Preparation and Characterization of Superabsorbent Polymer (SAP) by Graft Polymerization of Carboxymethyl Cellulose

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Abstract. The synthesis of superabsorbent polymer with Carboxymethyl cellulose using ceric ammonium nitrate (CAN) initiated acrylamide (AA) monomer through a solution based graft copolymerization has been conducted. The characterizing studies were performed using Fourier transform infrared (FTIR) spectroscopy, Atomic force microscopy (AFM) and swelling studies. FTIR spectra established crosslinked polymeric network structure of hydrogels through graft copolymerization reaction between CMC and acrylamide indicating incorporation of acrylamide monomer resulting the formation of carboxamide group ($>C=O$). AFM showed the surface morphology or properties of superabsorbent. The hydrophilic properties of the superabsorbent were identified by the swelling percentage or degree of swelling.

Introduction

Superabsorbent polymers (SAPs) (also called slush powder) are polymers that can absorb and retain extremely large amounts of a liquid relative to their own mass [1]. These polymers, when cross-linked, absorb aqueous solutions through hydrogen bonding with water molecules [2]. Owing to their unique physico-chemical properties, SAPs have been found showing extended absorption capacity, swelling behavior and permeability. These coupled with surface properties, optical properties and mechanical properties make them promising materials for a wide variety of applications [3]. As a result, superabsorbents are widely used in many fields, such as agricultural and horticultural, disposable diapers, feminine napkins, pharmaceuticals, textile and medical applications [4] and [5]. Carboxymethyl cellulose is a derivative of cellulose obtained by the chemical modification of natural cellulose [6].

In present work an endeavor has been taken to modify the properties of Carboxymethyl cellulose (CMC) gels by graft copolymerization with Acrylamide monomer to form super absorbent polymer (SAP), followed by subsequent study of the properties of the SAP so prepared.

Materials and methods

Materials

Carboxymethyl Cellulose Sodium salt was purchased from BDH Chemicals Ltd. Poole, England. Acrylamide monomer and Ceric Ammonium Nitrate was purchased from Loba Chem. Pvt. Ltd. Mumbai, India. Acetone was obtained from Merck, Germany. Potassium bromide was obtained from Sigma ultra, USA.

Methods

Preparation of superabsorbent polymer (SAP)

Acrylamide monomer and ceric ammonium nitrate were dissolved in water separately. A modifying bath for CMC was prepared by adding required percentage of a monomer (60% acrylamide on the basis of CMC) and Initiator (20% ceric ammonium nitrate on the basis of

CMC). Freshly prepared solution of ceric ammonium nitrate and acrylamide were added subsequently to the reaction mixture of CMC with constant stirring with 1: 50 sample liquor ratio. Modification of CMC was carried out at temperature 65°C for 90 min with occasional stirring and then allowed for further 30 min as the bath cools down [7] and [8].

Extraction of homopolymer from prepared superabsorbent polymer (SAP)

The product was purified by extracting the homopolymer of polyacrylamide (that might be produced during the polymerization) from the crude product by washing with acetone-water mixture (30:70), followed by acetone washing and air drying for 24h at room temperature [9].

Determination of degree of swelling of superabsorbent polymers (SAP)

After extraction the sample was dried to a constant weight for 24 h [10] and [11]. Degree of swelling (DS)

$$DS = (W_t - W_0) / W_0$$

where W_t is the weight of swelling superabsorbent polymer (SAP) after soaking time, W_0 is the initial weight of dry polymer.

Determination of water desorption of superabsorbent polymer (SAP)

The prepared hydrogel samples were weighted initially and then placed in an open environment for water desorption. At every 1 h interval the weight of the samples were taken for the first four hours and it was continued after 24, 48 and 72 h until constant weight is established. Finally, the percentage of water desorption was calculated gravimetrically at room temperature and average humidity was 50-55%, respectively [12]. Water desorption

$$WD\% = [(W_0 - W_t) / W_0] * 100$$

where, W_t is the weight of the dry superabsorbent polymer (SAP) after air drying time, W_0 is the weight of the prepared superabsorbent polymer (SAP).

Determination of water absorption of superabsorbent polymer (SAP)

Gel samples after extraction of sol, were dried to a constant weight and immersed in distilled water at room temperature. Gel swells in water. At first, weight of swelled gel was taken for the first four hours and it was continued after 24, 48 and 72 h. After completion of absorbing period, the hydrogels were taken out and then the adhering solvent (water) was removed using tissue paper. The hydrogel is then weighted as quickly as possible [11]. Finally, the percentage of hydration or water absorption was calculated gravimetrically as, Water absorption

$$WA\% = [(W_t - W_0) / W_0] * 100$$

where, W_t is the weight of the swelling superabsorbent polymer (SAP) after soaking time, W_0 is the weight of the dry superabsorbent polymer (SAP).

Results and discussion

FTIR Observation

The grafting of superabsorbent polymer (SAP) is confirmed by comparing FTIR spectra of pure carboxymethyl cellulose and the polymer so prepared. Fig 1. (a) shows the FTIR spectra of pure carboxymethyl cellulose. The spectrum showed peak at 3391 cm⁻¹ due to the stretching of -OH group of Carboxylic acid. The peak at 2922 cm⁻¹ indicates dimer -OH stretching vibration of Carboxylic acid. The peak at 1595 cm⁻¹ indicated >C = O stretching vibrations due to the presence of carboxylate (asymmetric). The peak at 1417 cm⁻¹ and 1325 cm⁻¹ could be assigned to CH₂ and CH₃ bending modes of alkanes respectively. The peak at 897 cm⁻¹ and 710 cm⁻¹ suggested the presence of alkenes =C-H stretching. The peak at 604 cm⁻¹ suggested the presence of alkynes of C-H bending.

Fig 1. (b) shows the FTIR spectra of carboxymethyl cellulose-g-acrylamide hydrogel. The peaks at 3435 cm^{-1} indicated -NH stretching of amide. The characteristic peak at 1636 cm^{-1} was due to the amide-I band of carboxamide group ($>\text{C}=\text{O}$ stretching vibration frequency). The presence of a band at 1400 cm^{-1} was due to carboxylate (symmetric). The peak at 612 cm^{-1} suggested the presence of alkynes of C-H bending. By comparing the spectrum of superabsorbent polymer (SAP) with pure carboxymethyl cellulose, some new absorption bands are observed in addition to characteristic hydrogel absorption bands. The existence of a rather sharp intense peak at 1636 cm^{-1} ($\text{C}=\text{O}$, carboxamide group) in IR spectra of the graft copolymers is a certain evidence of grafting [13]. Most of the other peaks of superabsorbent polymer (SAP) are related to pure carboxymethyl cellulose with the functional groups. So the presence of appreciable amounts of carboxamide groups in reaction product after extraction is the proof for grafting of acrylamide onto carboxymethyl cellulose producing superabsorbent hydrogel.

Table 1: Characteristic FTIR peaks shows by superabsorbent polymer (SAP)

Functional groups	Absorption (cm^{-1}) ^a	Absorption (cm^{-1}) ^b
Carboxylic acid	2800-3400	2922, 3391
Carboxamide	1630-1690	1636
Carboxylate (symmetric)	1400-1465	1400
Carboxylate(asymmetric)	1525-1595	1595
Amide	3400-3500	3435

Figure 1: (a) FTIR transmittance spectra of pure carboxymethyl cellulose (b) superabsorbent polymer (SAP)

AFM analysis

Atomic force microscopy is commonly used for determining the surface properties of the hydrogel. AFM is performed using a cantilever. As the cantilever passes over surface just touching the tip it experiences fluctuation due to presence of pores in hydrogels, giving rise characteristics amplitude and phase. As the Fig 2. (a) and Fig 2. (b) show the AFM images in terms of amplitude of pure carboxymethyl cellulose. Fig 3. (a) and Fig 3. (a) show the AFM images of superabsorbent polymer (SAP) prepared in our laboratory. The surface of pure carboxymethyl cellulose is showing the presence of regular building blocks (BB) of sizes $\sim 1\text{-}2\ \mu\text{m}$. The shapes of the building blocks are irregular with no visible pores. The surface morphology of the superabsorbent polymer (SAP) reveals the presence of sub-micron building blocks (SBB) with visible pores on the surface. The presence of visible pores reveals the proof of superabsorbent [14].

Figure 2: (a) Amplitude of pure carboxymethyl cellulose (b) Amplitude of superabsorbent polymer (SAP)

Figure 3: (a) Phase of pure carboxymethyl cellulose and (b) Phase of superabsorbent polymer (SAP)

Swelling and Shrinkage Study

Table- 4. shows, the water desorption of superabsorbent polymer (SAP) increased with the increase of air drying time. A regular increase is observed upto 12 hour. But, after this period, no remarkable desorption of superabsorbent polymer (SAP) was observed as the test continues upto 72 hrs with constant water desorption and it is seen the desorption in superabsorbent polymer (SAP) increases drastically initially and after 24h it becomes stable. After this time no more desorption was occurred. It can be concluded that the gel has no ability to contain its unbounded water.

Water absorption of superabsorbent polymer (SAP) has been conducted and it is seen swelling of hydrogel takes place as the times pass by. A regular increase is observed upto 12 hour. But, after this period, no remarkable absorption of superabsorbent polymer (SAP) was observed as the test continues upto 72 hrs with constant water absorption and it is seen the absorption in superabsorbent polymer (SAP) increases drastically initially and after 24h it becomes stable. After this time no more absorption was found and it is said the hydrogel is saturated with water.

Table 2: Determination of degree of swelling of superabsorbent polymer (SAP)

Number of sample	Weight of the dry gel, w_0 (g)	Weight of the swelling hydrogel after soaking time, w_t (g)	Degree of swelling, $ds=(w_t-w_0)/w_0$	Average degree of swelling
Batch 1	0.17	1.08	5.35	5.24
Batch 2	0.19	1.16	5.10	
Batch 3	0.15	0.94	5.26	

Table 3: Determination of water desorption of superabsorbent polymer (SAP)

Number of sample	Weight Of the prepared hydrogel, w_0 (g)	Weight of the dry hydrogel after air drying time, w_t (g)	Percentage of water desorption, $wd\%=[(w_0-w_t)/w_0]*100$	Average percentage of water desorption
Sample 1	1.02	0.15	85	86
Sample 2	1.13	0.18	84	
Sample 3	1.17	0.13	89	

Table 4: Interaction of superabsorbent polymer (SAP) with water

Super Absorbent Polymer (SAP)	Time (hr)						
	1	2	3	4	12	24	72
Water absorption (%)	55	92	194	208	524	524	524
Water desorption (%)	10	19	30	42	86	86	86

Conclusions

In this work, an approach have been taken for preparing superabsorbent polymer (SAP) by a simple chemical route with a high holding and absorbing water capacity. The surface properties are measured as a function of the tip deflection as it moves over the surface. In absence of visible pores in pure carboxymethyl cellulose superabsorbent polymer (SAP) reveals the presence of sub-micron building blocks (SBB) with visible pores on the surface. The hydrophilic properties of the hydrogels in terms of water absorbing capacity were due to the presence of visible pores in the superabsorbent polymers (SAP). In present work modified properties of Carboxymethyl cellulose (CMC) gels prepared by graft copolymerization with Acrylamide monomer will open up door for application in industrial sector after subsequent process optimization.

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