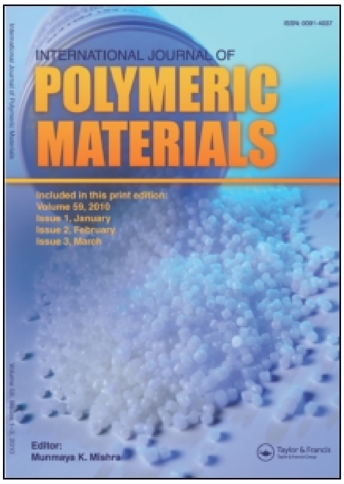

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Poly(acrylamide-chitosan) Hydrogels: Interaction with Surfactants

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Poly(acrylamide-chitosan) Hydrogels: Interaction with Surfactants

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Semi-interpenetrating hydrogels were prepared from hydrophilic acrylamide and cationic natural biopolymer chitosan, N,N^1-methylenebisacrylamide and water-soluble redox initiating system (ammonium persulfate/N,N,N^1,N^1-tetramethylethylenediamine). The interaction of these hydrogels with different surfactants such as sodiumdodecylsulphate (SDS, anionic), N-cetyl N,N,N-trimethyl ammonium bromide (CTA, cationic) and Tween20 (T20 non-ionic) was studied. The chemical structure of the hydrogels treated with surfactant was characterized by FTIR spectroscopy and the morphology of hydrogels was characterized by scanning electron microscopy (SEM). The thermal properties of surfactant-treated hydrogels were evaluated by TGA analysis.

Keywords chitosan, hydrogels, hydrophilic, semi-interpenetrating, surfactant

INTRODUCTION

Polymeric hydrogels are one of the most promising and widely studied types of polymer materials due to their water-insoluble nature. These hydrogels can significantly respond to a number of external stimuli, such as pH and temperature, by undergoing changes in their volume and other physicochemical

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properties [1]. The swelling properties of these hydogels have attracted the attention of researchers and found widespread applications in drug delivery devices, separation process sensors and many other fields [2]. However, these hydrogels have one major drawback, namely they have very poor mechanical strength. Therefore, to increase their mechanical strength, attempts have been made to crosslink the hydogels with various polymers, some of which are biodegradable. Among the biodegradable polymers, chitosan is the one of the best biodegradable polymers [3–5]. Chitosan is a linear polysaccharide with a good chemical entity for synthesizing hydrogels because of its greater crosslinking ability due to the presence of the amino ($-NH_2$) group [6]. The biodegradability, biocompatibility and other unique properties of chitosan have been used in a variety of areas, such as medicine [7], pharmaceuticals [8–11], tissue engineering [12] antimicrobial agents [13], chromatography [14] and biomedical applications [15–17].

Swelling studies and other properties of the biodegradable hydrogels can also be increased by using surfactants, which have found good applications in various fields such as food [18], surface coating [19] and cosmetics [20]. The ability of surfactants to self-assemble in water into a large variety of morphologically different structures makes them prime candidates for many systems. The effect of surfactants on the phase transition behavior of hydrogels has been extensively investigated [21–27]. Similarly, the changes in transition temperature by surfactant molecules in a hydrogel have been studied [28–30]. The information from surfactant-based hydrogels about the nature of polymer—solvent interaction with hydrogels helps us to understand the structures and functions of biopolymers [31].

The present work involves the preparation of poly(acrylamide-co-chitosan) (PAC) hydrogels and study of their swelling studies and interaction with different surfactants (SDS,CTA,T20) as well as the swelling behavior of these hydrogels in different swelling media (pH and NaCl solutions). The physical properties of the prepared hydrogels were characterized, including FTIR, morphology and thermal analysis.

EXPERIMENTAL

Materials

Analytical reagent grade samples of acrylamide (AAm) and chitosan (CS, $M_n \sim 1.5 \times 10^5$; Switzerland) were purchased from Flucka Chemicals. Sucrose (SR), N,N^1-methylenebisacrylamide (MBA), ammonium persulfate (APS) and N,N,N^1,N^1-teramethylethylenediamine (TMEDA) were purchased from S.D. Fine Chemicals (Mumbai, India). All of the chemicals were used without further purification. Throughout the experiments, double-distilled water was used.

Table 1: Feed composition of poly(acrylamide-co-chitosan) semi-IPN hydrogels.

	Concentration in the feed mixture of the gel networks				
Semi-IPN code	**AAM mM**	**Chitosan g**	**MBA mM**	**APS mM**	**TEMAD mM**
CS1	14.06	**0.1**	0.648	2.91	0.172
CS2	14.06	**0.15**	0.648	2.91	0.172
CS3	14.06	**0.2**	0.648	2.91	0.172
CS4	14.06	**0.25**	0.648	2.91	0.172
CSM1	14.06	0.2	**0.12**	2.191	0.172
CSM2	14.06	0.2	**0.25**	2.191	0.172
CSM3	14.06	0.2	**0.38**	2.191	0.172
CSM4	14.06	0.2	**0.51**	2.191	0.172
CSM5	14.06	0.2	**0.77**	2.191	0.172
CSM6	14.06	0.2	**0.90**	2.191	0.172
CSA1	14.06	0.2	0.648	**0.131**	0.172
CSA2	14.06	0.2	0.648	**0.198**	0.172
CSA3	14.06	0.2	0.648	**0.263**	0.172
CSA4	14.06	0.2	0.648	**0.328**	0.172
CSA5	14.06	0.2	0.648	**0.434**	0.172
CSA6	14.06	0.2	0.648	**0.876**	0.172

Preparation of PAC Hydrogels

5 g of chitosan flakes were dissolved in 5% of acetic acid solution in stirring condition for 36 h at ambient temperature. The chitosan solution prepared in this manner was used for the preparation of hydrogels. The hydrogels consisting of AAm and CS units were prepared by free radical polymerization using APS/TEMDA redox-initiator in the presence of MBA as a crosslinker. In this preparation 14.6 mM of AAm and 0.10 g of the above stock solution of chitosan were dissolved in 2 ml double-distilled water, added into the same beaker. To this reaction mixture, 1 ml of MBA (1 g/100 ml), 1 ml of APS (5 g/100 ml) and 1 ml of TMEDA (1 g/100 ml) solutions were sequentially added by stirring at 100 rpm on a magnetic stir plate. After the reaction was completed, the hydrogel was immersed in distilled water at ambient temperature for 24 h to remove the unreacted materials present in the hydrogel network. Finally, the hydrogel was dried at ambient temperature for 2 days. Similarly, other hydrogels were prepared in a similar manner. The feed compositions of the hydrogels are presented in Table 1.

CHARACTERIZATION

FTIR Analysis

The dry, unmodified and surfactant-modified hydrogels were analyzed as KBr pellet by FTIR spectroscopy (Perkin–Elmer FT-IR spectrometer spectrum 2000 model) in the region of 4000–600 cm^{-1}.

SEM Analysis

The internal surface morphology of the PAC semi-IPN hydrogels were studied with a Hitachi S-570 scanning electron microscope.

Thermal Analysis

Thermal stability of the hydrogels was studied with a TA-2050 thermal analyzer from room temperature to 800°C at a heating rate of 10°C/min under nitrogen flow (40 ml/min).

Swelling Studies

The swelling of PAC hydrogels was studied by conventional gravimetric method. In these swelling studies, about 0.50 g of the hydrogels was immersed in a 100 ml beaker containing the swelling medium (distilled water, surfactant, pH and NaCl solutions). The weight of swollen gels was determined at different time intervals and the swelling experiment was continued to a constant weight. At the end, the excess of water was removed superficially by filter paper and the gels were weighed. The swelling ratio was calculated using the following equation:

$$\text{Swelling ratio } (S_{g/g}) = [(Ws - Wd)/Wd]$$

where, Wd and Ws denote the weight of dry and swollen gel, respectively.

RESULTS AND DISCUSSION

FTIR Studies

The prepared hydrogels were characterized by FTIR spectroscopy between 600–4000 cm^{-1}. From the IR spectrum (Figure 1a–1d), peaks at 1657 cm^{-1} indicate $CONH_2$ unit of AAm. The peaks at 3415–3430 cm^{-1} are due to the hydroxyl groups of chitosan units. A clear variation can be seen for surfactant-modified hydrogels. The peak at 1124 cm^{-1} is due to the presence of sulphate groups of SDS. Actually the sulphate groups appear at 1250 cm^{-1}. But due to interaction with acrylamide units, the peak shifts from 1250 cm^{-1} to 1124 cm^{-1}. From (Figure 1c), in the IR spectra of hydrogel modified with T20, a new absorption peak at 773 cm^{-1} corresponding to the presence of T20 is found. Similarly, the cationic modified hydrogels show two peaks at 2920 cm^{-1} and 2851 cm^{-1}. These peaks are due to the stretching vibrations of methyl groups of N-cetyl N,N,N-trimethyl ammonium bromide. All the surfactant-modified hydrogels show a common peak at 1657–1658 cm^{-1} and 3415–3431 cm^{-1} due to AAm and chitosan units, respectively. The above

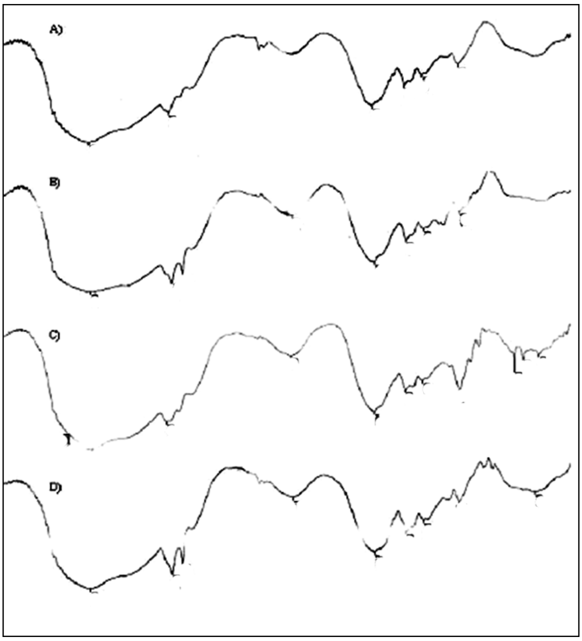


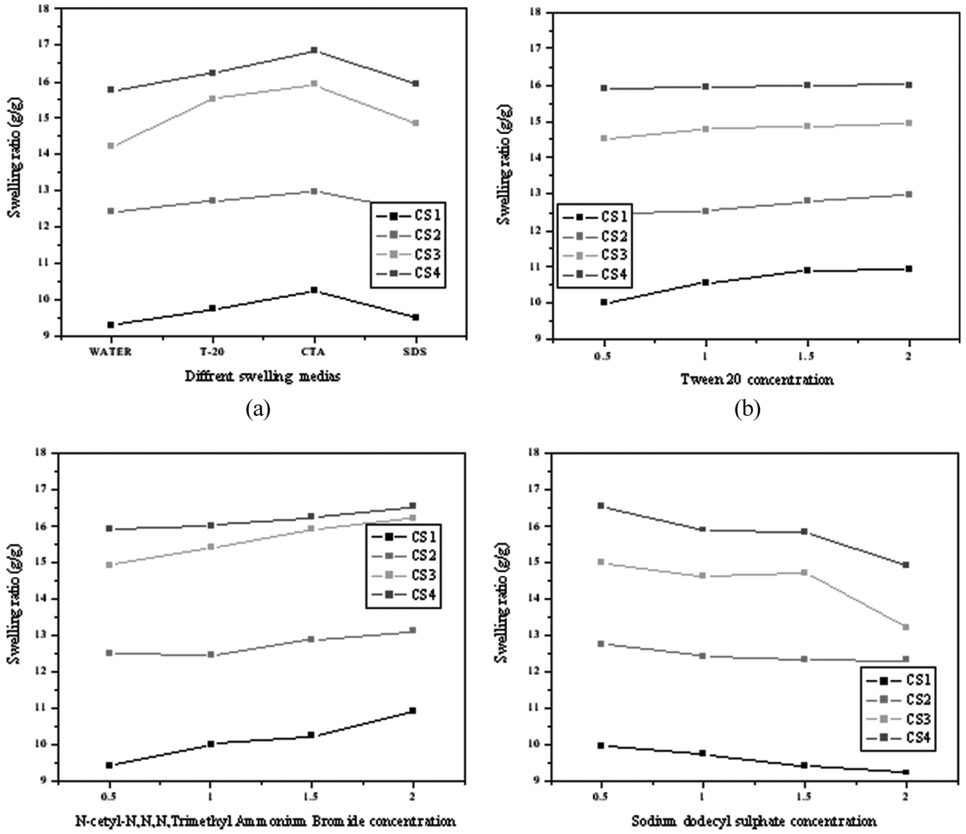
Figure 1: FTIR spectrum of surfactant interacted PAC hydrogels (a) Blank hydrogel (plain PAC), (b) SDS interacted PAC, (c) T20 interacted PAC, and (d) CTA interacted PAC.

data indicates the modification of hydrogels with different surfactants when compared to the IR spectrum of blank PAC hydrogel.

Effect of Different Surfactant Solutions on the Swelling Behavior of PAC Hydrogels

For the past few years, there have been many studies on the interaction of surfactants with different hydrogel networks or by modification of hydrogels with surfactants. A recent report by Noguchi et al. [32] revealed an approach for fast temperature-responsive hydrogel networks with surfactant-grafted PNIPAM hydrogels that is highly superior to the conventional graft/comb type gels. To know the effect of chitosan (0.1 to 0.25 g) on the swelling ability of the hydrogel, the reaction system was fixed at concentration AAm (1 g), MBA (0.648 mM), APS (2.18 mM), and TMEDA (0.86 mM). Figure 2a shows that as the chitosan concentration increases, the swelling ratio increases in different swelling media such as water, nonionic, cationic and anionic surfactant solutions, which is due to the increases of a number of hydrophilic groups (-OH) present in the chitosan.

Figures 2b–2d graphs show the swelling studies of CS1 to CS4 hydogels in the above surfactant solutions. The swelling ratio of hydrogels in nonionic



(a) (b)

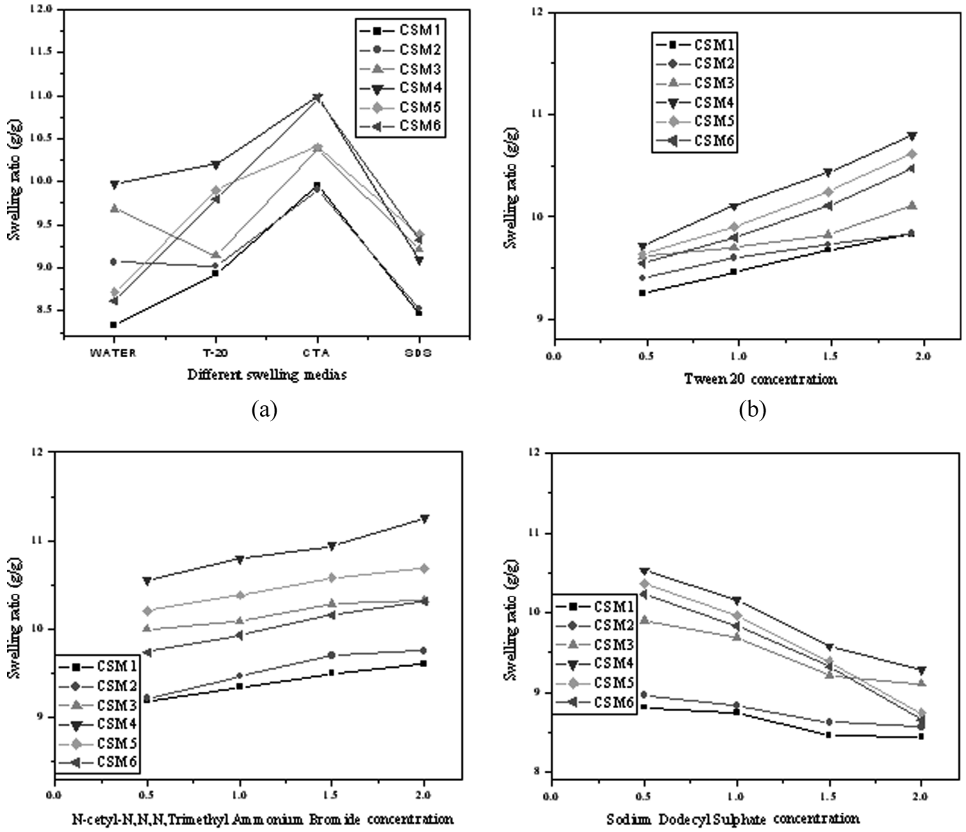
(c) (d)

Figure 2: Swelling behavior of CS semi IPN formulations in various surfactant solutions (a) in water, T-20, CTA, and SDS, (b) in T-20, (c) in CTA, and (d) in SDS.

surfactant solution (SDS) is presented in Figure 2b. The sodium ions present in SDS makes the increasing behavior of these hydrogels and the hydrophilic -OH groups also responsible for this increasing behavior.

The swelling studies of chitosan-based hydrogels in a cationic surfactant are shown in Figure 2c. The positive sites of cationic surfactant molecules may attack the negative site (-OH) of chitosan and thereby network size increases, and as a result, more water is held. Therefore we observe a gradual increase in the swelling ratio. Figure 2c shows the swelling studies in an anionic surfactant. These hydrogels show the decreasing behavior, which is due to repulsion of the counter ions of polymer chains with surfactant molecules.

The effect of a crosslinker (CSM1-CSM6) is known from the graphs in Figures 3a–3d. The graphs illustrate the swelling behavior of crosslinker-varied PAC hydrogels in water, nonionic (T-20) cationic and SDS solutions. When we consider crosslinker concentrations, these hydrogels behave as



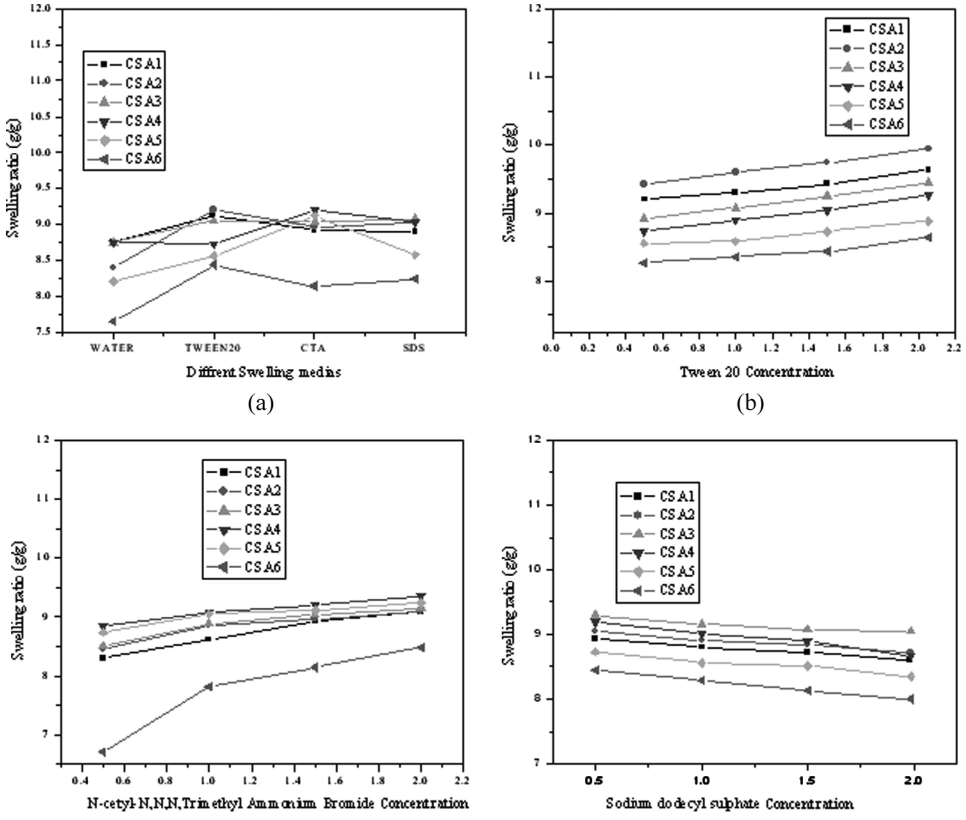
(a) (b)

(c) (d)

Figure 3: Swelling behavior of CSM semi IPN formulation in various surfactant solutions (a) in water, T-20, CTA, and SDS, (b) in T-20, (c) in CTA, and (d) in SDS.

common hydrogel, i.e., as crosslinker concentration increases the swelling ratio increases and attains a maximum equilibrium ratio and then decreases their swelling ratio with increases of crosslinker concentration. From Figure 3b, it is found that as surfactant concentration is increasing, the swelling ratio also increases. This is due to the entanglement of polyethylene glycol chains within the network of hydrogel, and thus a higher hydrophilicity of the network which promotes water absorbance. Figure 3c predicts the swelling capacity of the crosslinked varied PAC hydrogels in cationic surfactants. In fact, in cationic surfactant solution, hydrogels tend to decrease the swelling capacity, but here these gels show the opposite trend. This reverse trend is due to the NH_4^+ groups, which are hydrophilic in nature and make more swelling. But the same hydrogels (Figure 3d) show a reverse trend in anionic surfactant solutions. The pendant nature of -O-SO_3 groups of SDS makes a difference in their swelling ratio. These are highly repulsive and thereby a smaller amount of water holds between these.

In addition to crosslinker variation hydrogels, swelling studies on initiator-varied hydrogels were also performed (CSA1-CSA6) (Figures 4a–4d). From Figure 4a it is found that first there is an increase in their swelling ratio, after that are a decrease in the swelling ratio. After a certain time the number of free radicals increases and these radicals increase the numbers of chains and form a network structure. Therefore a decrement in the swelling ratio is found. The swelling studies of the same initiator-varied hydrogels were done in nonionic surfactant, cationic, and anionic solutions (Figures 4c, 4d). The swelling studies in the nonionic surfactant solution were similar to that of crosslinker-varied hydrogels, which is due to the hydrophilic groups of polyethylene glycol units. The swelling studies of these initiator-varied hydrogels in cationic and anionic hydrogels also show similar behavior to that of crosslinked varied hydrogels. The reasons are found in the previous explanation.

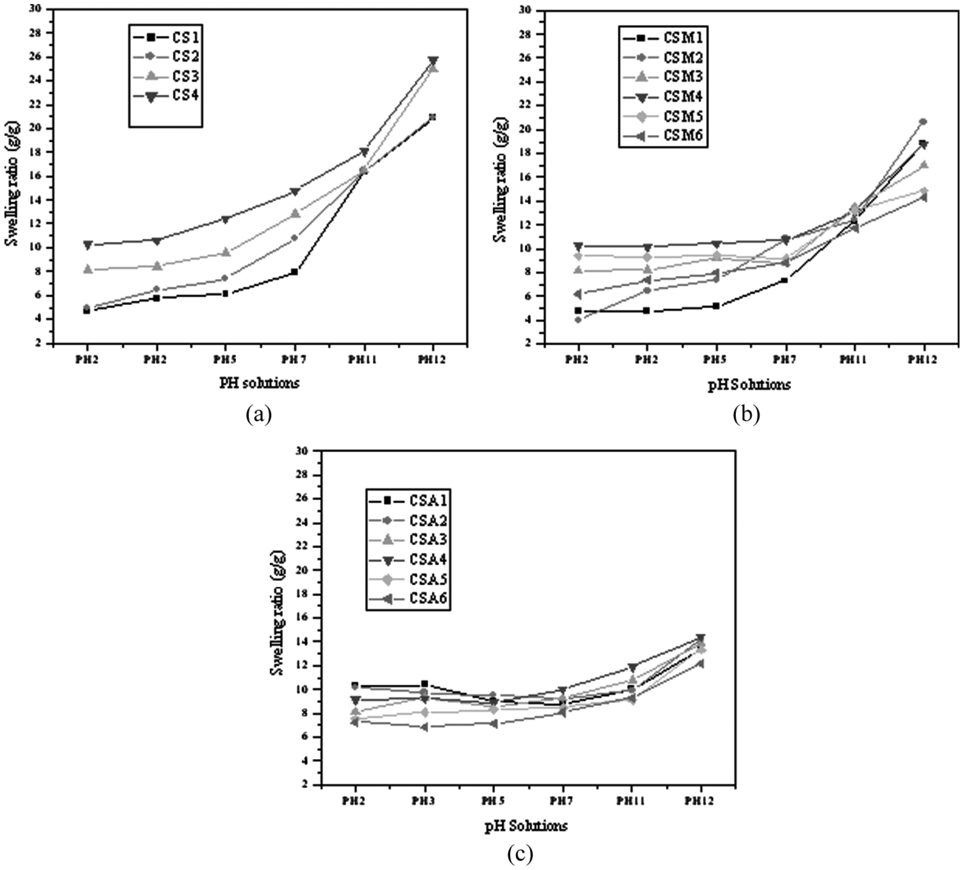


(a) (b) (c) (d)

Figure 4: Swelling behavior of CSA semi IPN formulations in various surfactant solutions (a) in water, T-20, CTA, and SDS, (b) in T-20, (c) in CTA, and (d) in SDS.

Swelling Studies in the pH Solutions

The pH-responsive character of hydrogel was investigated by swelling in different buffer solutions of 2, 3, 5, 7, 11, and 12 at 25°C as shown in Figures 5a–5c. The PAC (CS code) hydrogels exhibit the highest swelling ratio and a responsive character within the investigated pH values. However, the % of swelling ratios is continuously increased to exhibit the highest values overall of the studied pH values. It is well-known that below the pKa values, carboxylic acid groups are in the form of COOH. As pH of the solution increases COOH become ionized (COO-) and the resulting electrostatic repulsions cause this hydrogel exhibit. In conclusion, it may indicate that this hydrogel exhibits pH-responsive character below 7 pH, in which the hydrogel contracts and increases in volume above 7 pH, particularly at equilibrium.



(a)

(b)

(c)

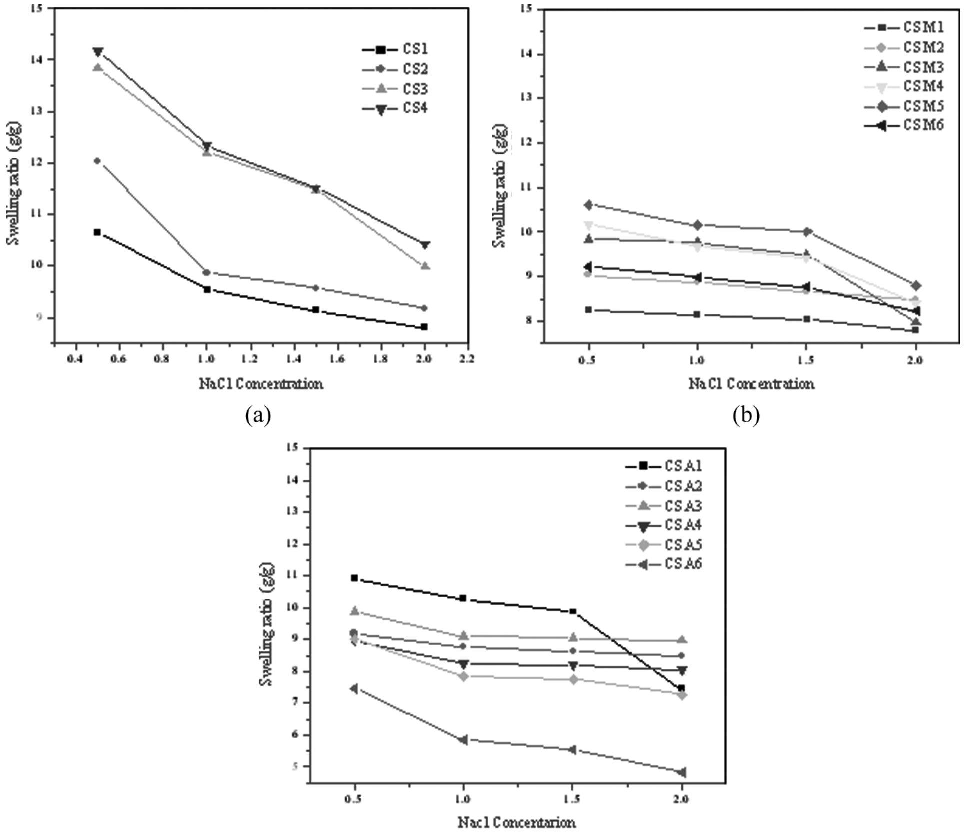
Figure 5: Swelling behavior of hydrogels in pH solutions (a) Swelling studies of CS hydrogels in different pH, (b) swelling studies of CSM in different pH, and (c) swelling studies of CSA in different pH solutions.

Swelling Behavior in Salt Solution

In the current investigation the effect of different concentrations of NaCl solution on the swelling behavior of PAC and surfactant semi-IPN hydrogels were studied (Figures 6a–6c). Here all hydrogels show similar behavior in that the swelling studies decrease with an increase in NaCl concentration. This nature is due to decrement in the expansion of the hydrogel networks, which is caused by the repulsive forces of counter ions on the polymeric chains shielded by the bound ionic charges.

SEM Analysis

The variations in the equilibrium swelling ratios of these hydrogels can be explained by using SEM images (Figures 7a–7d). Most hydrogel swelling properties depend upon their physicochemical properties, as well as their



(a)

(b)

(c)

Figure 6: Swelling behavior of hydrogels in NaCl solution (a) Swelling studies of CS hydrogels in different NaCl solution, (b) swelling studies of CSM in different NaCl solution, and (c) swelling studies of CSA in different NaCl solution.

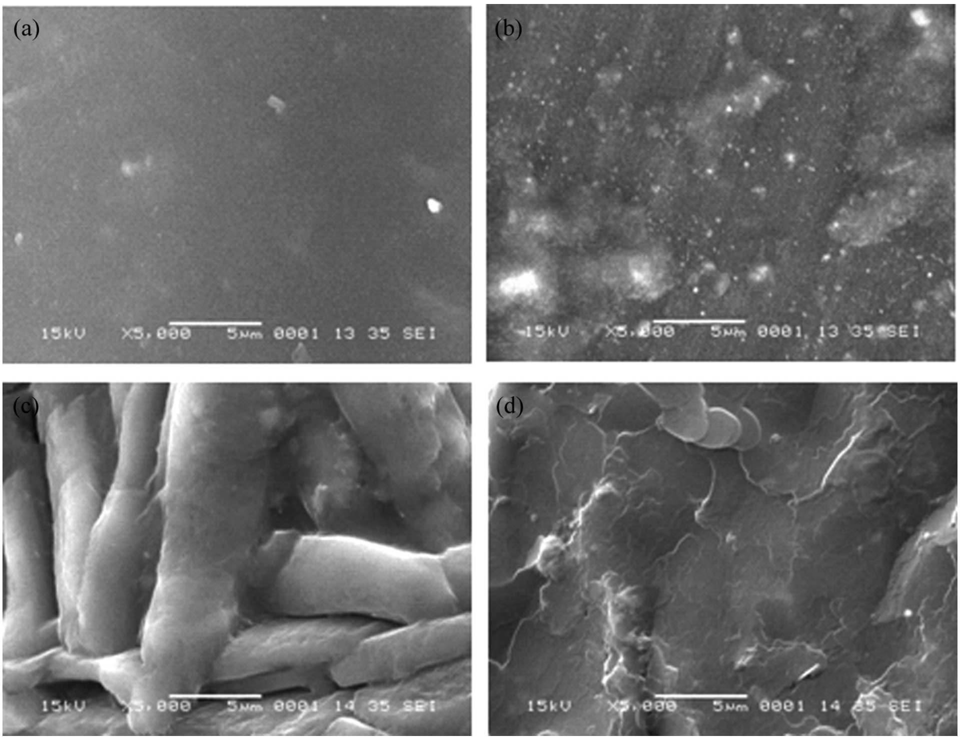


Figure 7: Scanning electron microscopic images of (a) PAC hydrogel, (b) nonionic surafactant interacted PAC, (c) cationic surfactant interacted PAC, and (d) anionic interacted PAC.

interaction with corresponding molecules. The highly repulsive groups like -O-SO_3 of the SDS cause a network structure to develop. Therefore that uniform layers are observed in SEM images of Figure 7d. In the case of cationic surfactant (CTA) modified hydrogels (Figure 7c) the positive sites may reduce the network size and thereby decreasing the swelling ratio. The aggregation of surfactant molecules onto the network results in a planar view along with the aggregated surfactant molecules in various parts of the hydrogel networks as shown. Following this we observe that the SEM images (Figure 7b) of T20-modified hydrogels show a uniform aggregated structure. This is due to the coverage of polyethylene glycol units on the entire hydrogel network. All of these SEM images show different behavior when compared with a blank hydrogel image (Figure 7a).

Thermogravimetric Analysis

The TGA results of modified hydrogels with surfactant hydrogels are depicted in Figure 8. From these results we learned that the three hydrogels show a good thermal stability. This is due to the physical crosslinking between

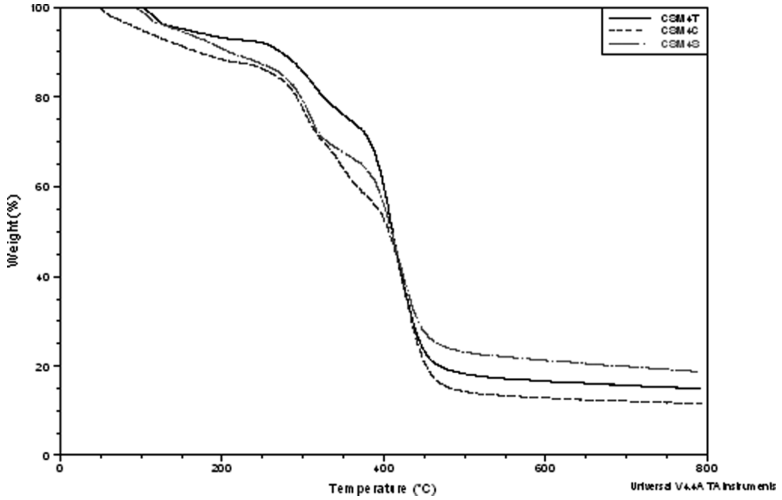


Figure 8: Thermo gravimetric analysis of surfactant interacted PAC (a) T-20 interacted PAC, (b) CTC interacted PAC, and (c) SDS interacted PAC.

PAC hydrogel and SDS. This SDS solution-treated PAC hydrogel shows a reasonable thermal stability when compared with other hydrogels. The other surfactant-modified hydrogels shows 90–95% decomposition at 800°C. This suggests a highly crosslinked nature, which eventually possesses a very poor swelling capacity.

CONCLUSIONS

Poly(acrylamide-co-chitosan) hydrogels were prepared by employing different amounts of chitosan, crosslinker and initiator. The swelling behavior of these hydrogels was done in water as well as different surfactant solutions like anionic, cationic and nonionic. These results suggested that chitosan hydrogels depend on chitosan concentration, initiator concentration and crosslinker concentration. The results as well suggested that the swelling behavior of hydrogels is greatly influenced by surfactant solutions, which is a key application for drug delivery. The morphology behavior of these surfactant-modified hydrogels was analyzed by SEM. The modification of hydrogel by surfactant can be known from FTIR and thermal behavior, and also studied using TGA analysis.

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