbents and extending their applications, especially for agriculture, hygienic products, the swelling behaviour of the superabsorbent hydrogel, H-Na-PCMPsy-g-PAN has been studied in low conductivity water as well as different saline solutions. The presence of ions in the swelling medium has a profound effect on the swelling behaviour of the superabsorbent hydrogels. The underlying principle behind the ionic dependence of swelling is well explained by the Donnan Equilibrium theory (Scheme 2). According to this theory, the balance between the osmotic pressure of the swelling system and elastic response of the polymeric network that controls the extent of swelling. The osmotic pressure results from the difference in concentration of mobile ions between the interior of the hydrogel network and the external solution. The fundamental feature within the hydrogel, bringing about the unequal distribution, in the present case, is the presence of the ionizable, carboxylate groups (anionic sites) attached to the polymeric network.



Scheme 2. Representation of swollen anionic superabsorbent hydrogel in equilibrium with electrolyte solution.

In the present work, the swelling behaviour of the “anionic” superabsorbent hydrogel, H-Na-PCMPsy-g-PAN, has been studied by carrying out its absorbency measurements in low conductivity water, 0.15M salt (NaCl, CaCl₂ and AlCl₃) solutions and simulated

urine (SU) at different timings. The results obtained are depicted in Fig. 1. The swelling of the anionic hydrogel is found to be increased steadily and continuously with time in low conductivity water up to 8h beyond which it almost levels off. The hydrophilic

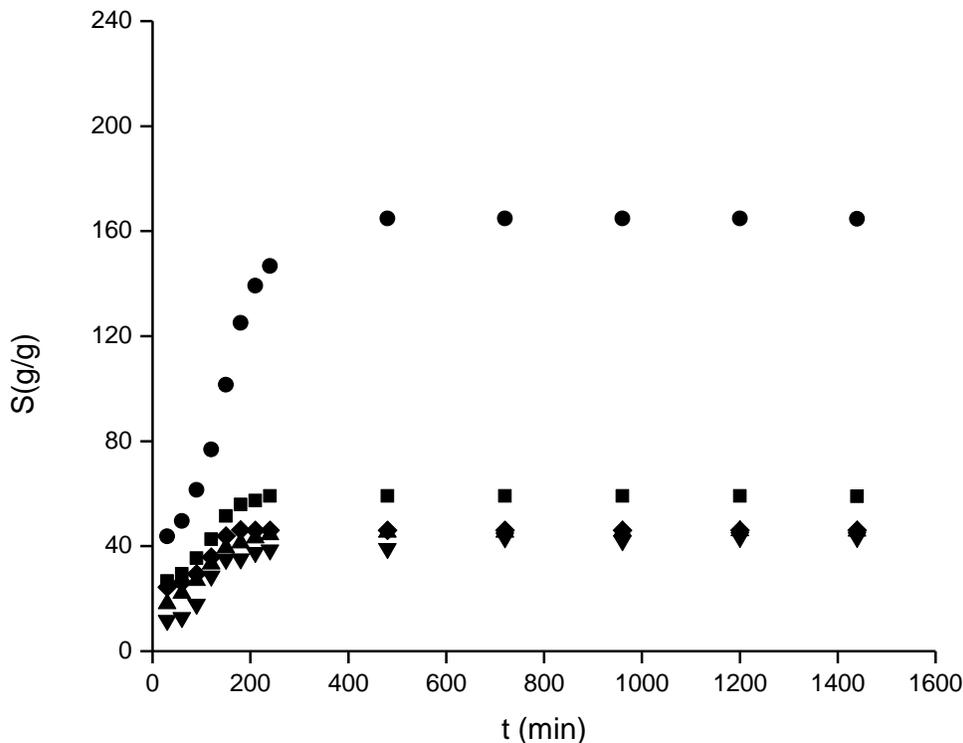
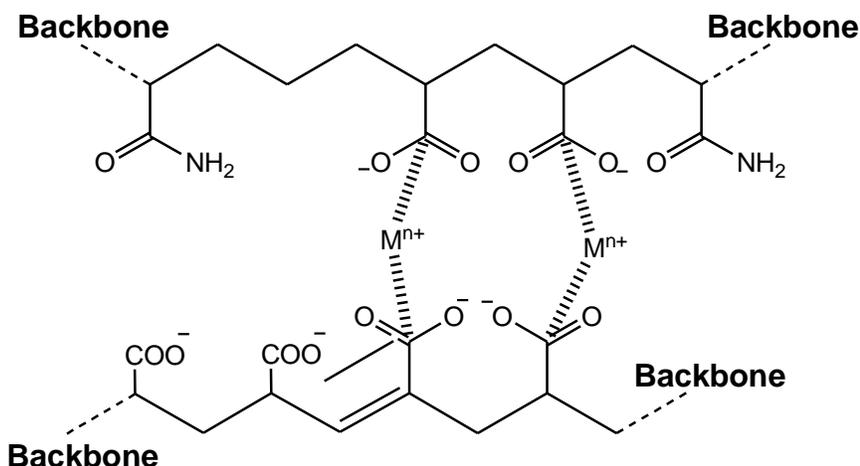


Figure 1. Kinetic swelling curves of the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN in low conductivity water (●), 0.15M NaCl (■), 0.15M CaCl₂ (▲), 0.15M AlCl₃ (▼) and SU (◆).

groups such as carboxylate and carboxamide groups absorb the penetrating water through the formation of hydrogen bonds. The swelling is driven by repulsion of ionic and hydrophilic groups inside the network and osmotic pressure difference between the hydrogel and the external solution. It is also evident from this figure that the hydrogel absorbs water quickly as good swelling (43.67g/g gel) is achieved within half an hour. Therefore, at this point (30 mins), the hydrogel absorbs water with a rate of about 1.46 g/g. min. However, the swelling ability of the anionic hydrogel in different salt (NaCl, CaCl₂ and AlCl₃) solutions, having same concentration (0.15M), as well as in simulated urine (SU) is found to be decreased dramatically at all different timings in comparison with the values measured in low conductivity water (cf. Fig. 1). This well known undesired swelling loss, which is commonly being observed in the swelling of ionic hydrogels (Castel et al., 1990), is attributed to a “charge-screening” effect of the additional counter ions (cations) causing a non-perfect anion-anion electrostatic repulsion (Flory, 1953). The water-absorption properties are thought to result from osmotic pressure and interaction through hydrogen bonding of the carboxylate and carboxamide groups of the polymeric network with water molecules. When low conductivity water is used as swelling agent, the absorption capacity is found to be higher. At the swelling equilibrium, the chemical potential of water in the polymer network will be equal to that of the water surrounding to it. However, when a certain amount of salt (NaCl or CaCl₂ or AlCl₃ or SU, as in the present study) in low conductivity water is used as a swelling agent then the attraction of the strong electrostatic forces exist between the fixed anionic sites or the negatively charged carboxylate groups on the polymer chain and the cations (counter ions) of the salt, as a result of which these cations, by screening the fixed charges on the polymer chain, reduce the electrostatic repulsion tremendously as compared with what it would be in their absence (cf. Fig. 1). Thus, because of the strong electrostatic forces, the concentration of the cations (e.g. Na⁺ or Ca⁺² or Al⁺³) will be higher inside the hydrogel than outside (Scheme 2) as a result of which the osmotic pressure outside the hydrogel will decrease drastically and consequently the absorbency amounts will be diminished (cf. Fig. 1).

The effect of different cations with a common anion (Cl⁻) on the absorbency of the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN can also be explained from the results of Fig. 1. It can be seen from this figure that the absorption capacity of the hydrogel decreases with an increase in the charge of the metal cation (Al³⁺ < Ca²⁺ < Na⁺) in the solutions having the same concentration (0.15M). This can be attributed to the complexing ability arising from the coordination of the multivalent cations with carboxylate groups of the hydrogel to induce the formation of intramolecular and intermolecular complexes (Scheme 3). This leads to an increase

in the crosslinking density, which makes network shrink (Pourjavadi and Mahdavinia, 2006). Thus, in the case of $AlCl_3$, due to the high complexing ability of the Al^{3+} ions with the carboxylate groups of the hydrogel, the crosslink density of the network ultimately



Scheme 3. Ionic crosslinking between a multivalent metal cation and anionic groups of the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN.

increases but it may hinder the approach of the water molecules leading to the lowering of the water uptake compared to that of NaCl (cf. Fig. 1). This ‘ionic crosslinking’ phenomenon mainly occurs at the surface of the particles and as a result, in the present case, the hydrogels are found to be rubbery and very hard to the touch when they swell in Ca^{2+} or Al^{3+} solutions, so that it cannot swell well. In contrast to this, the hydrogel particles are found to be swollen in NaCl and water, exhibiting lower gel strength to the touch. Similar results are also reported in the literature (Zohurian-Mehr and Pourjavadi, 2003; Pourjavadi and Mahdavinia, 2006; Trivedi et al., 2013).

The dimensionless salt sensitivity factor (f) was calculated for 0.15M salt solutions according to the equation (Zohurian-Mehr and Pourjavadi, 2003):

$$f = 1 - (S_{salt}/S_{water}) \quad \dots(5)$$

where S_{salt} and S_{water} are the values of the swelling ratio in a given saline solution and low conductivity water, respectively. Thus, the values of f calculated for the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN, in 0.15M different salt solutions and simulated urine at different timings are recorded in Table 1. The influence of increasing cation charge on the ultimate absorption for the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN can be evident upon comparing the average salt sensitivity values (Table 1). 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.

Table 1 Dependency of the dimensionless Salt Sensitivity (f) of the superabsorbent hydrogel, H-Na-PCMPSy-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 ^a
0.5	0.388	0.583	0.732	0.441	
1.0	0.407	0.553	0.740	0.472	
1.5	0.424	0.560	0.709	0.520	
2.0	0.445	0.566	0.627	0.532	$f_{NaCl} = 0.546$
2.5	0.492	0.611	0.655	0.567	
3.0	0.552	0.669	0.718	0.631	
3.5	0.588	0.689	0.730	0.668	$f_{CaCl_2} = 0.657$
4.0	0.597	0.697	0.737	0.685	
8.0	0.641	0.725	0.762	0.720	$f_{AlCl_3} = 0.720$
12.0	0.641	0.724	0.737	0.720	
16.0	0.641	0.722	0.744	0.720	
20.0	0.641	0.721	0.736	0.720	$f_{SU} = 0.624$
24.0	0.641	0.721	0.737	0.720	

^acalculated as per Eq.(5), on the basis of the Experimental Equilibrium Swelling Ratio (g/g gel) values (Table 2) for different swelling media.

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 (Mg²⁺ and Ca²⁺) 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 the literature (Burugapalli et al., 2001; Mahdavinia et al., 2004).

3.2.3. Swelling kinetics

In order to evaluate the mechanism of the swelling process of hydrogels, several kinetic models are used to test the experimental data. However, in the present work, for evaluating the dynamic swelling properties of the superabsorbent hydrogel, H-Na-PCMPsy-g-PAN, a simple kinetic analysis based on the second order kinetics model was adopted and accordingly the second order equation can be expressed as (Peniche et al., 1997):

$$\frac{dS}{dt} = k_S (S_{eq} - S)^2 \quad \dots(6)$$

where S_{eq}, S and k_S denote the equilibrium swelling (theoretical), swelling at any time, and swelling rate constant respectively. The integration of Equation (6) over the limits S = S₀ at t = t₀ and S=S at t = t, gives

$$t/S = A + Bt \quad \dots(7)$$

where B = 1/S_{eq} is the inverse of the maximum or equilibrium swelling, A = (1/k_S S_{eq}²) is the reciprocal of the initial swelling rate of the hydrogel (r_i), and k_S is the swelling rate constant.

For analyzing the experimental results of the present work in terms of the above kinetic model, the plots of t/S versus t were plotted for the hydrogel, H-Na-PCMPsy-g-PAN in different swelling media. The plots were found to be linear with good correlation coefficient (Table 2), indicating that the swelling behaviour of the hydrogel in the different swelling media follows the pseudo second

Table 2 Swelling Characteristics for the superabsorbent hydrogel, H-Na-PCMPsy-g-PAN, in different swelling media.

Swelling media	Experimental Equilibrium Swelling Ratio (g water/g gel)	^a t _{req} (h)	^b S _{eq} (g water/g gel)	^c EWC (%)	^d r _i [(g water/ g gel)min]	^e k _S x 10 ⁵ [(g gel/g water)/min]	R ²
low conductivity water	164.85	8	200	99.94	1.69	4.22	0.991
NaCl (0.15M)	59.11	4	62.50	99.83	1.78	45.60	0.998
CaCl ₂ (0.15M)	45.30	8	47.62	99.78	1.17	51.80	0.998
AlCl ₃ (0.15M)	43.21	12	47.62	99.77	0.55	24.40	0.994
Simulated Urine (SU)	46.11	3	47.62	99.78	2.04	89.80	0.998

^a Time required to achieve Experimental Equilibrium Swelling Ratio value

^bTheoretical Equilibrium Swelling Ratio

^cEquilibrium water content

^dInitial swelling rate

^eSwelling rate constant

order model. Fig. 2 represents such type of typical plot of t/s versus t obtained for the hydrogel, H-Na-PCMPsy-g-PAN in water as swelling media. The values of the initial rate of swelling (r_i), swelling rate constant (k_S), and theoretical equilibrium swelling (S_{eq}) were calculated from the slope and intersection of the lines obtained in the graphs for the hydrogel, H-Na-PCMPsy-g-PAN in different swelling media and are summarized in Table 2. The values of the Experimental equilibrium swelling ratio for different swelling media are reported in Table 2 along with the corresponding time required to achieve these swelling ratio values. As per Equation (4), the equilibrium water content (EWC%) values were also calculated for the hydrogel in different swelling media and are included in Table 2. It can be further evident from Table 2 that the values of the experimental equilibrium swelling ratios are reasonably in good agreement with those of the theoretical equilibrium ratio (S_{eq}). Mohan et al. have also compared the values of the

experimental equilibrium swelling ratios with the values of the theoretical equilibrium ratio in the case of Semi-IPN hydrogels crosslinked with 1,4-butanediol diacrylate (BDDA) and 1,2-ethyleneglycol dimethacrylate (EGDMA) and their observations are also in line with our observations.

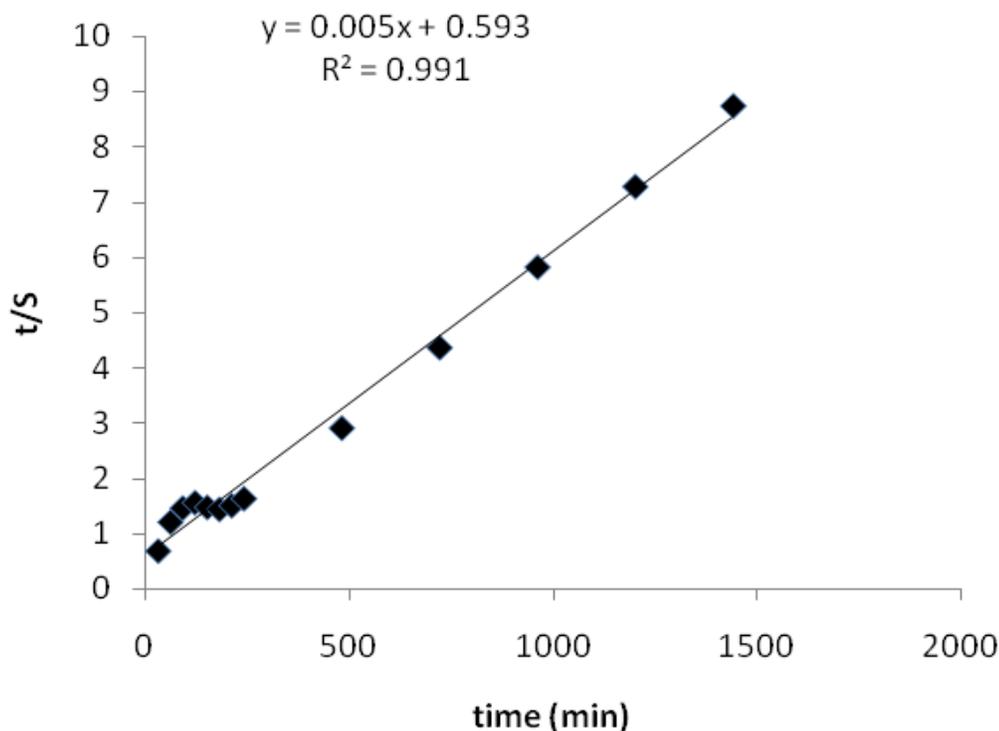


Figure 2. Plot of t/S versus t for the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN in low conductivity water as swelling medium.

IV. CHARACTERIZATION

4.1. Viscosity measurements

The viscosity measurements of the (isolated) polyacrylonitrile (side chains) sample were carried out at 25°C in dimethyl formamide using an Ubbelohde Viscometer in the usual manner. The viscosity-average molecular weight (\overline{M}_v) was calculated from the $[\eta]$ value using the following equation (Rodehed and Ranby, 1986) and it was found to be 2.04×10^4 g/mole.

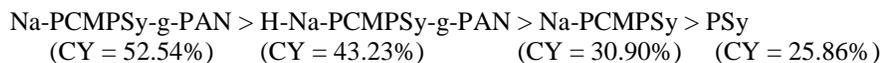
$$[\eta] = 3.92 \times 10^{-4} \overline{M}_v^{0.75} \text{ dL/g} \quad \dots(8)$$

4.2. FTIR spectroscopy

The spectra of the graft copolymer [Fig. 3(b)] showed absorption bands of Na-PCMPSy ($\overline{DS} = 0.13$) [Fig. 3(a)] as well as an additional band at $\sim 2244 \text{ cm}^{-1}$, which has been attributed to $-\text{C}\equiv\text{N}$ stretching mode indicating that photo-grafting of AN onto Na-PCMPSy ($\overline{DS} = 0.13$) has taken place. Fig. 3(c) represents the IR spectrum of the hydrogel, H-Na-PCMPSy-g-PAN. The disappearance of the nitrile sharp peak at $\sim 2244 \text{ cm}^{-1}$ [cf. Fig. 3 (b)] and appearance of the two distinct bands at $\sim 1578 \text{ cm}^{-1}$ and $\sim 1409 \text{ cm}^{-1}$, indicating the respective presence of C=O asymmetric and symmetric stretching modes of the carboxylate anions and the absorption band appeared at $\sim 1671 \text{ cm}^{-1}$ indicating C=O stretching in carboxamide functional groups are the measure proofs for the conversion of the nitrile groups into carboxamide and carboxylate groups after alkaline hydrolysis of the graft copolymer.

4.3. Thermogravimetric analysis

From the primary thermograms of PSy [Fig. 4(S₁)], Na-PCMPSy ($\overline{DS} = 0.13$) [Fig. 4(S₂)], Na-PCMPSy-g-PAN [Fig. 4(S₃)], the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN [Fig. 4(S₄)] and PAN [Fig. 4(S₅)] samples, obtained at a scan rate of 10°C/min in an inert atmosphere, the temperature characteristic values as well as the decomposition temperature (T_D) values at every 10% weight loss were calculated and recorded for all the samples in Table 3. Upon comparing the char yield (CY) values at 750°C, the following order of decreasing thermal stability is observed:



Thus, the observed increase in thermal stability of PSy upon carrying out its carboxymethylation is attributed to the introduction of the polar groups into it leading to the increased inter-and intra-molecular interactions which ultimately imparts higher thermal stability to it.

The thermal stability of the homopolymer, PAN (isolated from the graft copolymer) is found to be higher than the graft copolymer sample. The thermal stability of both grafted and hydrogel grafted copolymers is found to be improved in comparison with Na-PCMPSy itself. The increased ring formation at higher temperatures may be responsible for the observed higher value of the thermal stability, for the Na-PCMPSy-g-PAN compared to Na-PCMPSy (Trivedi et al., 2005). On the other hand, although there is no nitrile group in H-Na-PCMPSy-g-PAN structure, but the existence of COO⁻Na⁺ and CONH₂ groups improve its thermal stability over Na-PCMPSy.

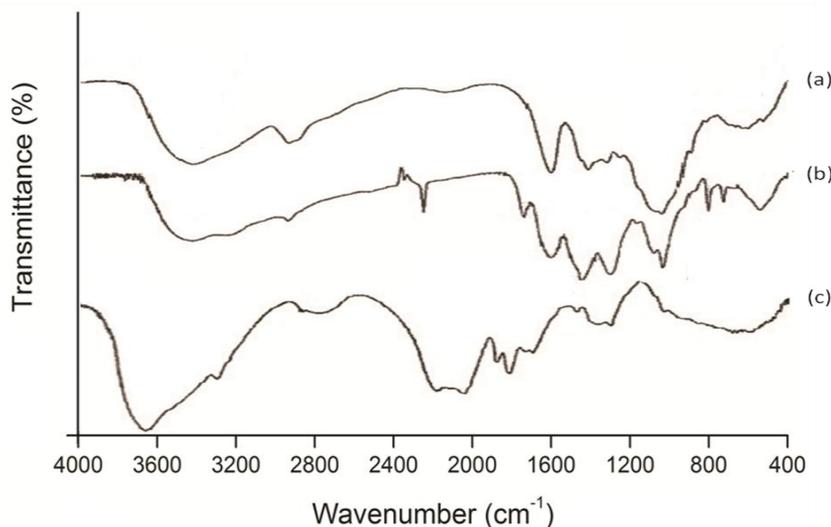


Figure 3. FTIR Spectra of (a) Na-PCMPSy ($\overline{DS} = 0.13$), (b) Na-PCMPSy-g-PAN (%G = 219.62) and (c) the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN.

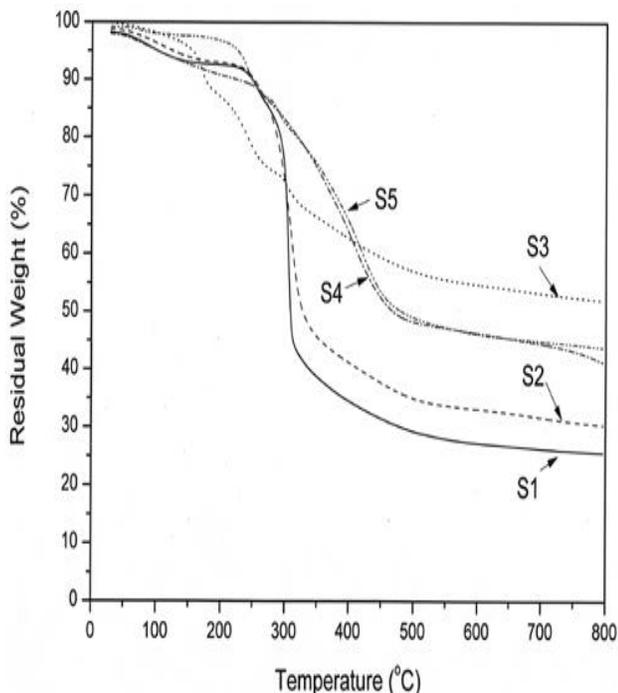


Figure 4. Thermogravimetric curves (TG) for Psyllium (S₁), Na-PCMPsy ($\overline{DS} = 0.13$) (S₂), Na-PCMPsy-g-PAN (%G = 219.62) (S₃), H-Na-PCMPsy-g-PAN (S₄) and PAN (S₅) samples in nitrogen atmosphere at a heating rate of 10°C/min.

Table 3 Thermogravimetric analysis of Psyllium (PSy), Na-PCMPsy ($\overline{DS} = 0.13$), Na-PCMPsy-g-PAN (%G = 219.62), PAN and the superabsorbent hydrogel, H-Na-PCMPsy-g-PAN samples

Sample	T _i °C (IDT)	T _f °C (FDT)	T _{max} (°C)			Char Yield at 750°C (wt%)	Decomposition temperature (T _D) at every 10% wt. loss						
			Step-1	Step-2	Step-3		T _D (°C)						
							10%	20%	30%	40%	50%	60%	70%
PSy (S ₁)	209	711	305	–	–	25.86	248	292	302	305	308	338	481
Na-PCMPsy (S ₂)	193	771	311	–	–	30.90	251	287	302	312	328	416	796
Na-PCMPsy-g-PAN (S ₃)	117	764	170	241	302	52.54	175	241	311	440	797 ^b	–	–
H-Na-PCMPsy-g-PAN (S ₄)	211	730	264	410	–	43.23	224	319	372	414	469	796 ^c	–
PAN ^a (S ₅)	145	707	242	289	421	44.37	248	317	379	421	482	796 ^d	–

^a $\overline{M}_V = 2.04 \times 10^4$ g/mole ($[\eta] = 3.92 \times 10^4 \overline{M}_V^{-0.75}$ dl/g in DMF at 25°C)

^b T_D (°C) value at 48% wt. loss

^c T_D (°C) value at 59% wt. loss

^d T_D (°C) value at 56% wt. loss

4.3. Scanning Electron Microscopy (SEM)

Upon comparing the morphology of the grafted sample [Fig. 5(b)] with ungrafted material [Na-PCMPsy, Fig. 5(a)] it is clearly evident that the grafted chains have drastically changed the topology of the Na-PCMPsy ($\overline{DS} = 0.13$) sample. Fig. 5(c) represents the micrograph of the hydrogel, H-Na-PCMPsy-g-PAN. Upon comparing with the morphology of the graft copolymer [cf. Fig. 5(b)], a totally different morphology (porous structure) is observed as the graft copolymer (i.e. Na-PCMPsy-g-PAN) was treated in the alkaline medium to yield the superabsorbent hydrogel, H-Na-PCMPsy-g-PAN [cf. Fig. 5(c)]. It is supposed that these pores are the regions for the penetration of water into the polymeric network, and ultimately it helps in enhancing the water absorbency of the hydrogel.

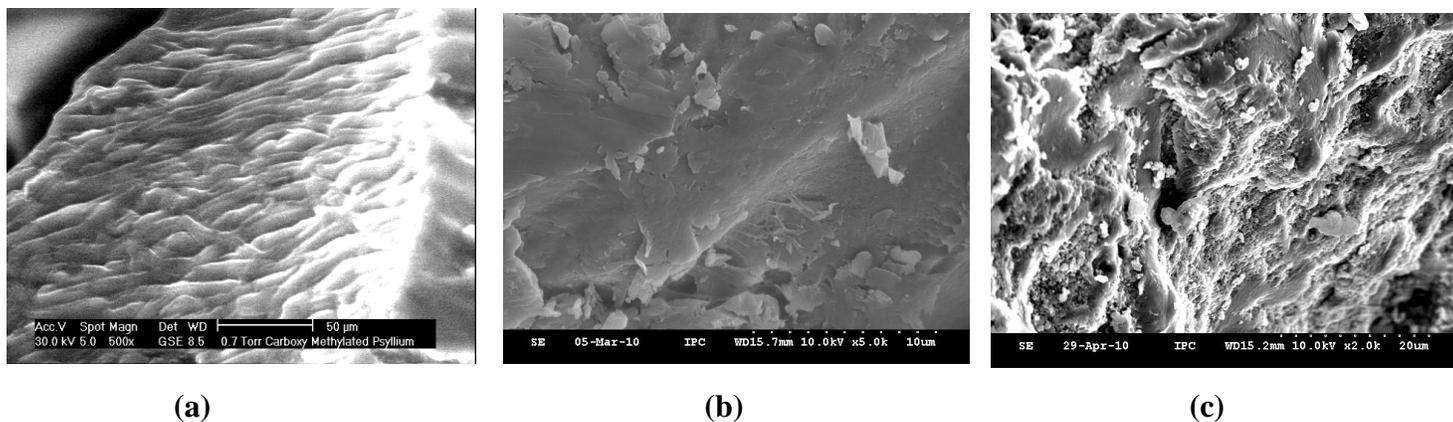


Figure 5. Scanning Electron micrographs of (a) Na-PCMPSy ($DS = 0.13$) (X500), (b) Na-PCMPSy-g-PAN (%G = 219.62) (X 5.0k) and (c) the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN (X 2.0k) samples.

V. CONCLUSIONS

The nitrile groups of Na-PCMPSy-g-PAN (%G = 219.62) were completely converted into a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis, followed by in situ crosslinking of the grafted PAN chains in order to synthesize the superabsorbent hydrogel, H-Na-PCMPSy-g-PAN. The swelling behaviour of the synthesized superabsorbent hydrogel was studied in different swelling media and the results regarding its absorbency measurements have been successfully explained on the basis of the “charge screening effect” and “ionic crosslinking” phenomenon. The experimental data suggested clearly that the swelling process of the hydrogel obeys second order kinetics. The observed retention of about 46 g of water by the hydrogel in the presence of simulated urine and that too within 3h is good enough to make the hydrogel as potential candidate for personal health care application. FTIR, XRD, TGA and SEM techniques have been successfully used to characterize all the products.

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