

Photo initiating system to synthesize an absorbent hydrogel

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Abstract

In order to synthesis absorbent hydrogel, Carboxymethyl cellulose (CMC) was prepared by different DS.

A superabsorbent hydrogel of carboxymethylcellulose (CMC) was initiated by UV system using methylenebisacrylamide (MBA) as a crosslinking agent and Photo initiator.

For investigation the reaction of water absorbency of the hydrogels, the synthetic conditions were systematically optimized through studying the influential factors.

The maximum water absorbency was achieved under the optimum condition of poly CMC that found to be CMC (DS 0.76) / 10 g, MBA =0.5 gm, PI = 0.08 g, L.R 1:10, temp. 30⁰ C and time 3 h.

Key words: Carboxymethylation, hydrogel, cross linking, photo initiation UV and swelling

Research background

Using the photo initiation system in order to create super absorbent hydrogel to absorb liquid solutions

1-INTRODUCTION

The photosensitized vinyl monomers and acrylic monomers onto a range of polymeric substrates has been the subject of particular interest in the recent past⁽¹⁾. Much of this interest originates in the recognition that many of the co-polymeric products possess an interesting range of physical and/or chemical properties.

Among the various methods allowing the generation of radicals, e.g. γ irradiation, redox chemical initiation, heating, dye-sensitized reaction and UV light-induced grafting, sensitized reactions are more attractive. UV light-induced grafting allows the use of larger wavelengths of excitation, thus increasing the possibility of potentially valuable commercial exploitation

However, this kind of reaction requires knowledge of the photo-reactivity of the initiator with respect to the chemical nature of the monomer and of the macroradical. Since polymers absorb light below 300 nm, photosensitiser or photoinitiator that absorb near UV or visible light have been generally added to formulations. The excited molecule may then split and/or react with the subsequent formation of reactive radicals that are capable of attacking the polymeric backbone.

Free radical generation in cellulose, by photosensitized excitation, has shown unequivocally that UV irradiation, both in photosensitized and unsensitized experiments, results in chain scission and radical generation on the glucosidic cycle. By proper choice of the sensitizer, the scission of glucosidic bonds can be reduced and radical generation can be enhanced, thus resulting to a lower degradation of the polymer and an increase in the rate of photochemical reaction.

The reason of this study to produce poly (MBA)-CMC graft copolymer with superabsorbent character

In the current study, a water-soluble photosensitizer, 4- (trimethyl ammonium methyl) benzophenone chloride, symbolized as PI, was used to initiate the graft copolymerization of methylenbisacrylamide onto CMC in an aqueous medium. Factors affecting the graft copolymerization reaction i.e., loading of the photoinitiator and methylenbisacrylamide, irradiation time, polymerization temperature, material: liquor ratio and the DS of the CMC used were studied. ⁽²⁻⁶⁾

2- Experimental

2- 1-Materials

2-2- Raw materials

-Native wood pulp (WP) was kindly supplied by the Egyptian National Research Center, Cairo, Egypt.

2-3-Chemicals

-Carboxymethylation (CMC preparation)

Sodium hydroxide (NaOH), sodium carbonates anhydrous (Na_2CO_3), Monochloroacetic acid (ClCH_2COOH) were of laboratory grade, and Ethanol was of commercial grade.

-Grafting (CMC by UV)

-Photo initiator (PI), N, N-Methylen Diacrylamide (MBA) $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_2$, Acrylamide(AAM) $\text{C}_3\text{H}_5\text{NO}$, were of laboratory grade chemicals, supplied by Merck- Schuchardt –German & Fine Chemicals.

-Ethyl alcohol absolute, sodium hydroxide (NaOH) ⁽¹⁾

3- Practical procedure

3-1- Carboxymethylation

A certain amount of smashed wood pulp (WP) was placed in sealable bottle and mixed together with a known volume of the solvent at room temperature. An aqueous solution of sodium hydroxide was added drop wise to the cellulose-solvent mixture under stirring until the whole amount of sodium hydroxide was added. The sodium salt solution of

monochloroacetic acid prepared by the reaction of monochloroacetic acid with sodium carbonate monohydrate was added drop wise to the cellulose -solvent-sodium hydroxide mixture under continuous stirring until complete addition of the sodium monochloroacetate solution.

Stirring was then stopped and the bottle was closed and kept in thermostat shaking water bath at 70°C for certain reaction time. After Carboxymethylation, the samples were washed with ethanol: water solution (80:20) while excess alkali was neutralized using acetic acid. After washing, samples were filtered, oven dried at 100°C. ⁽¹⁾

This method was done by different moles of monochloro acetic to study the effect of degree of substitution (DS)

3-2- Preparation of poly (MBA)-CMC Composite

A known weight of the photoinitiator (PI) was dissolved in a known volume of distilled water using a mechanical stirrer. After the dissolution of the (PI), the CMC (10 g.) powder was added portion wise to the solution of the (PI) and left under continuous stirring until complete dissolution of the CMC was obtained. Doing so, the (PI) was distributed regularly on the surface of the CMC molecule. A known volume of the N,N-Methylen Diacrylamide (MBA) was then added drop wise to the aqueous solution of the (PI) and the CMC and left for about 10 minutes under continuous stirring. The whole contents were then transferred to the irradiation vessel where the irradiation was provided by a water-cooled 125 W medium-pressure Hg lamp assembly (wavelength distribution, 190 nm to the visible region with some IR energy output as well). The total dose of the UV irradiation was controlled by controlling the time of exposure, i.e., the reaction time. The reaction temperature was controlled using a thermostated water bath. The whole contents were kept at the polymerization temperature for a required known period of time under continuous stirring in the presence of air. After polymerization, the gel-like, poly (MBA)-CMC* composite was collected from the irradiation vessel and kept in a closed bottle at 30°C.

3-3-Extraction of grafted copolymer

-The gel-like poly (MBA)-CMC and composite was repeatedly stirred thoroughly with 100% commercial ethanol at 25°C (using mechanical stirrer) in order to remove any trace quantities of unwanted, attendant homopolymer and residual monomer. The insoluble poly (MBA)-CMC graft copolymer was removed by centrifugation. The stirring/centrifugation process was repeated many times for six hours. The extracted poly (MBA)-CMC graft copolymer was oven dried at $100 \pm 5^\circ\text{C}$ and kept dry for the analyses.

Dried at then kept over P₂O₅ for at least 48h before analysis.

3-4-Analyses and characterizations

3-4-1- Swelling

Swelling or water uptake was measured according to Siripriya et al ⁽⁷⁾ by impregnation 1 gm of the powder in PBS (Phosphate Buffered Saline, PH 7.4) at 37 °C for 24 hours in a numbered cylinder in order to measure the swelling

4- Results and discussion

4-1- Effect of MBA Concentration on the swelling of CMC-PMBA graft copolymer

Most of the hydrogels or superabsorbent polymers are usually prepared by using N, N1-methylenebisacrylamide (MBA) as a crosslinker. We know that the type of crosslinking agent and its concentration greatly affects the network formation which ultimately influences the swelling behavior of the hydrogels. In order to examine the influence of concentration of crosslinker was studied.

N, N1-methylenebisacrylamide was chosen as a crosslinker for testing its effect on the swelling capacity of (CMC-P-MBA) hydrogels. The concentration of MBA was varied from 0.01 to 1.5 gm MBA/10gm CMC and the swelling of the (CMC-P-MBA) results are depicted in table (1) and Figure (1). ⁽⁸⁾

It is observed that as the concentration of MBA increases from 0.01 to 1.5gMBA/10g CMC the swelling ratio increased then decreases according to increasing MBA concentration and highest swelling degree is obtained at 0.5gMBA/10g. It is a well-known rule in all of hydrogels that a small increase in degree of crosslinking causes an appreciable decrease in swelling capacity. In fact, more crosslinking concentration causes a higher crosslinking density and decreases the space between the copolymer chains and consequently, the resulting highly crosslinked rigid structure can not be expanded and hold a large quantity of water. ⁽⁹⁻¹⁰⁾

Table (1): Effect of MBA Concentration on the swelling of CMC-PMBA graft copolymer

[MBA]gm	0.1	0.2	0.3	0.4	0.5	1	1.5
Swelling (Vol.)	12	18	20	22	36	32	20

Experimental condition: CMC (DS 0.73) = 10 g , PI = 0.1 g , M:W 1 : 10 , Temp . 30 °c and time 60 min

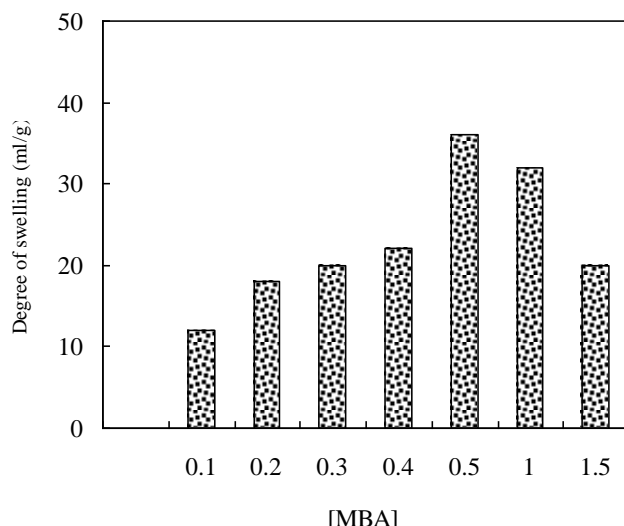


Fig. (1): Effect of MBA Concentration on the swelling of CMC-PMBA graft copolymer.

4-2- Effect of PI Concentration on the swelling of CMC-PMBA graft copolymer

The influence of photo initiator concentration on final swelling capacity of the hydrogel has been studied by varying the PI concentration from 0.0 to 0.1gm/10gm CMC (table 2). Maximum swelling (40ml /g) was obtained at 0.08 gm/10gm CMC of initiator concentration, the lowest result of swelling was obtained at without point and that may have related to the presence of the crosslinker, more or less than this concentration gives hydrogel with decreased swelling capacity (fig. 2). The number of active free radicals on the polysaccharide (CMC) backbone is decreased at lower concentrations than 0.08 gm/10gm CMC which, in turn, resulting in lower graft polymerization extent and consequently lower final water absorbency. Subsequent swelling loss can be explained on the basis of (I) an increase in terminating step reaction via bimolecular collision, which is referred to as “self-crosslinking” and (II) the decrease in molecular weight (M_w) of grafted PMBA of the hydrogel causes to decrease the swelling value. The latter reason is due to the inverse relationship between M_w and initiator concentration. Also, the free radical degradation of polysaccharide (CMC) backbones by sulfate radical-anions is an additional reason for swelling loss at higher PI concentration. ⁽¹¹⁾

Table (2): Effect of Photoinitiator Concentration on the swelling of CMC-PMBA graft copolymer

[PI]g	0	0.03	0.06	0.08	0.1
Swelling (Vol.)	13	18	20	40	36

Experimental condition: CMC (DS 0.73) = 10 g, MBA =0.5 g, L. R= 1:10, Temp. 30 °c and time 60 min.

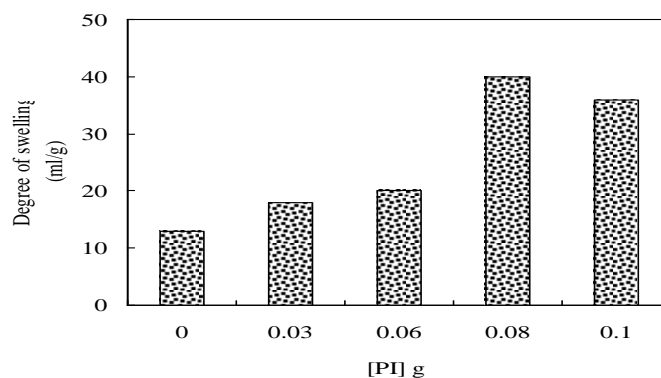


Fig. (2): Effect of Photoinitiator Concentration (PI) on the swelling of CMC-PMBA graft copolymer.

4-3- Effect of reaction temperature on the swelling of CMC-PMBA graft copolymer

The sensitivity of the photopolymerization reaction towards increasing the polymerization temperature was studied using polymerization temperature range from 30°C to 60°C. The polymerization reaction was allowed to take place for 1 hours using 10 g of CMC at liquor ratio of 1:10.

Figure (3) and table (3) show the effect of increasing the polymerization temperature on water absorption (swelling) of the CMC-PMBA graft copolymer produced respectively. The results obtained show that increasing the polymerization temperature from 30°C to 60°C is accompanied by a sharp decrease in the swelling of the graft copolymer produced.

The decrease in the swelling, as a result of increasing the temperature, could be due to the favourable effect of the increased temperature on many reactions that take place during the photopolymerisation, such as the formation of the PI_2^\bullet radical, the formation of the pinnacol derivative and glucosidic bond scission.

It is expected that the more the formation of PI_2^\bullet radicals, as a result of the increased temperature, the more would be the graft copolymer produced. However, the chance of formation of the pinnacol derivative increases also on increasing the polymerisation temperature. This derivative as mentioned earlier, has an adverse effect on the formation of the graft copolymer.

At the same time, there arise glucosidic bond scission forms the $Cello^\bullet$ radical which leads to the chain scission and to the oxidative degradation that are favoured by the increased temperature and the presence of oxygen in the polymerisation system. Very short CMC* molecules might result i.e., the viscosity of the CMC* would be much less. ⁽¹⁾

Also, an increase in the temperature favors the increasing of radical centers, causing high crosslinking points in the hydrogel. So, the swelling capacity of the hydrogel is decreased. ⁽¹²⁻

To increase the polymerization temperature of the current system to more than 30°C is not recommended. ⁽¹⁾

Table (3): Effect of Reaction Temperature on the swelling of CMC-PMBA graft copolymer

(Temp.) ⁰ C	30	40	50	60
Swelling (Vol.)	40	29	26	20

Experimental condition: CMC (DS 0.67) =10g, MBA =0.5g, PI =0.08g, M: L. R= 1:10, and Time 60 min

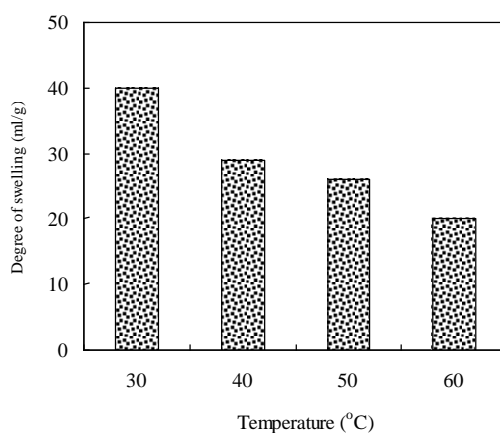


Fig. (3): Effect of Reaction Temperature on the swelling of CMC-PMBA graft copolymer.

4-4- Effect of Liquor Ratio on the swelling of CMC-PMBA graft copolymer

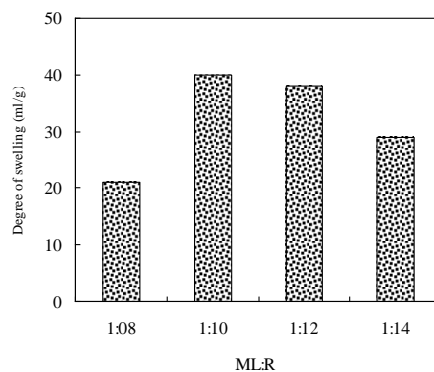
The effect of the material ratio to water (10g CMC: x g water) of CMC - poly (MBA) and on the swelling of the copolymer produced was studied using a material ratio to water range from 1:08 to 1:14, The PI loading and the MBA were kept constant. The homopolymerization was then allowed to take place using 10 g of CMC at 30°C for 1 h of irradiation using the method mentioned before.

Figures (4) and table (4) show the effect of the liquor ratio on water absorption (swelling) of the copolymer produced, respectively. The swelling increases with increasing the liquor ratio from 1:08 to 1:10. Increasing the liquor ratio by more than 1:10 (1:12 to 1:14) was accompanied by a decrease swelling, hence, the number of MBA molecules in the vicinity of the CMC decreases so that the swelling of MBA of poly(MBA)-CMS* graft copolymer decrease. ⁽¹⁾

Table (4) Effect of Liquor Ratio on the swelling of CMC-PMBA graft copolymer

Material: Liquor Ratio [L:R]	1:08	1:10	1:12	1:14
Swelling	21	40	38	29

Experimental condition: CMC (DS 0.73) =10g, PI=0.08g, Temp. 30°C and Time 60 min

**Fig. (4): Effect of Liquor Ratio on the swelling of CMC-PMBA graft copolymer**

4-5- Effect of Degree of Substitution (DS) on the swelling of CMC-PMBA graft copolymer

In order to obtain a perfect crosslinked CMC with, it is necessary to investigate the influence factors on the adsorption capacity. In our previous work, adequate studies suggested that the adsorption capacities of the crosslinked CMC. So herein the effect of DS of CMC was investigated.⁽¹⁴⁾

Figure (5) shows the influence of DS of CMC-PMBA on water adsorption. It is observed that the water adsorption increase with increasing the DS at the range of 0.67–0.73 and then decreasing rate up to about a DS of 0.8 .

It is important to note that the rate of absorbent shown an opposite effect decreasing almost at a DS greater than 0.73⁽¹⁴⁾

The large increase in swelling at low Ds is probably related mainly to the opening up of tightly hydrogen bond cellulose structure by the bulky carboxyl substituents.

The distribution of the substituents along the cellulose backbone will influence the properties of the polymer. Uneven distribution normally gives a tendency of high “gel-blocking” of the superabsorbent and consequently low rate of absorption.

The gel blocking phenomenon occurs when an absorbent polymer swells an effectively prohibits fluid distribution in an absorptive pad.⁽¹⁴⁾

Table (5): Effect of Degree of Substitution on the swelling of CMC-PMBA graft copolymer

(DS)	0.67	0.73	0.8
Swelling (Vol.)	19	40	38

Experimental condition: CMC =10g, PI=0.08g, L.R= 1:10, Temp. 30°C and Time 60 min.

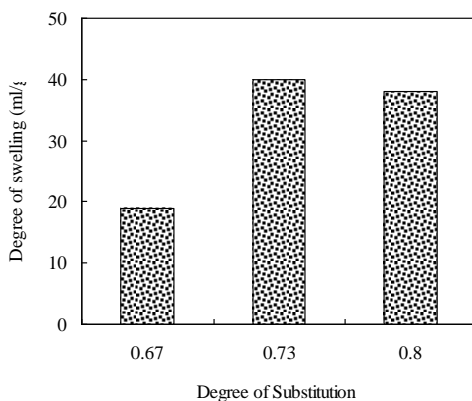


Figure (5): Effect of Degree of Substitution on the swelling of CMC-PMBA graft copolymer.

3-6- Effect of Reaction Time on the swelling of CMC-PMBA graft copolymer

The influences of the time on the grafting reactions are presented in Figure (6) and table (6). It is observed that the absorbency increases substantially with increasing the reaction time up to 3h.

The initial increasing in swelling value can be attributed to increase carboxylate-to-carboxamide ratio values. Intensive electrostatic repulsion of the anions leads to higher swelling of the hydrogel. ⁽¹¹⁾

Table (6): Effect of Reaction Time on the swelling of CMC-PMBA graft copolymer

(Time)h	0.5	1	2	3
Swelling (Vol.)	18	40	42	85

Experimental condition: CMC (DS 0.76) =10g, PI=0.08g, L. R= 1:10, and Temp. 30°C

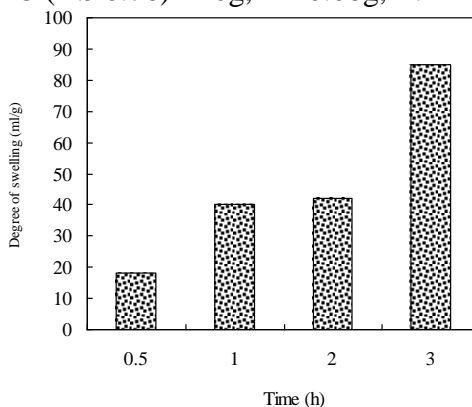


Figure (6): Effect of reaction time on the swelling of CMC-PMBA graft copolymer.

Conclusion

Carboxymethylation was done by different molecular weight of monochloroacetic acid in order to have different DS of both CMC

Hydrogels based on Carboxymethylation (poly CMC- was prepared by UV system using MBA as a crosslinking and photo initiator.

Factors affecting the graft copolymerization reaction i.e., loading of the photo initiator and methylenebisacrylamide, irradiation time, polymerization temperature, material: liquor ratio and the DS of the CMC used were studied.

The reactions of grafted copolymer variables that affect the swelling of the hydrogels were optimized. The maximum water absorbency was achieved under the optimum conditions of poly CMC that found to be. CMC (DS 0.76) 10g, MBA 0.5 gm, PI 0.08g, L.R 1:10, Temp. 30°C and time 3h,

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