Water absorbency of chitosan grafted acrylic acid hydrogels

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**Abstract.** Acrylic acid (AA) monomer was directly grafted onto chitosan (CTS) using potassium persulfate (KPS) as an initiator and methylenebisacrylamide (MBA) as a crosslinking agent under an inert atmosphere. One factor affecting the swelling capacity of the obtained hydrogel, KPS concentration, were studied. The hydrogel products were characterized using Fourier Transform Infrared spectroscopy (FTIR) for chemical structure and scanning electron microscopy (SEM) for morphology. Swelling of the hydrogel samples in distilled water and saline solution (9% NaCl) was examined. Swelling capacity of the CTS-g-PAA hydrogels in distilled water (88.53 g/g) was higher than in NaCl solution (29.94 g/g). The highest swelling capacity value was obtained when the grafted reaction was carried out using 2.5 wt% initiator.

1. **Introduction**

With growing worldwide ecological awareness, there has been a trend to produce low cost, biodegradable materials with improved properties. Lately, there has been a great interest to produce thermoplastic composites reinforced with natural products [1]. The chemical modification of synthetic and natural polymers is a convenient route to obtain materials with different chemical and physical properties. Considerable interest has been focused on the modification by grafting synthetic polymers onto the most abundant naturally occurring polysaccharides such as cellulose, starch, and alginites. Many actual as well as potential applications for products obtained from natural and chemically modified polysaccharides exist as, for example, products with enhanced hydrophilic characteristics. For instance, modified polysaccharides containing carboxyl functions as anionic groups are adequate for the preparation of ionotropic gels. Ionotropic gels are products capable of interacting with polyvalent metal cations. These are water insoluble but they swell considerably with the addition of water or aqueous metal salt solutions. Much recent research deals with this topic and its metal chelating capacity [2]. This type of material, with a large capacity for water retention, is known as a hydrogel. In particular, chitosan (CTS) is becoming popular because it has lower cost, lower density and exhibit better processing ability. Nowadays, CTS is no longer a waste by-product from the seafood processing industry because currently this material is being used by biomedical and pharmaceutical industry [3,4].
CTS, a high molecular weight polysaccharide from chitin, is the second most abundant natural polymers after cellulose in the world, and is excellent biodegradable material and can be degraded into nontoxic products in vivo. Reactive −NH$_2$ and −OH groups present in CTS repeating unit are convenient for graft polymerization of hydrophilic vinyl monomers, making it an efficient way to acquire hydrogels with novel properties (chemical structure is provided below in Figure 1) [5–7]. Grafting polymerization of hydrophilic monomers onto CTS could enhance hydrophilicity and water uptake capacity of the backbone [8].

![Figure 1. Structure of chitosan](image)

Due to its excellent biocompatibility and biodegradability, CTS and its derivatives were widely applied in the fabrication of biomedical materials, enzyme and cell immobilization, especially for drug delivery. Since CTS is easily soluble in acidic solutions, crosslinking of CTS to form a network is the only way to prepare chitosan hydrogels. When an anionic monomer such as acrylic acid is grafted onto CTS (in the presence of a crosslinking agent monomer), an ampholytic hydrogel containing both cationic and anionic charges is prepared. Therefore, by introducing anionic charges (−COO−) onto CTS, a hydrogel with swelling ability at various pHs is prepared [10].

Graft copolymerization of vinyl monomers onto polysaccharides is an efficient route for the preparation of hydrogels. Because of the presence of certain functional groups along the polymer chains, hydrogels are often sensitive to the conditions of the surrounding environment, which are referred to as “intelligent materials” or “smart materials”. For example, the water uptake of these materials may be sensitive to temperature, pH, or ionic strength of the swelling solutions [11,12]. The aims of this work are to synthesize graft copolymer of CTS onto acrylic acid using KPS as initiator in aqueous medium and under nitrogen atmosphere. The resulting CTS grafted acrylic acid was characterized by using Fourier-Transform Infrared Spectroscopy and Scanning Electron Microscopy.

2. Materials and Methods

2.1. Materials

Acrylic Acid (AA) and potassium persulfate (KPS) from E-Merck, chitosan (CTS) and $N,N$-methylenebisacrylamide (MBA) from Sigma-Aldrich
2.2. Instrument and Apparatus

FTIR spectra of the hydrogel samples were recorded on a FTIR spectrophotometer (IR Prestige-21 Shimadzu) in the range of 4000–400 cm\(^{-1}\), using KBr pellets. SEM studies were carried out in a SEM instrument (JSM-6360LA, JEOL, Ltd) after coating the sample with gold film.

2.3. Preparation of CTS-g-PAA

A series of hydrogel from CTS and AA, were synthesized according to the following procedure. Appropriate amount of CTS was dissolved in 50 mL acetic acid solution (1%) in a 1L four-neck flask, equipped with a mechanical stirrer, a reflux condenser, a funnel and a nitrogen line. The reactor was placed in a water bath preset at 60°C. After being purged with nitrogen for 30 min to remove the oxygen dissolved from the system, and certain amount of KPS was introduced to initiate CTS to generate radicals. Ten minutes later, the mixed solution of 7.2 g AA, certain amount of MBA and 90 mL water was added. The water bath was kept at 80 °C for 3 h to complete the polymerization, and then the resulting product was poured into (6 N) NaOH solution to pH 7.0 by neutralization. The swollen product was dehydrated with acetone and dried at 70°C to a constant weight.

2.4. Swelling Measurements

CTS-g-poly(acrylic acid) sample (0.10 g) was put into a weighed teabag and immersed in 100 mL distilled water and allowed to soak for 24 h at room temperature [13]. The equilibrated swollen gel was allowed to drain by removing the teabag from water (~10 min). The bag was then weighed to determine the weight of the swollen gel. The absorbency (equilibrium swelling) was calculated using the following equation:

\[
\text{Absorbency} (Q_e) = \frac{(W_s - W_d)}{W_d}
\]  

Where, \(W_s\) and \(W_d\) are the weights of the samples swollen in water and in dry state, respectively. So, absorbency was calculated as grams of water per gram of resin (g/g) [14].

2.5. Measurement of Swelling Rate

The swelling rate of the samples was measured according to the following process. Sample (0.10 g) was immersed amount of distilled water and 9 wt% NaCl solution in several 500 ml beakers. At certain time intervals, the water absorbency (Qt) of the sample was measured. The measurement condition is the same as that for equilibrium water absorbency [4].

3. Results and Discussion

3.1. Characterization of CTS-g-PAA
Chemical modifications are promising ways to obtain various utilizations of polysaccharides, such as CTS in this study. Of possible modifications, graft copolymerization is expected to be quite promising for developing sophisticated functions [15]. Cross-linked CTS-g-poly(AA) was formed through free-radical polymerization mechanism. The –OH groups present in the backbone polymer are the active sites for the formation of CTS-g-poly(AA) and takes place through the following mechanism as described in Scheme 1. The persulfate was decomposed under heating and produced sulfate anion-radicals that remove hydrogen from –OH groups of CTS backbones. Therefore, this persulfate-saccharide redox system results in active centers capable of radically initiating polymerization of AA leading to graft copolymer. One of the most important features of graft polymerization is unwanted formation of homopolymer, homopoly(AA), that is not chemically bonded to the substrate poly (CTS). Homopolymer can result if the initiator used is one that produces free radicals in solution (in the presence of vinyl monomer AA initiating homopolymerization) before creating the macroradicals. Once a grafted chain has been initiated and begins to propagate, chain transfer from the growing grafted chain end can occur with some species in the medium to yield free radicals that could initiate the growth of homopoly(AA) chains. Since the CTS is an anionic polysaccharide [16] the cross-linking of the MBA takes place through secondary bonding forces with the backbone as well as through multiarmed cross-linking of MBA with CTS [17,18].

The infrared spectra of CTS and CTS-g-PAA are depicted in Figure 2. The FTIR spectrum of CTS has strong peak around 3448 cm⁻¹ due to the stretching vibration of O–H, the extension vibration of N–H, and inter-molecular hydrogen bonds of the polysaccharide. In addition, the typical absorption bands of CTS at 1654, 1594 and 1328 cm⁻¹ are assigned to amide I, amide II and amide III, respectively. In the region of 1000–1200 cm⁻¹, CTS presents a broad absorption band centered at 1091 cm⁻¹, corresponding to stretching of C–O bond of secondary –OH. The band of 1034 cm⁻¹ is derived from C–O stretching of primary –OH. The asymmetric stretching of C–O–C appears at 1155 cm⁻¹ [19]. After the reaction, these characteristic absorption bands get weaken or masked with other absorption bands, implying that reactive functional groups of CTS, such as –NH₂ and –OH, have took part in the copolymerization reaction. The absorption bands in the spectrum of CTS-g-PAA at 1722, 1556, 1454 and 1407 cm⁻¹ are arisen from PAA and assigned respectively to stretching C-O vibration, asymmetric –COO− stretching vibration, bending vibration of C–H and symmetric –COO− stretching vibration. The occurrence of these bands in CTS-g-PAA spectrum is a powerful evidence of PAA existence. From above analysis, it is no doubtful that during the reaction, PAA has been grafted on the backbone of CTS [15].
One of the most important properties that must be considered is hydrogel microstructure morphologies. The surface morphology of the samples was investigated by scanning electron microscopy. Figure 3 shows an SEM micrograph of the polymeric hydrogels (CTS-g-PAA) obtained from the fracture surface. The hydrogel has a porous structure. It is supposed that these pores are the...
regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers [14].

![Figure 3. SEM micrographs of (a) CTS and (b) CTS-g-PAA](image)

### 3.2. Effect of Initiator Content on Water Absorbency

The effect of initiator content on water absorbency for CTS-g-PAA hydrogel is shown in Figure 4. As can be seen, the water absorbency in distilled water increases with increasing KPS content from 1.0 to 2.5 wt%, and then decreases with further increase in the content of KPS. When the content of KPS reaches 2.5 wt%, the water absorbency in distilled water is 88.53 g g\(^{-1}\). The curve of water absorbency did not change in 9 wt% NaCl solution and the water absorbency is in the range of 26.8 to 29.9 g g\(^{-1}\). The increase in water absorbency with increasing the ratio of initiator may be ascribed to the increase in the active sites on the backbone of CTS, arising from the attack of sulfate anion-radical. The increase in the number of active sites on the CTS led to an increase in PAA grafting onto CTS backbones [4]. As the KPS content increased, a large amount of radical was produced, which in turn created more macroradicals in the main chain of CTS. However, if the massratio is increase further, the water absorbency is decreased. This was attributed to the fact that more radicals would enhance the terminating step via bimolecular collision, and the molecular weights of the branched chains are thus decreased [20, 21].
Figure 4. Variation of water absorbency in distilled water and in 9 wt% NaCl solution for the CTS-g-PAA hydrogel with KPS contents.

Figure 5. displays the swelling rate of hydrogel in distilled water and 9 wt% NaCl solution. It was found that the swelling rate of the hydrogel is higher in 0–20 min, and the time of reaching swelling equilibrium is about 2.0 h. The ratios of water absorbency in 1 min to that of swelling equilibrium of CTS-g-PAA with 2.5 wt% KPS, are 91.47% and 76.48% in water and 9 wt% NaCl respectively.

Figure 5. Swelling rate in distilled water and in 9 wt% NaCl solution for CTS-g-PAA with 2.5 wt% of KPS.
4. Conclusions

Superabsorbent hydrogels, CST-g-PAA, were synthesized through grafting of AA onto CTS. Swelling capacity of the hydrogels was found to be affected by initiator concentrations. The water absorbancy both in distillate water and in 9 wt% NaCl solution increased with increase in initiator content. Swelling capacity of the CST-g-PAA hydrogels in distilled water (88.53 g/g) was higher than in NaCl solution (29.94 g/g). The highest swelling capacity value was obtained when the grafted reaction was carried out using 2.5 wt% initiator. The changes of chemical structure were characterized by FTIR spectroscopy which showed a new band at 1722 cm\(^{-1}\) attributed to the carbonyl group of acrylic acid.

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