



Chemical Modification of Carboxymethyl Cellulose via Graft Copolymerization and Determination of the Grafting Parameters

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ABSTRACT

The graft copolymerization of acrylamide(AAm) onto Carboxymethyl cellulose in aqueous medium was investigated, using Ceric Ammonium Nitrate (CAN). The graft copolymer was characterized by Fourier transform infrared spectra. The effects of reaction variables, such as concentration of the initiator, monomer and CMC were investigated, and the grafting conditions were optimized.

Key words: CMC, Acrylamide, Graft copolymerization, Ceric Ammonium Nitrate.

INTRODUCTION

Carboxymethylcellulose (CMC), an anionic water-soluble polysaccharide, is important modified cellulose which is used in various fields such as detergent, food, paper and textile industries. The application potential of CMC has been demonstrated because of its promising characteristics including those of mentioned above(1-3). Indeed, CMC is an important derivative of cellulose and comprises carboxylate functional groups in its structure. This natural polymer is a hydrophilic polymer that dissolving of this polymer in water causes a viscose solution(4). recently, considerable interest has been focused on chemical modification by grafting synthetic polymers onto natural polymers such as CMC, chitosan, chitin, Na-Alginate, carrageenane and starch. Graft

copolymerization with various vinyl monomers can be carried out with different initiator systems and by different mechanisms(5-6). Graft copolymerization of vinyl monomers onto CMC to preparation of hydrogels have been reported. The present work reveals graft copolymerization of acrylamide monomer onto CMC in the presence of Ceric Ammonium Nitrate as a initiator.

EXPERIMENTAL

Materials

CMC sample (DS 0.52) was purchased from Merch Co. Acrylamide (AAm, Fluka), was used after crystallization in acetone. Ceric Ammonium Nitrate (CAN, Merck) was used without purification. All other chemicals were of analytical grade.

Graft copolymerization procedure

CMC solution was prepared in a one-liter reactor equipped with mechanical stirrer and gas inlet. CMC was dissolved in degassed distilled water. In general, 0.50 g of CMC was dissolved in 30.0 mL of distilled degassed water. The reactor was placed in a water bath preset at 60 °C. Then 0.10 g of CAN (dissolved in 5 mL water-HNO₃) as an initiator was added to CMC solution and was allowed to stir for 10 min at 60 °C. After adding CAN, variable amounts of AAm were added to the CMC solution. The total volume of reaction was 40 mL. After 60 min., the reaction product was allowed to cool to ambient temperature and methanol (500 mL) was added to the gelled product. After complete dewatering for 24 h, the product was filtered, washed with fresh methanol (2'50 mL) and dried at 50 °C(5).

Homopolymer extraction

The graft copolymer, namely CMC-g-PAAm, was freed from poly acrylamide homopolymer, by pouring 0.50 g of the product in 50 mL of ethanol solution. The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymer, the CMC-g-PAAm was filtered, washed with methanol and dried in oven at 50°C to reach a constant weight⁹.

Instrumental analysis

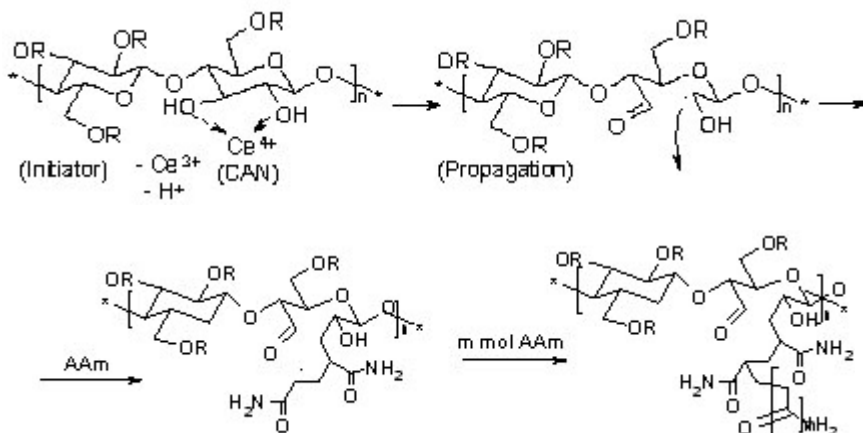
Fourier transform infrared (FTIR) spectroscopy absorption spectra of samples were taken in KBr pellets, using an ABB Bomem MB-100 FTIR spectrophotometer (Quebec, Canada), at room temperature.

RESULTS AND DISCUSSION

Synthesis, mechanism

PAAm was simultaneously grafted onto CMC in a homogenous medium using Ceric Ammonium Nitrate as a radical initiator under an inert atmosphere. The initiator, polysaccharide and the monomer concentration, as well as the reaction temperature four important variables affected on graft copolymerization, were investigated. The mechanism of copolymerization of AAm onto CMC is shown in Scheme 1. At the first step, a complex between the Ce⁴⁺ ion with the oxygen atom at the C-3 position and the hydroxyl group at the C-2 position was formed. This ceric-CMC complex is then dissociated to produce CMC macroradicals. The acrylamide molecules, which are in vicinity of the macroradical sites, become acceptor of CMC radicals resulting in chain initiation and thereafter themselves become free radical donor to the neighboring molecules leading to propagation. These grafted chains are terminated by coupling to give the graft copolymer⁵.

For identification of the graft copolymer, infrared spectroscopy was used. Figure 1 shows the IR spectroscopy of CMC-g-PAAm copolymer. The graft copolymer product comprises a CMC backbone with side chains that carry carboxamide functional groups that are evidenced by peaks at 1660 cm⁻¹. In fact, In the spectrum of the copolymer (Fig. 1-b), new peaks are appeared at 3206 and 1660 cm⁻¹ that may be attributed to amide NH stretching, asymmetric and symmetric amide NH bending, respectively.



Scheme 1: General mechanism for CAN-initiated graft copolymerization of acrylamide onto CMC

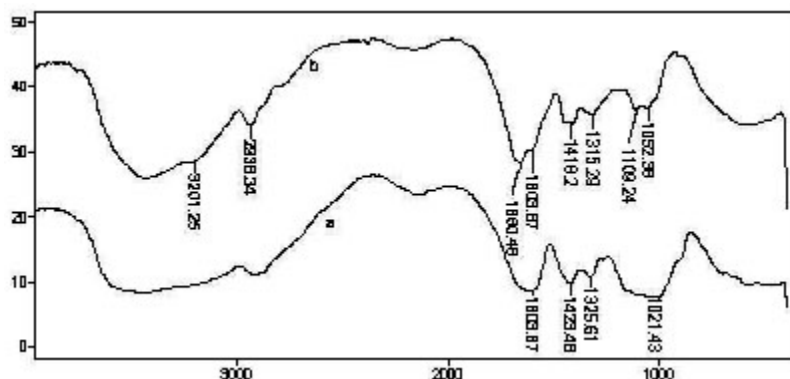


Fig. 1: FTIR spectra of pure CMC(a) and homopolymer-free CMC-g-PAAmc copolymer (b)

Characteristic important-grafting parameters

The percentage of grafting ratio (%Gr), add-on (%Ad) and homopolymer (%Hp) were evaluated with the following weight-basis expressions as reported by Fanta⁹:

$$\%Gr = \frac{(PAAm \text{ grafted}) - \text{Initial CMC}}{\text{Initial CMC}} \times 100 \quad \dots(1)$$

$$\%Hp = \frac{\text{total product} - (PAAm \text{ grafted})}{\text{total product}} \times 100 \quad \dots(2)$$

$$\%Ad = \frac{(PAAm \text{ grafted}) - \text{Initial CMC}}{(PAAm \text{ grafted})} \times 100 \quad \dots(3)$$

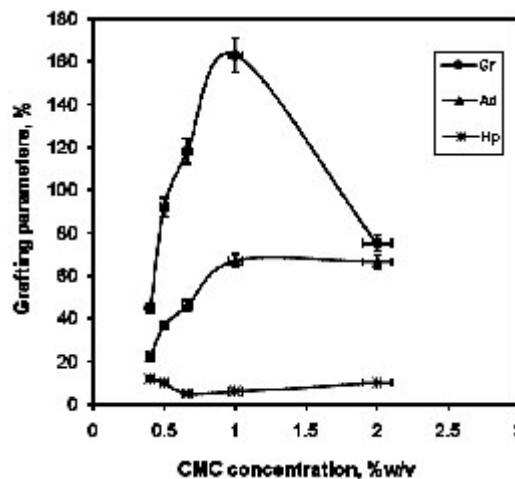
Optimization of the reaction conditions

In the present investigation, the effect of concentration of CMC, CAN and AAm, along with temperature of reaction was studied, to optimize the reaction conditions. It may be found from the related curves (next figures) that the trends of the "changes" are similar for grafting parameters Gr, Hp, and Ad. The reason is the similar concepts applied for defining the grafting parameters (Eqs. 1-3).

Effect of CMC concentration

The effect of CMC concentration on graft copolymerization was depicted in Figure 2. With increasing the CMC amount, more reactive grafting sites are formed which is favorable for grafting. This can account for initial increment in grafting parameters up to 1.0 %W/V of CMC value. Beyond

this amount, the grafting values were diminished. This may be ascribed to the increase in viscosity of reaction mixture and the termination reaction between macroradical-macroradical and macroradical-primary radicals as well. This observation is in close agreement with the results obtained by other investigators¹⁰⁻¹⁴.



Reaction conditions: CAN 0.0005 M, AAm 1.30 mol/L, temperature 40°C, time 120 min.

Fig. 2: Effect of CMC concentration on the grafting parameters

Effect of initiator concentration

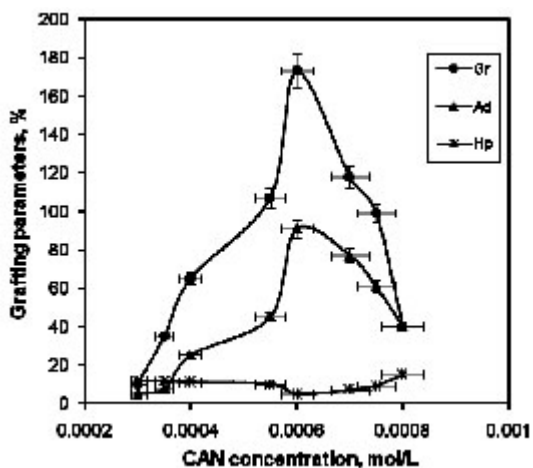
The grafting dependence on CAN concentration can be concluded from Figure 3. The highest grafting ratio (321%) was achieved at 0.0006 mol/L of CAN where homopolymer content was 5%.

Increased CAN concentration resulted in more radical sites on the polysaccharide backbone that in turn led to higher Gr and add-on values and lower homopolymer formation. However, since the CAN initiator solution is used as dilute HNO_3 , at CAN concentration higher than 0.0006 mol/L, a more acidic pH probably causes partial termination of the macroradicals on CMC. As a result, increased free radicals on CMC are compensated by partial termination of the macroradicals. Thus Gr and add-on values were diminished at higher amounts of the initiator¹⁰⁻¹⁴.

The percent of graft decreased with the increase of the initiator concentration beyond the optimum condition. This behavior can be attributed to:

- A relatively high concentration of the initiator may cause a reduction of the grafting of AAm due to an increase in the number of CMC radicals terminated prior to AAm addition.
- At high concentration of CAN, was an increase in the homopolymer (PAAm), which competed with the grafting reaction for available monomer.

These observations are in agreement with similar observations reported by others¹⁶.

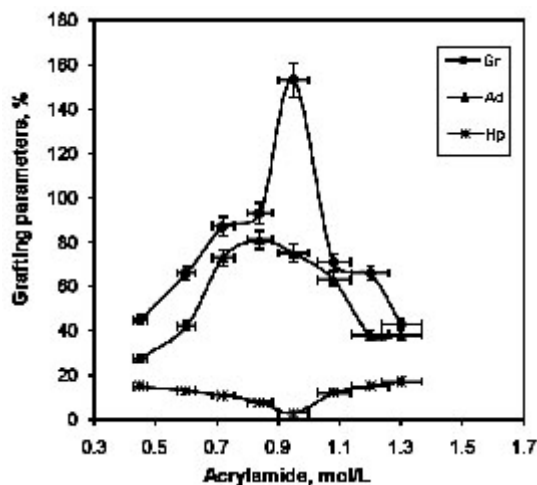


Reaction conditions: CMC solution 1 %W/V, AAm 1.30 mol/L, temperature 40°C, time 120 min

Fig. 4: Grafting parameters as functions of initiator concentration

Effect of Monomer Concentration

The Acrylamide concentration was varied from 0.45 to 1.30 mol/L to study its effects on grafting parameters (Figure 5). These parameters were found to be increased by enhancement of AAm concentration from 0.45 up to 0.95 mol/L. This behavior can be attributed to the increase of monomer concentration in the vicinity of the CMC backbone and consequent greater availability and enhancement chances for molecular collisions of the reactants. The decrease in %Gr and %Ad after a certain level of AAm (0.95 mol/L) is probably due to preferential homopolymerization over graft copolymerization as well as increasing the viscosity of reaction medium, which hinders the movement of free radicals¹⁷⁻¹⁹.



Reaction conditions: CMC solution 1 %W/V, CAN 0.0006 mol/L, temperature 40°C, time 120 min.

Fig. 5: Effect of the acrylamide concentration on the grafting parameters

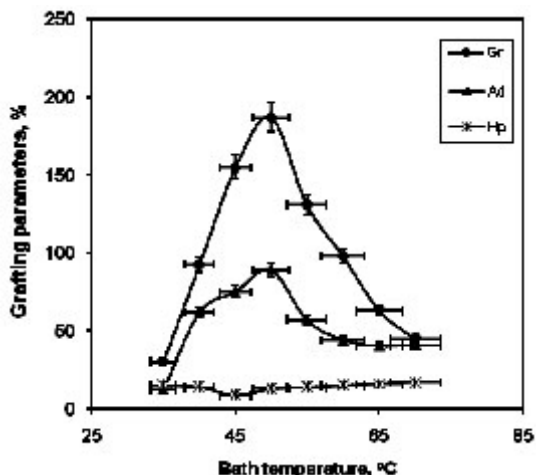
Needless to say, the increase in the chain transfer to monomer molecules may be other possible reason for the diminished grafting at higher AAm concentrations. Similar observations have been reported for the grafting of ethyl acrylate onto cellulose and methyl acrylate onto starch.

Effect of reaction temperature

The grafting reactions were carried out at different temperatures between 35 and 70°C, keeping the other variables constant.

As shown in Figure 6, it is found that %Gr and %Ad increase initially and then decrease to some extent with further increase in temperature. This is attributed to the fact that increasing the temperature favours the activation of macroradicals as well as accelerates the diffusion and mobility of the monomers from the aqueous phase to the

backbone. However, a further increase in temperature decreases %Gr and Ad parameters, which can be ascribed both to the acceleration of termination reaction and to the increased chance of chain transfer reaction, accounting for the increase in the amount of homopolymer. This observation indicates that the optimal reaction temperature is 45°C. Similar behavior was observed in the case of grafting of acrylic acid onto methyl cellulose and acrylamide onto xanthan gum²¹⁻²².



Reaction conditions: CMC solution 1 %W/V, CAN 0.0006 mol/L, AA 0.95 mol/L, time 120 min.

Fig. 7: Effect of the water bath temperature on the grafting parameters

CONCLUSION

Graft copolymerization was employed as an important technique to obtain a chemically modified natural polysaccharide, CMC. The grafting of acrylamide onto CMC was carried out using CAN as an efficient initiator. The characteristic absorbing peaks in the FTIR spectra have proven that CMC participates in graft copolymerization with AAm. The main factors affecting the grafting parameters, including concentration of the initiator, monomer and CMC and reaction temperature was studied. The optimum reaction conditions were found to be CAN 0.0006 mol/L, AAm 0.95 mol/L, CMC 1 %W/V, and reaction temperature 45°C. Under the optimized conditions the grafting parameters were calculated to be Gr 173 %, Ad 91 %, and Hp 5.0 %.

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