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Graft copolymerization of 2-hydroxyethylmethacrylate onto carboxymethyl chitosan using CAN as an initiator

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Abstract

O-Carboxymethyl chitosan (CMCH) was prepared and characterized by FTIR spectroscopy. Graft copolymerization of 2-hydroxyethylmethacrylate (HEMA) onto CMCH using ceric ammonium nitrate (CAN) as an initiator was carried out in an aqueous solution. Evidence of grafting was confirmed by comparison of FTIR spectra of CMCH and the grafted copolymer as well as scanning electron micrograph (SEM) of the products. The effects of concentration of CAN, HEMA, reaction time and temperature on graft copolymerization were studied by determining the grafting percentage, grafting efficiency. With keeping other condition constant, the optimum grafting conditions was obtained as following: CMCH, 2 g; CAN, 0.2 M; and HEMA, 0.384 mol/l; reaction temperature, 40 °C; and reaction time, 4.5 h.

Keywords: Carboxymethyl chitosan; 2-Hydroxyethylmethacrylate; Ceric ammonium nitrate

1. Introduction

Cellulose and chitin as biopolymers is the most abundant organic compound in nature and estimated to be at levels approaching 10^{11} ton annually [1]. Chitin has been a major structural exoskeleton since the Cambrian Period, more than 550 million years ago. The total amount of chitin harvestable without unbalancing the marine ecosystem is estimated to be 1.5×10^{8} kg/year [2], mostly from the shells of crustaceans such as crab, shrimp and krill. Chitosan is the *N*-deacetylated derivative of chitin, though this *N*-deacetylation almost never complete [3,4]. Actually, the names 'chitin' and 'chitosan' corresponds to a family of polymers varying in acetyl content. Therefore the degree of acetylation determines whether the biopolymer is chitin or chitosan. Chitosan [(1→4)-2-amino-2-deoxy-β-D-Glucan] is a biocompatible polymer and have found a number of applications as biomaterials in tissue engineering and in a controlled drug release system for various route of delivery [5–9]. Chemical modification of chitosan is an important topic for production of bifunctional material.

Considerable interest has been focused on chemical modification by grafting synthetic polymers onto chitin and chitosan [10–17]. Graft copolymerization of vinyl monomers onto chitosan and other natural polymers can introduce desired properties and enlarge the field of potential application of them by choosing various types of side chains. In recent years number of initiator systems has been developed to initiate graft copolymerization. Initiators, such as ceric ammonium nitrate (CAN), potassium persulfate (KPS) and ammonium persulfate (APS) usually produce free radical sites on polymer. However, the properties of grafted chitosan have been improved but not so much because of its regular structure and the strong intermolecular hydrogen bonds. Recent researchers showed that grafting onto pre-modified chitosan is quite significant in view of preparing polysaccharide-based advanced materials with multi functions [18]. But there are very limited reports about the graft copolymerization of pre-modified chitosan derivatives [19–21].

In this paper, multiple-derivated chitosan (CMCH-*g*-HEMA) was prepared by etherification of chitosan with mono chloroaceticacid followed by the graft polymerization of 2-hydroxyethylmethacrylate, and the effects of reaction conditions like reaction time, reaction temperature, concentration of HEMA and concentration of CAN on graft copolymerization were investigated.

2. Experimental

2.1. Materials

Chitosan (molecular weight 8.4×10^{4}; the degree of deacetylation 85%) provided by Central Institute of Fisheries

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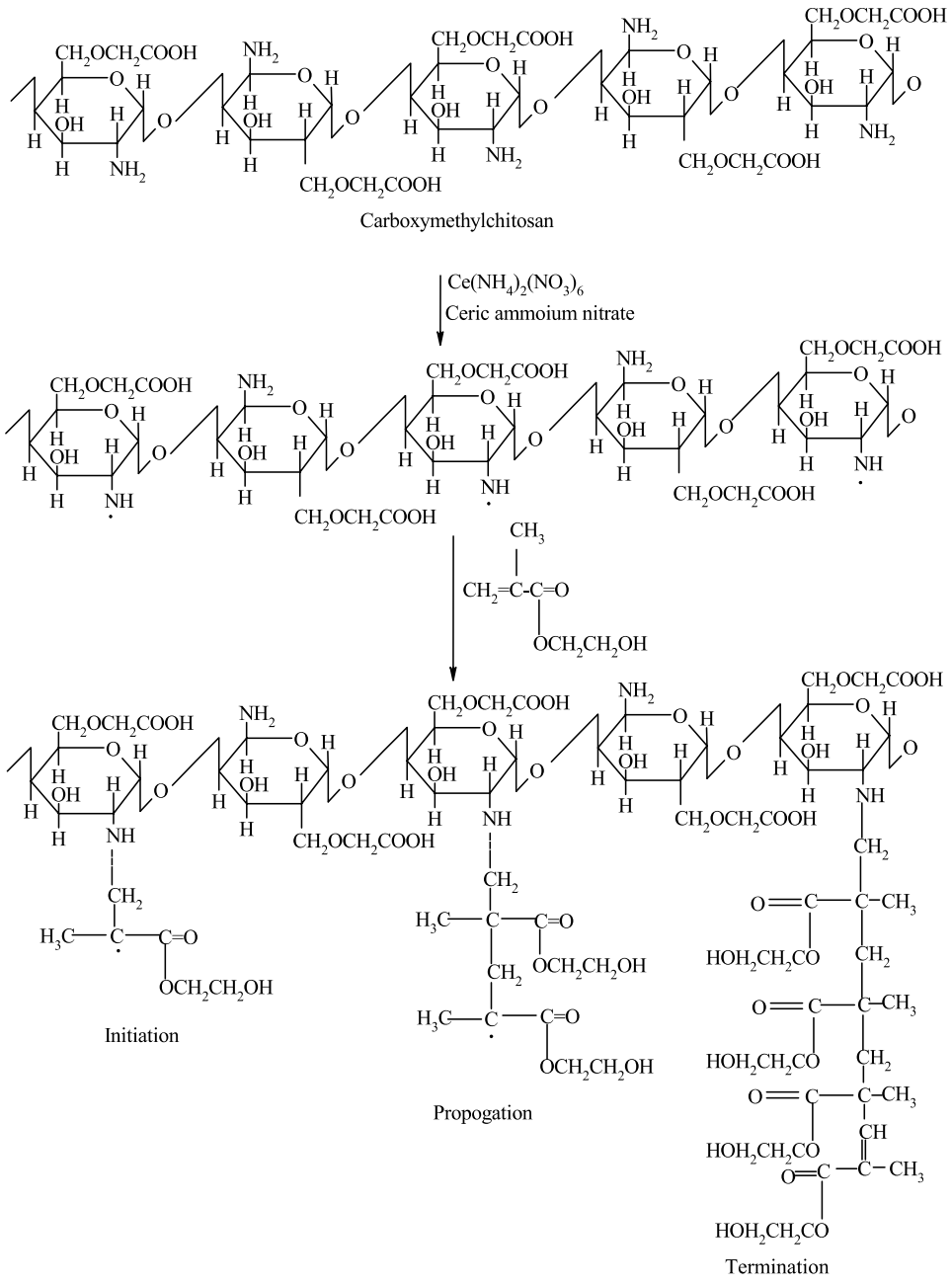

Fig. 1. Reaction scheme of CMCH-*g*-HEMA.

Technologies, India. Ceric ammonium nitrate (CAN) of analytical grade reagent was supplied from S.D. Fine Chemical, India. HEMA was obtained from National Chemical, India. All the other reagents are analytical grade and used without further purification.

2.2. Preparation of O-carboxymethylchitosan

To synthesize O-carboxymethylchitosan, chitosan (10 g), sodium hydroxide (13.5 g) and solvent isopropenol (100 ml) were suspended into a flask to swell and alkalize at room temperature for 1 h. The temperature was maintained in a water bath. The mono chloroaceticacid (15 g) was dissolved in isopropenol, and added into the reaction mixture drop wise within 30 min and reacted for 4 h at 55 °C. Then the reaction was stopped and isopropenol was discarded. Ethyl alcohol (80%) wad added and solid product was filtered and rinsed with 80–90% ethyl alcohol to desalt and dewater, and vacuum dried at 50 °C. The degree of substitution (DS) of CMCH was determined by pH-metry and found to be 0.31 [22].

2.3. Graft copolymerization

A small amount of CMCH (2 g), a predetermined amount of HEMA, and 100 ml double distilled water were charged into a three necked round bottom flask in a constant temperature water bath maintained at a 40 °C. Nitrogen gas was bubbled for 30 min to remove the dissolved oxygen under stirring. 0.20 M

CAN dissolved in 10.0 ml of 0.30 M HNO_3 was slowly added to the three necked flask to initiate graft copolymerization. Reaction products were neutralized by 10% NaOH, precipitated in acetone, filtered, washed with acetone and methanol/H_2O (90:10), so that all the unreacted CMCH and cerric salt were removed and dried under vacuum at 50 °C. Homopolymers were extracted with alcohol for 48 h, and dried at 50 °C for 24 h; reaction scheme of the graft copolymerization was shown in Fig. 1 [23]. The grafting parameters were calculated in following manner [24].

$$\text{Grafting percentage (G\%)} = \left[\frac{W_1}{W_0}\right] \times 100 \quad (1)$$

$$\text{Grafting efficiency (GE\%)} = \left[\frac{W_1}{W_0}\right] \times 100 \quad (2)$$

where W_0, W_1, and W_2 denote the weight of CMCH, weight of pure graft copolymer and weight of crude graft copolymer, respectively.

2.4. Characterization

IR spectra of chitosan derivatives were recorded with a Perkin–Elmer fourier-transform infrared (FTIR) spectrometer using KBr pellets. Scanning electron microscopy (SEM) of Chitosan, CMCH and graft copolymer were obtained by using SEM XL-Series from Philips, The Netherlands at 15 kV.

3. Results and discussion

3.1. Characterization of chitosan derivatives

Structural changes of chitosan and its derivatives were confirmed by FTIR spectroscopy (Figs. 2 and 3). The IR spectrum of chitosan shows peaks assigned to the saccharide structure at 1152, 1080, 1028 and 897 cm^{-1}, and a strong amino characteristic peak at around 3420, 1655 and 1325 cm^{-1}, are assigned to amide I and II bands, respectively [25]. In the IR spectrum of CMCH, the strong peak at 1412.3 cm^{-1} could be assigned to the symmetrical stretching vibration of COO^-. The asymmetrical stretching vibration of COO^- (1900–1550 cm^{-1}) overlapped with the deforming vibration of NH_2 at 1599.3 cm^{-1} to obtain a very strong peak. And C–O absorption peak of hydroxyl group became stronger and move to 1074.1 cm^{-1}. The results indicated that the substitution occurred at C_6 position. In the IR spectrum of CMCH-*g*-HEMA, characteristic peak of C=O obtained at 1725.53 cm^{-1}. From the IR data it is clear that the grafted copolymer CMCH-*g*-HEMA had both characteristic peaks of PHEMA and the saccharide of chitosan and its derivatives, which could be effective evidence of grafting.

The scanning electron micrograph (SEM) of chitosan, CMCH and its graft copolymer are shown in Figs. 4–6, respectively. Carboxymethylation and graft copolymerization modified the surface morphology and also its physical, chemical and biodegradable characteristics of chitosan. It is clearly seen from Figs. 4 and 5 flaky nature of chitosan was little modified in carboxymethylation process. The fibrous nature of CMCH was totally modified in the graft copolymer, wherein distinct morphological differences were discernible in their surface topography. Fig. 6, CMCH-*g*-HEMA showed the clustered irregular structure.

3.2. Effect of initiator concentration

The graft copolymerization was conducted at different concentrations of CAN. As shown in the Fig. 7 the %G and %GE increase with increase in the initiator concentration and reaches at a maximum value. It was observed that formation of homopolymer was considerably less at low initiator concentration while there was a significant homopolymer formation beyond a certain value. Increase the initiator concentration further resulted in a decrease of the %G and %GE. A relatively high concentration of the initiator may

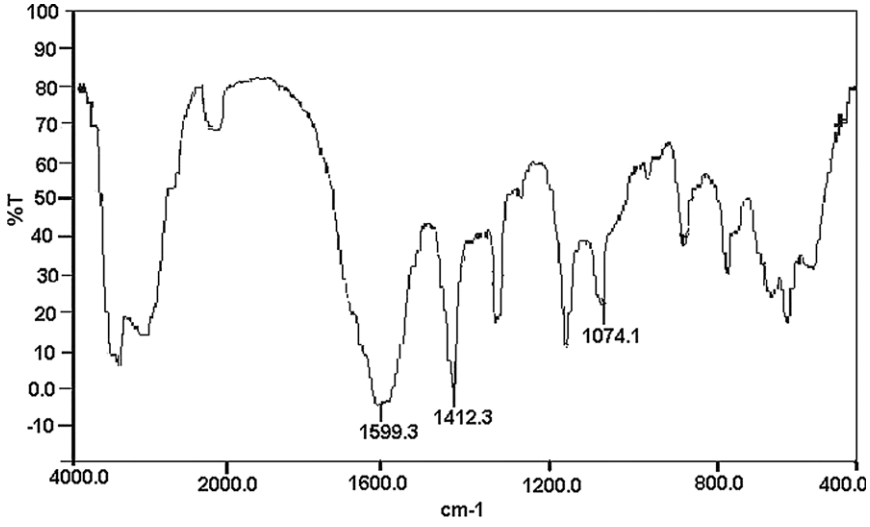

Fig. 2. FTIR of CMCH.

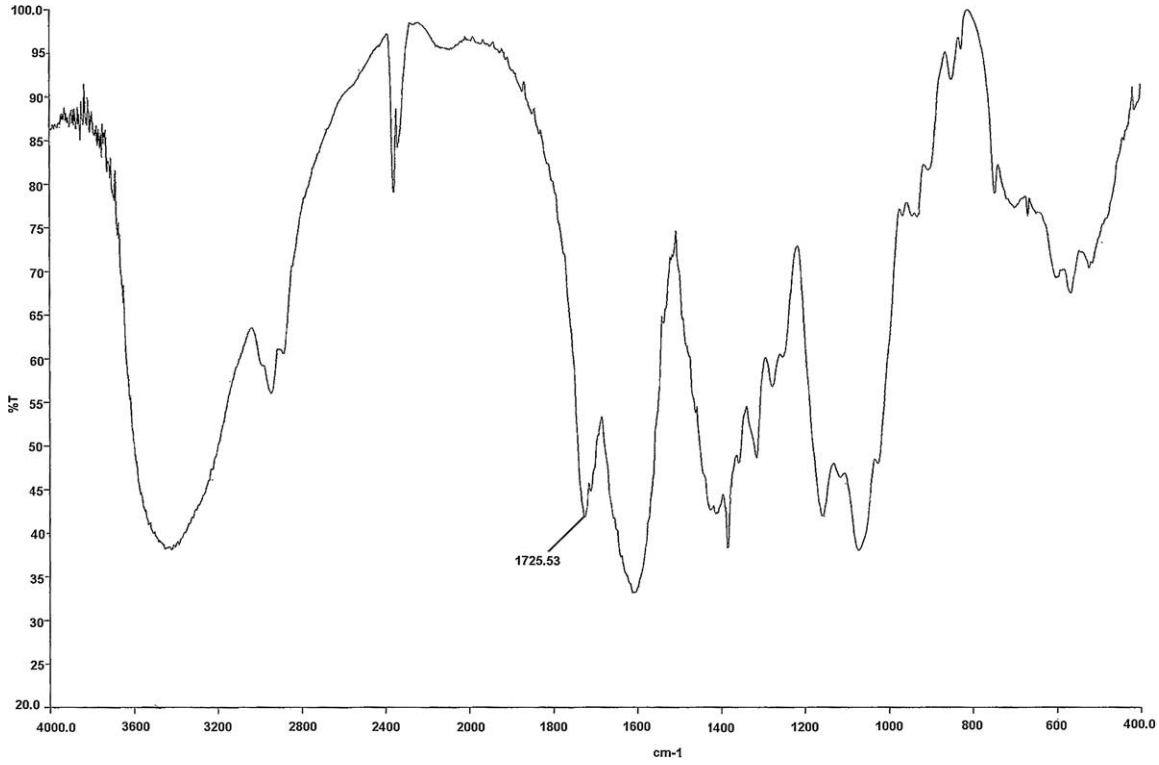

Fig. 3. FTIR of CMCH-*g*-HEMA.

cause a reduction of %G and %GE due to increase in the number of CMCH free radicals terminated prior to HEMA addition. Furthermore, homopolymer formation at higher initiator concentrations which compete with the grafting reaction for available monomer could lead to decrease in the %G and %GE.

3.3. Effect of monomer concentration

Fig. 8 showed the effect of concentration of HEMA on graft copolymerization. With increase in concentration of HEMA, %G increased continuously, reached the maximum value when the concentration of HEMA was 0.384 mol/l, and

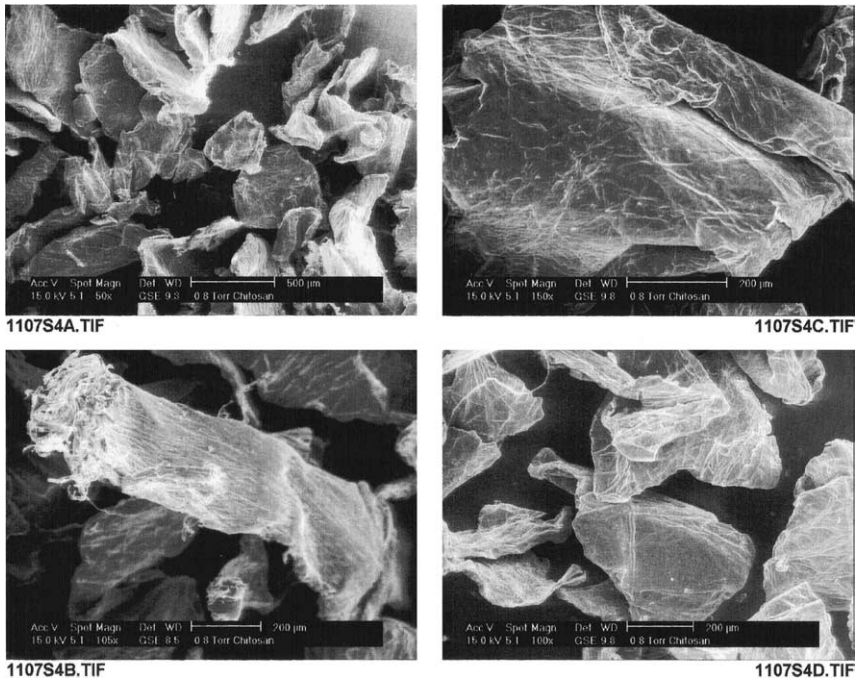

Fig. 4. SEM of chitosan.

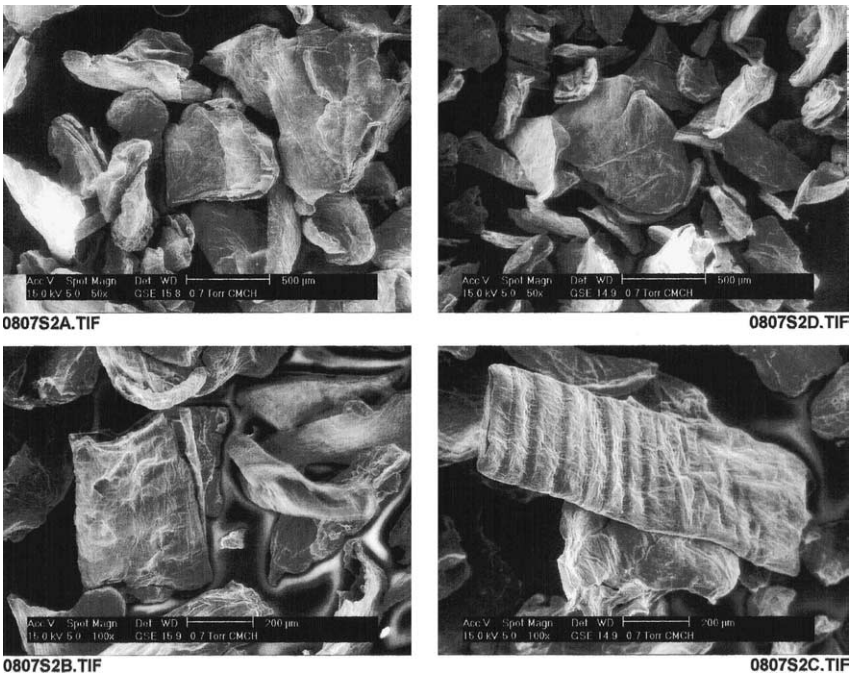

Fig. 5. SEM of CMCH.

then decreased. This behavior could explained by the fact that an increase of monomer concentration lead to the accumulation of monomer molecules in close proximity to the CMCH backbone. The decrease of %G after saturation could be associated with depletion in the available HEMA concentration as well as a reduction in the active sites on the CMCH backbone as graft copolymerization proceeds. With the higher monomer concentrations the primary radicals attack the monomer instead of reacting with the backbone polymer. It can also be noted that once the graft copolymer radical has formed, the excess monomer will shield the graft copolymer, which may inhibit the rate of graft

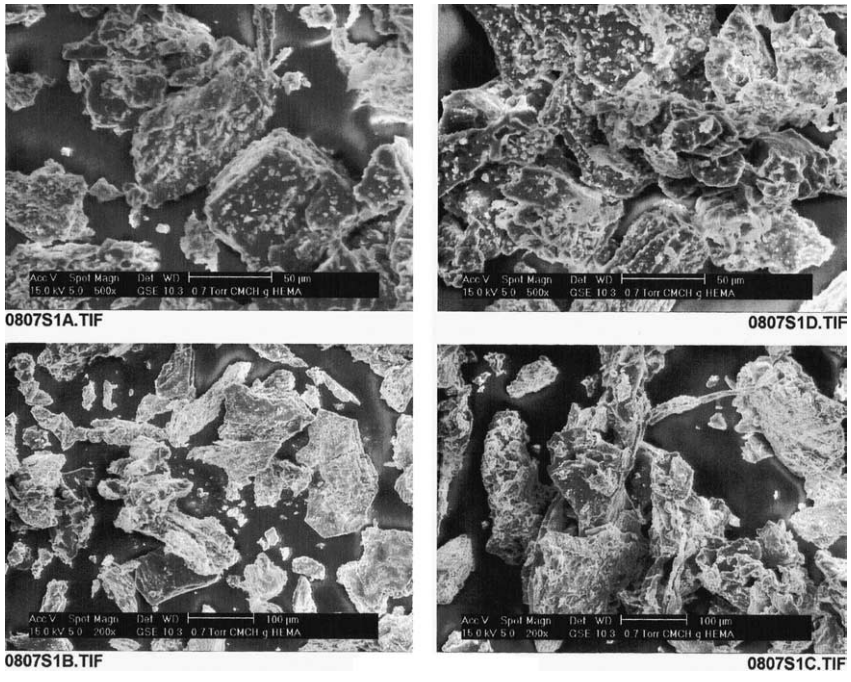

Fig. 6. SEM of CMCH-*g*-HEMA.

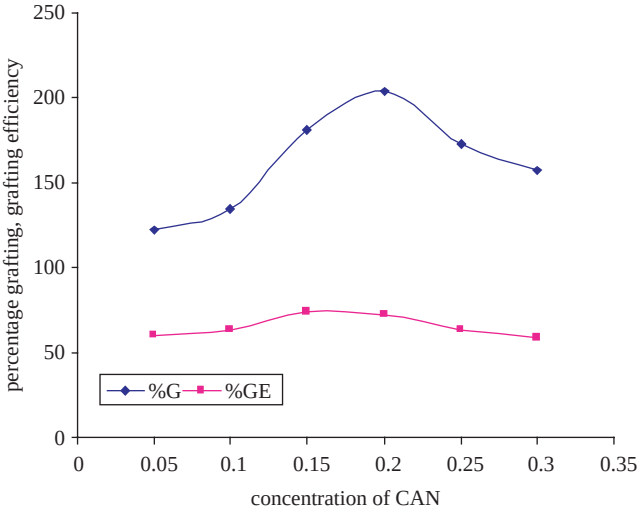

Fig. 7. Effect of initiator concentration (CAN) on percentage grafting (%G) and grafting efficiency (%GE).

copolymerization. In addition to this the excess monomer will be available for initiator radicals to initiate the homopolymerization reaction and there by decrease in the %GE.

3.4. Effect of reaction temperature

The effect of temperature was studied by changing the reaction temperature from 20 to 70 °C and keeping the other reaction condition constant. It can be seen from Fig. 9 that %G and %GE reached maximum value at 40 °C. At low temperature, a redox reaction between CAN and NH_2 group of CMCH was slow, the amount of radicals generated was small and thus %G was low. The increase in temperature the graft copolymerization occurs with poor selectivity, and various hydrogen abstraction and chain transfer reaction might be accelerated and thus lead to a decrease in %G. The decrease in %GE at higher temperature may be attributed

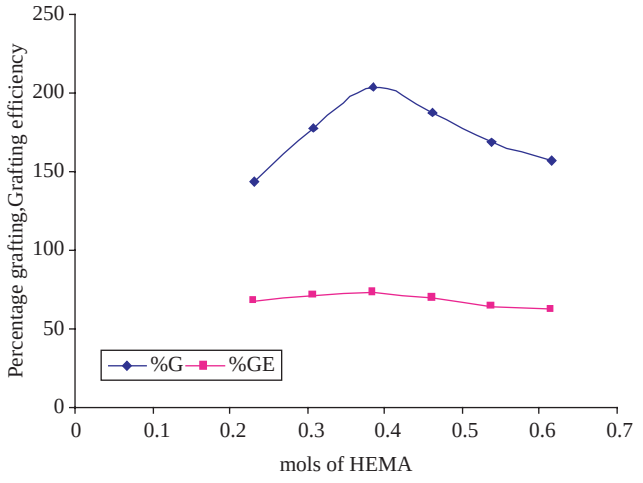

Fig. 8. Effect of monomer concentration (HEMA) on percentage grafting (%G) and grafting efficiency (%G).

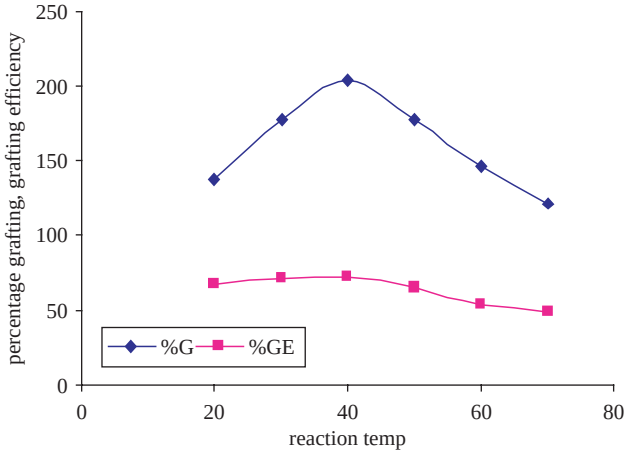

Fig. 9. Effect of reaction temperature on percentage grafting (%G) and grafting efficiency (%GE).

to the solubility of monomer in the aqueous phase and also to the acceleration of the termination reaction which leads to the formation of more homopolymer.

3.5. Effect of reaction time

Fig. 10 shows the effect of reaction time on the %G and %GE. It is clear from this figure that as reaction time increases %G and %GE increased gradually. The decrease in the %G and %GE with time could be attributed to decrease in concentrations of initiator and the monomer as well as a reduction in the number of free radicals accessible for grafting as reaction proceeds. The higher value of %G can be attributed to the fact that the presence of bulky groups, such as $–CH_2COOH$ in the CMCH, may open up its structure, thereby increasing the diffusion of the initiator and monomer into CMCH.

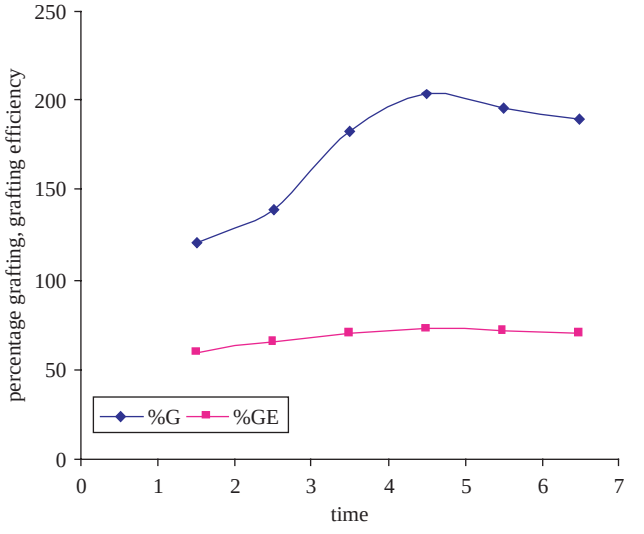

Fig. 10. Effect of reaction time on percentage grafting (%G) and grafting efficiency (%GE).

4. Conclusions

The feasibility of grafting HEMA onto CMCH by CAN as an initiator has been demonstrated by this work. The reaction condition such as initiator concentration, monomer concentration, reaction time and reaction temperature had great influence on graft copolymerization. The study of FTIR spectra and SEM provides the graft copolymerization do takes place. This multi-derivatived chitosan will have potential applications in controlled drug delivery system and food preservation.

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