Carboxymethylated Cellulose Hydrogel; Sorption Behavior and Characterization

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Abstract: Cotton linters pulp was furnished as raw material for production of CMC. Cotton linters pulp was carboxymethylated at different temperatures and then cross-linked with epichlorohydrin. The water solubility for cross-linked CMC decreased gradually with increasing the reaction temperature. The influence of the CMC composition and etherification temperature on the swelling behavior of CMC hydrogel was investigated. The optimum swelling percentage of CMC hydrogel was obtained on etherification of cotton linter at 40°C. The swelling of hydrogel is pH dependent; the swelling of hydrogel increases with increasing the pH of the bathing media, the highest swelling was in neutral and alkali solution. FTIR spectroscopy and SEM have been used to investigate the fine structure characteristics of the prepared samples. Thermogravimetry (TG) and derivative thermogravimetry (DTG) were carried out for studying the pyrolytic behavior of hydrogel samples.

Keywords: Cotton linter, carboxymethylation, CMC, cross-linking, hydrogel

1. Introduction:

The chemical modification of polysaccharides is the most important rout to modify the properties of the naturally occurring biopolymers and to use this renewable resource in the context of sustainable development. Alkali cellulose and carboxymethyl cellulose (CMC) is the most important cellulose derivatives. Carboxymethylation of polysaccharides is a widely studied conversion since it is simple and leads to products with a variety of promising properties. Sodium carboxymethyl cellulose, NaCMC, is cellulose ether and one of the most important commercial water soluble polymers used today. It is produced on large scale and is applied as an additive in a variety of products. Examples of products where CMC is used in detergents, oil drilling mud, wall paper glues and high purity CMC grade are found in pharmaceuticals, tooth past, food, etc.

The average degree of substitution (DS) of the CMC as well as its degree of polymerization (DP) can vary a lot depending on its use, but DS is usually between 0.5-1.5. CMC is produced from cellulose where the raw material is wood or cotton linters and it is therefore based on a sustainable raw material. It is well known that cellulose is not water soluble, but CMC is made water soluble as a result of a chemical reaction between cellulose and monochloroacetic acid (MCA) in the presence of sodium hydroxide. This reaction is carried in an aqueous alcohol system (Veronica, Göran, and Ulf, 2008), according to the equation [1]:

$$[C_6H_7O_2(OH)_3]_n + nNaOH \rightarrow [C_6H_7O_2(OH)_2ONa]_n + nH_2O$$

$$[C_6H_7O_2(OH)_2ONa]_n + nClCH_2COONa \rightarrow [C_6H_7O_2(OH)_2OCH_2COONa]_n + nNaCl$$

Equation [1]

Hydrogels are three dimensional network of polymers formed by either chemical or physical cross-linking in water (Machado, Bavaresco, Pino, Zavaglia and Reis, 2004). Hydrogels are unique class of polymeric materials which imbibe enormous amounts of water when left in a water reservoir for long times (Bajpai and Anjali, 2003). The underlying property for this unusual behavior of hydrogels is their transition from a glassy to a rubbery state when contacted with thermodynamically compatible solvents (Colombo, 1993). This water sorption property of hydrogels accounts for a great number of biomedical and technological applications such as artificial implants (Williams, 1990), contact lenses (Peppas, 1980), enzyme immobilization (Moustafa , Kahil and Faizalla, 2000), etc. other fields for hydrogel applications cover the area of controlled release technology which is being intensively used in pharmaceuticals and agriculture (Saraydın, Karadağ and Güven, 1998). Many hydrogels are thermo-reversible gels, meaning that they can exist in either liquid or gel form depending on their temperature.

Understanding the gelation of thermo-sensitive hydrogels will provide a useful insight in their applications for many important processes, including drug delivery (Lam, Sunil and Bee, 2007). Lately, hydrogels are used for controlled drug delivery systems when they are in contact with any surface. This could happen through channels or spaces inside the network and the matrix dissolution/disintegration (breaking up) effect. This process is possible due to hydrogels response capacity to temperature changes, pH variation, ionic interaction, chemical compounds, etc. These materials showed a principal reaction by changing shape and volume. Cellulose derivatives have high rigidity; some can swell and be soluble in water or solvents depending on the extent of their degree of substitution. They can provide biodegradable character to any material when they are mixed with other materials since they are polysaccharide derivatives. They can also enhance physical hydrogel properties (Rivas-Orta, et al, 2008). For the methods used to prepare water absorbents from cellulosic materials, the introduction of hydrophilic groups e.g. carboxymethyl (Tsukamoto, 1996) and sulfate (Arai and Goda, 1993) and their cross-linking are the main reactions. Na-CMC as an amylose with many hydroxyl and carboxylic groups can absorb water and moisture, so the hydrogel made of it has many excellent properties, such as high water content, good biodegradation and wide source of its low cost (Huarong et al , 2004). CMC is a key component in controlled drug release pills and in the manufacture of personal care products (Maile, 1990). It is also used in gels applied as protecting agent during heart, thorax and cornea surgery (Pannell, Blackmor and Allen, 1992). It is important to note that cellulosic water absorbents are also prepared by grafting acrylonitrile and acrylic acid onto cellulosic materials followed by hydrolysis in the former case (Rivas-Orta, et al, 2008, Leone, et al, 2008), estrification of sodium carboxymethyl cellulose (NaCMC) was done with acryloyl chloride which contains double bond, resulting in formation of new derivatives of (NaCMC). By this method we can incorporate double bonds in cellulosic structures which can help us to photopolymerize the cellulose for various biomedical applications (Leone, et al, 2008 ,Kunal, Banthia and Majumdar 2005). Nuknshina and other recently reported indicate that the water absorbance of cellulosic water absorbents prepared from carboxymethyl cellulose (CMC) and other cellulosic materials was much lower than those prepared from starch and synthetic polymers except for some grafted celluloses (Nuknshina, 1980, Miyata and Sakata, 1991). Cellulosic water absorbents are widely accepted around the world, probably because of their economical advantages and environmental amiability.

In this study we tried to develop water absorbents from cellulose. Cellulose was carboxymethylated and then cross-linked with epichlorohydrin. Therefore, a study of chemically cross-linked CMC was carried out in order to see the impact of CMC on hydrogel properties. Samples were characterized by FTIR spectroscopy, TGA and SEM. FTIR spectroscopy technique has been used to investigate the fine structure characteristics, relative intensity and assignment of absorption bands for hydrogel samples. Thermogravimetry (TG) and derivative thermogravimetry (DTG) were carried out for studying the pyrolytic behavior of hydrogel samples. Moreover, their swelling behavior at different pH values was measured.

2. Experimental

Cotton linters pulp was obtained from Abo Zaable Chemicals Company (Abo Zaable, Egypt) and used for CMC preparation. The standard testing method of Tappi was used for the determination of α-cellulose and hemicellulose content. The chemical composition of cotton linter was α-cellulose 96.2%, hemicellulose %3.5 and ash 0.08%. The fibers were milled using a 20-mesh screen. All chemicals and solvents used in this study were reagent grade and used without further treatment or purification.

Carboxymethyl cellulose synthesis:

The CMC was synthesized according to a slurry process (Veronica, et al, 2005). 10 g of pulp was first mercerized with aqueous NaOH (30%) for 2hrs at 27^{o}C. Then, filtered and pressed till the weight of the produced alkaline cellulose reached 30g. After that, 7.5g monochloroacetic acid in isopropanol (1:20 cellulose/isopropanol) at 30, 40, and 70^{o}C was added. The reaction was then allowed to proceed under mechanical stirrer for 3hrs. The CMC was neutralized with 0.4N HCl and washed with excess of ethanol (75%) after the reaction to remove the by-product. The carboxylic content was determined by titration using NaOH standard solution and phenolphthalein indicator.

Preparation of cross-linked CMC

CMC (5g dry weight) was mixed with 50g of 17.5% NaOH and stirred at 50^{o}C for 20min. Subsequently epichlorohydrin (50g) and NH_4OH (50g of a 28% solution) were added and the sample maintained at 40^{o}C under reflux for 4 hours. The insoluble cross-linked CMC product was collected by vacuum filtration, washing with ethanol and water, and finally vacuum drying.

Fourier transform infrared analysis (FTIR):

FTIR spectra were recorded by Jasco FT/IR, Nicolet, and a model 670. The samples were measured as thin films using the diffuse reflectance mode of IR spectroscopy. The unit cell used is model no. 0.0030-099 and serial no. 02107-003. The CO_2 of air, moisture oxygen and H_2O of air were eliminated by measuring the background spectra before every sample. Bands are in the region from 4000 to 400cm^{-1} detectors are DTGS.

Thermogravimetric analysis:

TG was recorded by Perkin-Elmer thermal analysis controller AC7/DXTGA7, using a heating rate of 10^{o}C min in nitrogen atmosphere.

Study of surface morphology:

Different samples were investigated via SEM with JEoL JXA-840A electron Probe micro analyzer (Tokyo, Japan). The samples were coated with a thin layer of gold before SEM with a SIS^{o}A Edward, Sputter coater (Crawley, UK).

Determination of hydrogel water absorption:

To test the water absorption capability, 0.1g of the hydrogel was placed in a sieve pouch. The pouch was then immersed to swell in distilled water (30ml). After a suitable period, the sample was taken out from the water. After removing the excess water, the weight of the swollen hydrogel was measured. The swelling ratio (w_c g/g) is calculated by: $\%\text{Swelling } (w_c) = [(ws - w_d)/ w_d] \text{ x}100$

Where w_c is the hold water in percentage absorbed by the hydrogel after 24 hours swelling, and w_s and w_d are hydrogel weights after and before swelling, respectively. Hydrogel swelling was carried out for three CMC samples prepared at different temperatures and different pH values (2, 7and 12).

Water solubility:

A weighed sample of known water content up to 0.1g was placed in 50 ml beaker containing 30ml of deionized water. After 24 hours at room temperature, the water-insoluble fraction was separated by a 1G2 sintered glass filter of known weight. Water solubility was calculated as follows:

Water solubility %=

$$[\{Ax\ (1 - C)\}\ -B/\{A\times\ (1-C)\}]\ \times 100$$

Solubility fraction= 100 - Water solubility

Where A is the initial weight of a sample (g), B is the oven dried sample weight after immersion in water and filtration (g) and C is the amount of water (g) in 1g of the sample **(**Yuehua and Gyosuke, 2001).

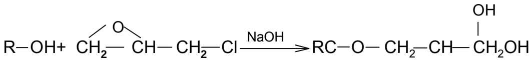
3. Results and Discussion

Carboxymethyl cellulose (CMC) is cellulose ether produced by reacting a dissolving pulp with strong alkali at room temperature in a mercerization stage, which transfers the cellulose to alkali cellulose. Monochloroacetic acid (MCA) is then added and the temperature is raised to facilitate a chemical reaction. The etherification reaction was carried out at 30, 40 and 70°C for 3 hours.

The degree of substitution (DS) for CMC prepared at 30, 40 and 70°C respectively using isopropanol as solvent are 0.51, 0.59 and 0.61 but it becomes 0.17 in water. As we can see the DS increases with increasing the etherification temperature and it was 0.61 at 70°C. It was shown that the etherification temperature during carboxymethyl cellulose preparation had a strong influence on the DS. The higher the temperature between 60 and 70°C during the etherification, the higher the accessibility of swollen alkali cellulose to react with carboxymethylating agent, thus the DS increased. Also using isopropanol as a reaction medium gave DS values more than that obtained in water medium.

The effect of cross-linking reaction on the water solubility of CMC synthesized at different temperatures

Crosslinking of CMC causes prevention or dissolution retardation and improves certain physical properties. Epichlorohydrin (E) is commonly used as a cross-linking agent effectively stabilizes agricultural residues for the preparation of cellulose derivatives (Laszlo, Dintzis, 1994, Nada and Adel, 2007) and brought an improvement in stability of functional group. The reaction of E with cellulose in presence of NaOH is represented by equation [2]:



$$R{-}OH + CH_2{-}\overset{O}{\frown}{-}CH{-}CH_2{-}Cl \xrightarrow{NaOH} RC{-}O{-}CH_2{-}CH{-}\overset{OH}{C}H_2OH$$

Cellulose Epichlorohydrine equation [2]

Figure 1 shows the effect of cross-linking reaction on the water solubility of CMC synthesized at different temperatures. It was found that, the water solubility decreased with the cross-linking reaction of CMC. When the etherification reaction was carried out at 30, 40, and 70°C followed by cross-linking using epichlorohydrin , the water solubility for cross-linked CMC decreased gradually with increasing the reaction temperature and about 37%, 94% and 98% of CMC became water insoluble after the cross-linking of CMC prepared at 30, 40, and 70°C respectively.

Swelling behavior of CMC hydrogel:

The influence of CMC composition on the swelling percent is shown in fig (2). It is obvious from the figure that, the swelling percentage of CMC hydrogel increased reasonably with increasing the etherification temperature from 30-40°C and decreased at etherification temperature 70°C. This is attributed to the creation of network between the CMC molecules and the strength of this network was higher if the etherification had been done at 40°C instead of 70°C. Thus, if a lower etherification temperature had been used the length of the CMC molecules were longer, and longer chain increases the possibility for hydrogen bonding between the chains to have an effect so, the swelling percentage of CMC hydrogel increases (Veronica, Göran and Ulf , 2008).

The swelling studies indicated that the etherified product is pH dependent. Carboxymethyl groups in the gel remain in equilibrium between their natural and ionized form. The dissociation degree is shifted to the right or left side of equation [3] due to the pH.

$$R\text{-}CH_2\text{-}COOH \longrightarrow R\text{-}CH_2\text{-}COO^- + H^+$$

equation [3]

On the other hand, crosslinking of CMC played an important role in the formation of hydrogels as shown from Fig (2). The swelling of hydrogels increases as the pH of the bathing media increases. It is the lowest in solution of pH ≈ 2 and the highest in neutral and alkali solution. The swelling capacity is directly related to both osmotic pressure and electrostatic repulsion according to the level of dissociation. In an acidic medium, no dissociation occurs, the gel structure is devoid of charge, and collapsing is observed as a result of hydrogen bonding formation. With increasing of pH, a dissociation of ionic bond takes place, expansion of the hydrogel occurs. Further neutralization causes only a slight enlargement of swelling and stabilization at a pH value over 7. Then, the electrostatic interactions of ionized carboxyl groups result in stretching of polymer chains, and the equilibrium of swelling is the highest. Ionization allows the hydration of charged oxygen atoms, which promote the formation of hydrogen bonds between polymer and water, and Van der Waals interactions (Radoslaw, et al 2003).

Infra red spectra of cotton linters, CMC and Crosslinked CMC:

Effect of sodium hydroxide treatment:

Fig (3) shows that the infrared spectra of cotton linters and cotton linters treated with sodium hydroxide solution. From Fig (3), it is clear that, the OH groups have a higher value in case of cotton linters treated with sodium hydroxide than untreated one. This is due to that, the sodium hydroxide decreases the hydrogen bonds between the OH groups of cotton linters. This can be confirmed by the shift of OH groups to the higher wave length 4320cm^{-1} in the case cotton linters treated with soda while in case of untreated one the OH group was found at 3320cm^{-1}. Also, from table (1) it is clear that crystallinity index of cotton linters treated with sodium hydroxide is lower than that of untreated one while the value of mercerization depth which has a higher value in case of treated cotton linters than untreated one. On the other hand, some degradation of cellulose chain during treatment with sodium hydroxide. This result was obtained from the relative absorbance of C—O—C bridge between glucose chains at 1162cm^{-1} which has lower value in case of treated cotton linters with sodium hydroxide than untreated one. Moreover, the relative absorbance of C=O at 1720cm^{-1} increases on treatment of cotton linters with sodium hydroxide. Also C=O at 1640cm^{-1} which characterize the aldehydic groups has a higher value in case of treated cotton linters than untreated one.

Effect of temperature:

Fig (4) shows the infrared spectra of cotton linters and the prepared carboxymethylcellulose at 30, 40, and 70°C. From table (2), it is clear that the relative absorbance of OH group at 3400cm^{-1} decreases due to the formation of carboxymethylcellulose as shown in equation [1].

On the other hand, the relative absorbance of CH_2 group at 2900cm^{-1} and 1425cm^{-1} increase by carboxymethylation. This relative absorbance of CH_2 group increases due to the reaction of cellulose with monochloroacetic acid which adds the CH_2 to the formed carboxymethyl cellulose. This quantity of CH_2 group increases by increasing the reaction temperature of carboxymethylation from 30 to 40°C and then decreased by increasing temperature to 70°C. The relative absorbance of C=O band which is characteristic to COOH at 1720cm^{-1} and to CHO at 1640cm^{-1} increases by carboxymethylation. On the other hand, a slightly increase in crystallinity index of carboxymethylcellulose due to heating and reaction of monochloroacetic acid with cellulose. The mercerization depth of the carboxymethylated cotton linters has a value higher than cotton linters itself. This mercerization depth increases by increasing the reaction temperature of carboxymethylation reaction from 30 to 40°C and then decrease by increasing the reaction temperature to 70°C.

Effect of carboxymethylation medium and crosslinking:

Fig (5) shows that the infrared spectra of CMC prepared in water and solvent medium at 70°C. Table (3) shows the different relative absorbance of different groups of the produced CMC in water, solvent medium and the crosslinked CMC at 70°C. It is seen that the relative absorbance of OH groups in the prepared crosslinked CMC in solvent medium have a higher value than that the prepared CMC in water medium. This can be attributed to that, a part of the prepared CMC and small chains dissolved in water medium which decreases from the reaction and consequently the DS of the formed CMC in water medium decreases.

The relative absorbance of C=O at 1720cm^{-1} which is characteristic to COOH groups has a higher value in case of CMC prepared in the solvent medium and crosslinked. This is due to the decrease of dissolution of the formed CMC in the solvent medium. On other hand, the crosslinked CMC has lower value of relative absorbance of COOH group due to the crosslinking which formed between OH groups of cellulosic chains. The crystallinity index of the prepared CMC in the solvent medium has a higher value than in water medium. The mercerization depth of CMC prepared in water medium is higher than that of CMC prepared in solvent medium. This is confirmed by the higher crystallinity index of prepared CMC in the solvent and crosslinking media. It is clear that, the crosslinked CMC has a lower mercerization depth than that of uncroslinked CMC. This due to that the crosslinker increases the net and branches between OH groups which found in crosslinked CMC.

Study of surface morphology:

Fig (6) shows SEM of cotton linter, cotton linter treated with NaOH and crosslinked CMC. It is seen from the figure that SEM of untreated cotton linters under various magnifications shows the shape and size distributions of the microfibrils in cotton linters. The surface of untreated cotton linters is almost free of trenches, but there are obvious bounding edges in different regions (Haibo, et al, 2007). The surface of mercerized linters was also studied and showed that the fibers bundles are loosened, moving then slightly apart. During the treatments, cellulose chains was degraded by the hydrolysis of glycosidic bonds, resulting in a rearrangement of the crystal packing of chains from native cellulose I (chains aligned in parallel) to cellulose II (anti- parallel) (Beatriz, Mohamed and Frollini, 2006), which causes collapsing of the fiber structure, resulting in roughness(deeper and broader strains).

As shown from the same figure, the SEM images of the Crosslinked CMC at different temperatures shows that, the microstructure was changed from fiber structure to closed-grained structure. During the solvent precipitation, the polymer was extensively swollen in water. When the organic solvent that is miscible with water was added, water was displaced from the network by the organic solvent. During this displacement process, the polymer retained its expanded porous structure. By vacuum drying the residual organic solvent was easily removed and shrinkage obtained for the dried hydrogel (Chen, Liu, and Tan, 2008).

Pyrolytic behavior of thermogravimetric analysis

The pyrolytic process of a solid material can be expressed by the following equation:

$$A(s) \rightarrow B(g) + C(s)$$

The rat of disappearance of solid reactant A(s) can be expressed by Arrhenius equation:

$$dx/dt = Z \exp(-E/RT)\, f(\alpha)$$

Where: α is the fraction of A(s) decomposed at time (t) and be defined by

$$\alpha = W/Wc$$

W: weight loss up to time (t) or temperature (T)
Wc: weight at the completion of the reaction.

The term (α) is a function of weight loss and can be expressed as follows:

$$f(\alpha) = (1-\alpha)n$$

The study of the thermal decomposition of cotton linters, cotton linters treated with NaOH, CMC, and CMC crosslinked samples has been achieved by using thermogravimetric curves based on the weight loss as a function of temperature as shown in fig (7). The calculation k of the activation energies (E) of the thermal decomposition has been accomplished for different samples by applying Coats-Redfern equation (Coats, and Redfern, 1964):

$$\log[-\ln(1-\alpha)/T^2]=\log[RZ/\phi E(1-2RT/E)]-E/2.303RT$$

Where: R: General gas constant (1.98 Cal/mol/K)
E: Activation energy (Cal /mol))
Z: Pre-exponential factor (min-1)
ϕ: Linear heating rate (K min-1)

A plot of log[- ln (1- α)/ T2] against 1/T, where the order of the reaction could be assumed first order, should result in straight line with slop (–E/2.303R).

Analysis of thermograms, fig (8), of cotton linters, cotton linters treated with NaOH, CMC samples (CMC prepared at 40°C and gel of CMC prepared at 40 and 70°C) shows thermal decomposition of different pyrolytic reactions of respective structural components. Based on the characteristics peaks observed on the thermograms of the different samples mentioned before, the thermal decomposition process could be divided into three major reaction zones:

In the first Zone (up to 190 °C), the weight loss has mainly attributed to vaporization of the hydrated water which is bounded in the pores system of the internal surface area of the superamolecular cellulosic structure leading to accessional chain scissions, but maintains the β-1,4 polysaccharide skeleton (Zanier, and Jachle, 1996).

The calculated energies of activation values in the first zone, table (4), increase with increasing the groups attracting the water molecules. The sharp decrease of energy of activation in the first zone for gel of CMC prepared at 70°C may be attributed to the destruction of the pore system of the cellulosic structure as a result of chain degradation during the formation CMC sample at high temperature 70°C, and consequently decreasing of the bounded water molecules which facilitate the dehydration process, i.e. the free water molecules associated to gel of CMC prepared at 70°C is the predominate which are easily removed (Kok, and Keskin, 2001).

In the second zone (from 200 to 400°C), the weight loss is due to dehydroxylation associated with the pyrolytic fragmentation leading to formation of aromatized entities. The activation energies values in the 2nd zone, table (4) decrease with formation of NaOH treated cotton linters or carboxymethylated cotton linters. Also, energies of activation in the 2nd zone decrease due to the crosslinking of CMC samples. This indicates that the thermal stability of cellulosic skeleton decreases with increasing the degree of substitution (carboxymethylation) or gel formation via crosslinking by epichlorohydrine **(**Santos, Souza, and Santos, 2001).

In the 3rd zone (above 400°C), the thermal decomposition is likely related to the combustibility of the highly crosslinked aromatized entities formed in the 2nd zone. The activation energies values in the 3rd zone of NaOH treated cotton linters or CMC samples have lower values than that of pure cotton linters. This may be attributed to the oxygen content in the combusted aromatized entity (Bermejo, et al, 1997).

Table (1): The relative absorbance of different bands of cotton linters and treated cotton linters with sodium hydroxide.

Band	Relative absorbance	
	Cotton Linters	Cotton linters treated withed with NaOH
OH (3400 cm^{-1})	1.49	1.60
CH_2 (2900 cm^{-1})	0.95	1.00
C=O (1720 cm^{-1})	0.26	0.57
Keto group (1640 cm^{-1})	0.52	1.39
CH_2 (1425 cm^{-1})	0.96	2.25
1162 cm^{-1}	1.29	0.67
1060 cm^{-1}	1.63	1.07
900 cm^{-1}	0.52	0.14
CrI (1425cm^{-1}/900cm^{-1})	1.92	1.10
Mercerization depth (1375cm^{-1}/1335cm^{-1})	1.08	1.35

Table (2): The relative absorbance of the different bands of cotton linters, CMC prepared at 30, 40 and 70°C.

Band	Relative absorbance			
	C.L	CMC 30°C	CMC 40°C	CMC 70°C
OH (3400 cm^{-1})	1.49	1.29	1.15	1.3
CH_2 (2900 cm^{-1})	0.95	1.22	1.30	1.25
C=O (1720 cm^{-1})	0.246	1.10	1.18	1.01
Keto group (1640 cm^{-1})	0.52	1.20	1.19	1.01
CH_2 (1425 cm^{-1})	0.96	1.11	1.16	1.12
1162 cm^{-1}	1.29	1.09	1.17	1.27
1060 cm^{-1}	1.63	1.11	1.62	1.43
900 cm^{-1}	0.52	0.55	0.52	0.53
CrI (1425cm^{-1}/900cm^{-1})	1.92	2.00	2.08	2.12
Mercerization depth (1375cm^{-1}/1335cm^{-1})	1.08	1.35	1.45	1.10

Table (3): The relative absorbance of the different bands of CMC cotton linters prepared in water and solvent and Cross-linker at 70°C.

Band	Relative absorbance		
	CMC 70°C (Water)	CMC70°C (Solvent)	CMC70°C (Cross linking)
OH (3400 cm^{-1})	1.49	1.52	1.86
CH_2 (2900 cm^{-1})	1.25	1.17	1.70
C=O (1720 cm^{-1})	0.57	1.10	0.62
Keto group (1640 cm^{-1})	1.01	1.54	1.32
CH_2 (1425 cm^{-1})	1.12	1.54	1.34
1162 cm^{-1}	1.27	1.24	1.14
1060 cm^{-1}	1.43	1.32	1.18
900 cm^{-1}	0.52	0.29	0.38
CrI (1425cm^{-1}/900cm^{-1})	2.12	0.29	3.52
Mercerization depth (1375cm^{-1}/1335cm^{-1})	1.10	0.91	0.82

Table (4): Energy of activation values of different samples calculated from the essential peaks on the thermograms.

Sample	Energy of Activation, K Joule mol Sample		
	1st Zone	2nd Zone	3rd Zone
Cotton linters	———	102	66.31
Cotton linters treated with NaOH	20.58	19.54	13.96
CMC prepared at 40°C	23.97	44.88	20.08
Gel of CMC prepared at 40°C	25.43	27.97	38.86
Gel of CMC prepared at 70°C	8.69	11.73	21.69

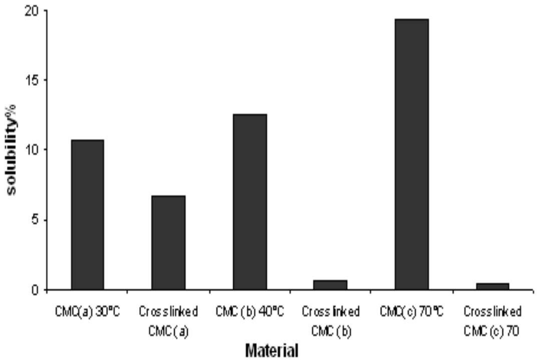


Fig (1): The effect of crosslinking reaction on water solubility of CMC prepared at different temperatures.

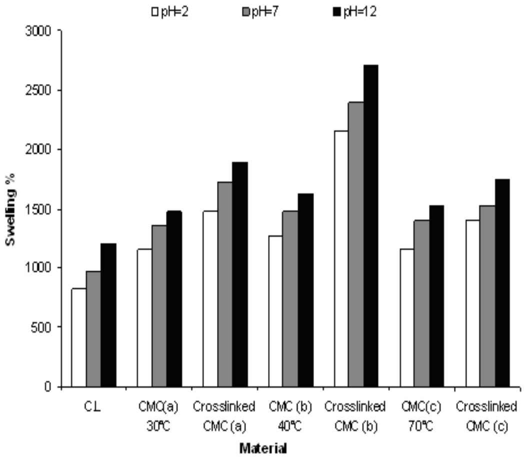


Fig (2): The effect of pH value on the swelling behavior of CMC.

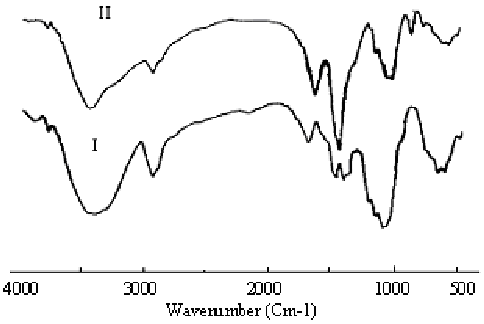


Fig (3): Infra red spectra of I- cotton linter and II- cotton linter treated with NaOH.

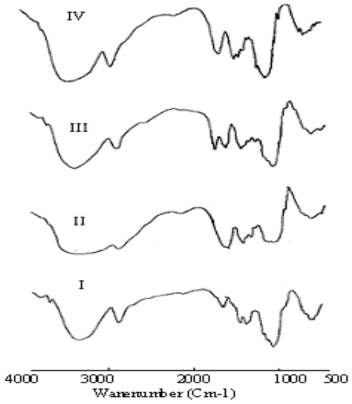


Fig (4):Infra red spectra of cotton linter (I) and CMC prepared at 30°C (II), at 40°C (III) and at 70°C(IV)

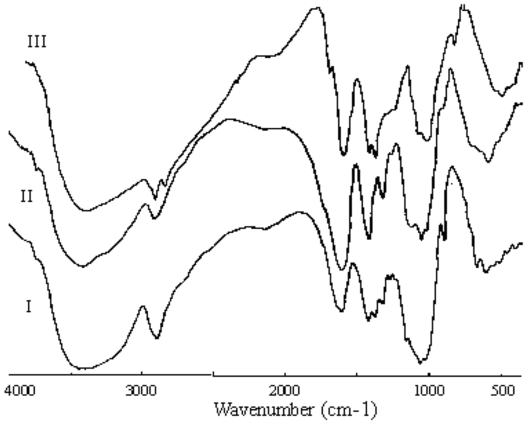
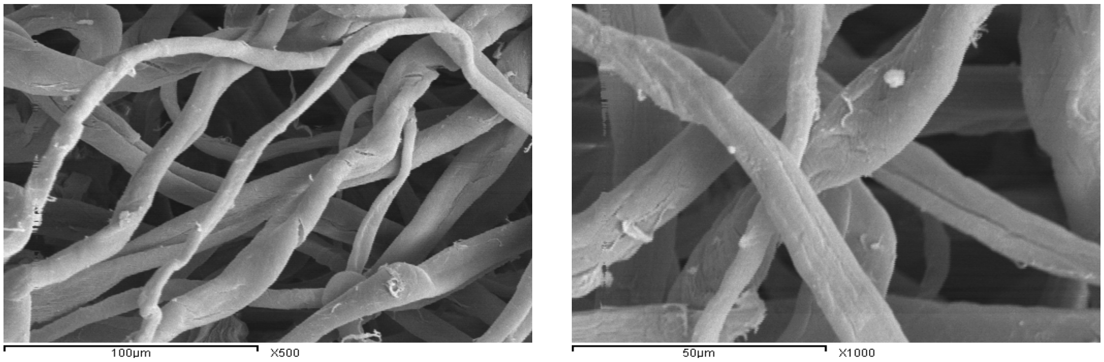
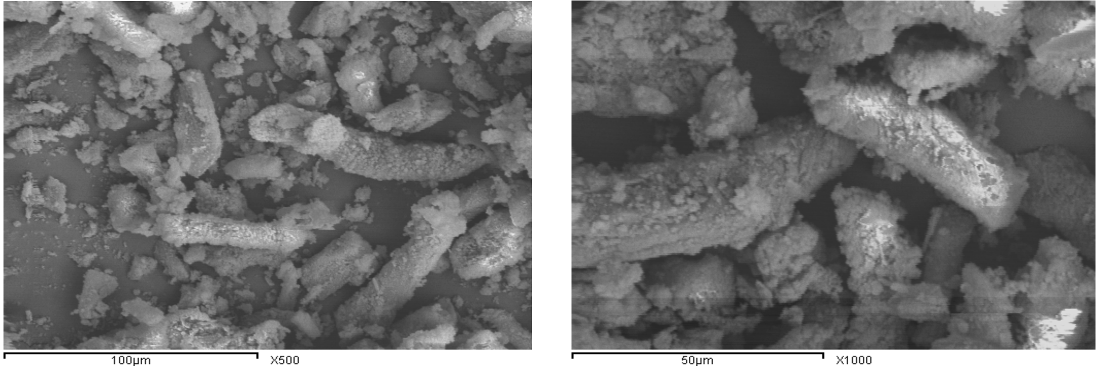


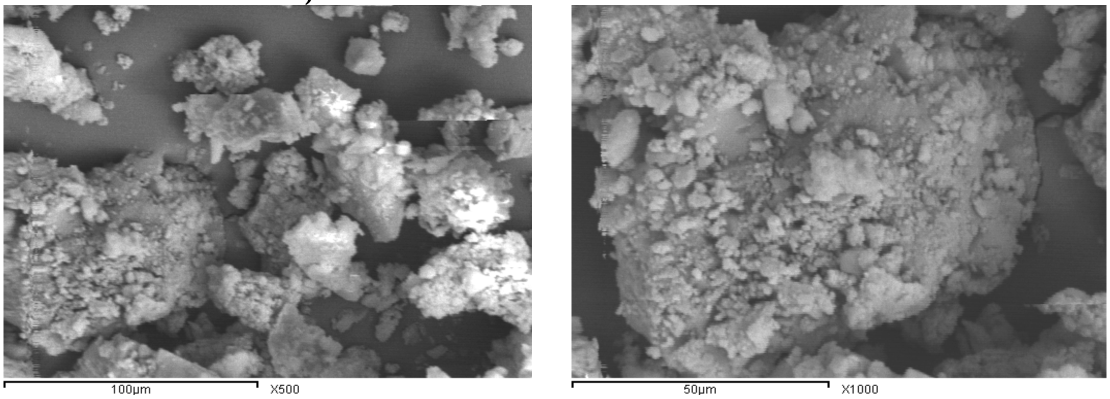
Fig (5): Infra red spectra of CMC prepared at 70°C in presence of I-water, II- solvent and III -cross linker



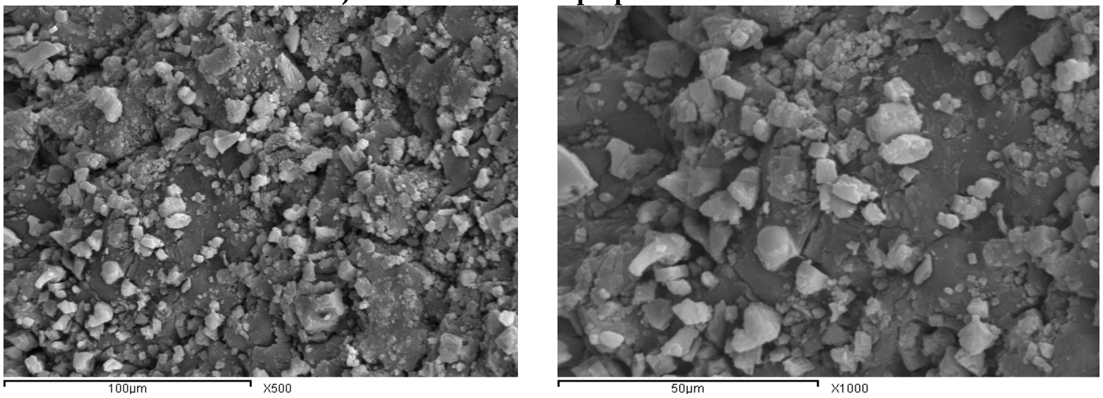
a) Cotton linter at 500 &1000



b) Cotton linter treated with NaOH at 500 &1000



c) Cross linked CMC prepared at 30°C



d) Crosslinked CMC prepared at 40°C

Fig (6): ESM of, a) Cotton linter, b) Cotton linter treated with NaOH, c) CMC crosslinked at 30°C and d) CMC crosslinked at 40°C.

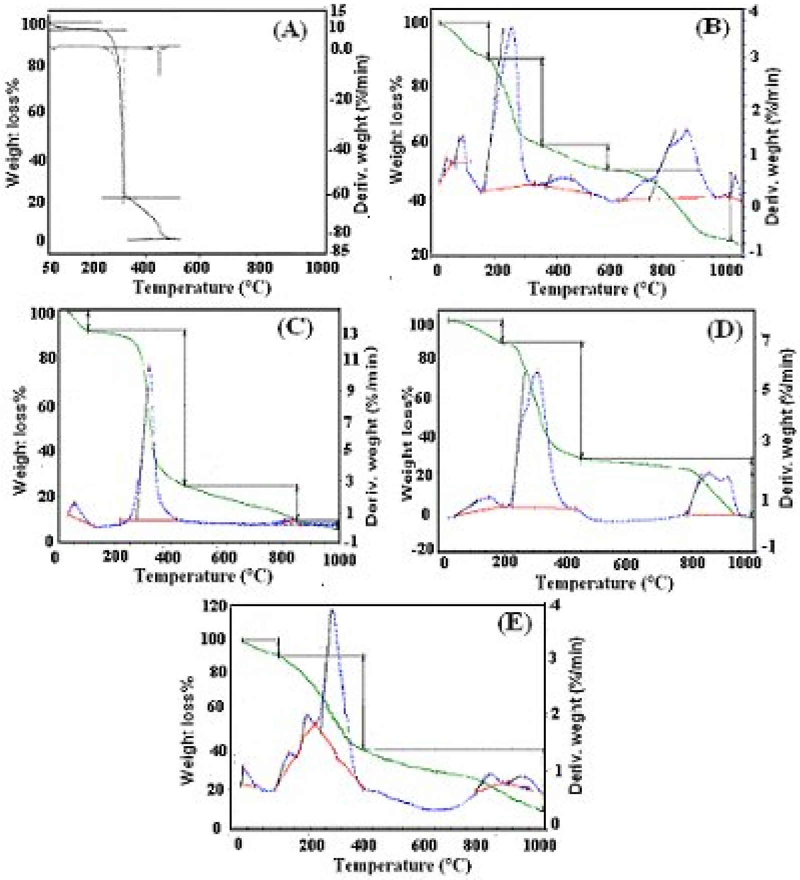
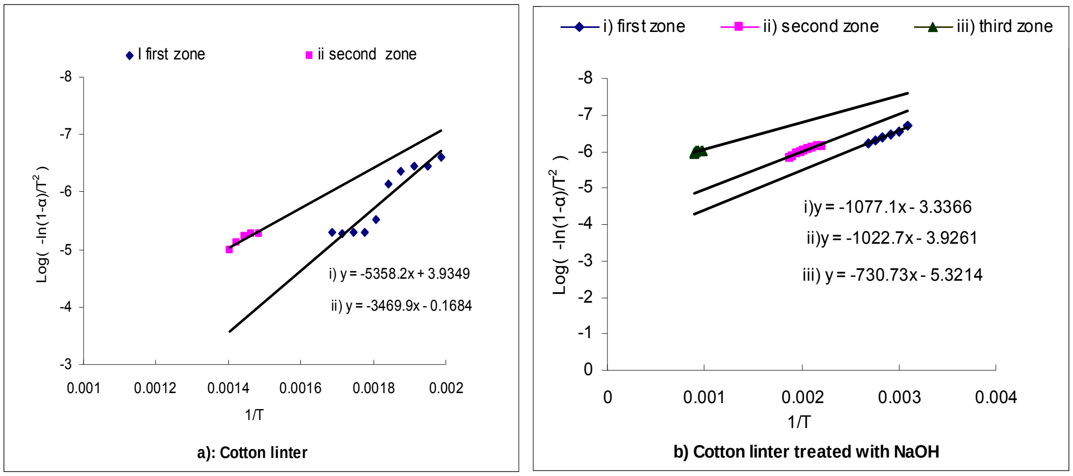
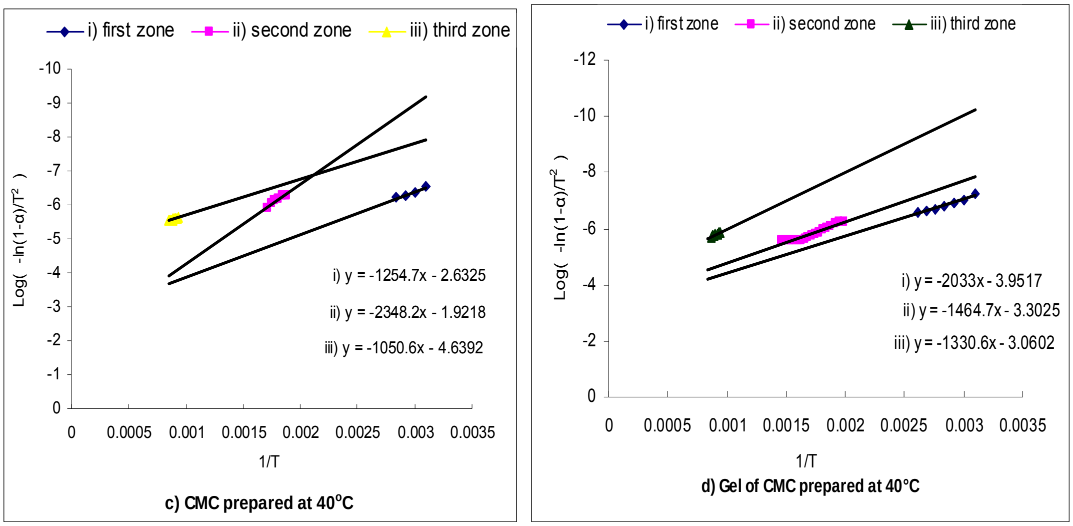


Fig (7): Thermogravimetric curves of Cotton linter (A), Cotton linter treated with NaOH (B), CMC prepared at 40°C (C), Gel of CMC prepared at 40°C (D) and Gel of CMC prepared at 70°C (E).



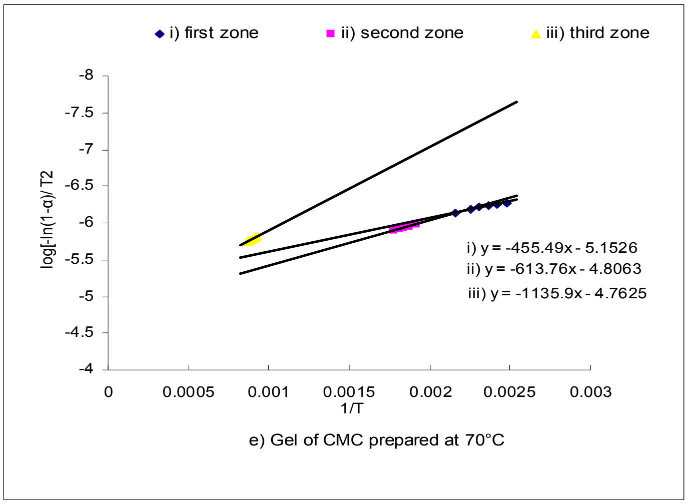
a): Cotton linter

b) Cotton linter treated with NaOH



c) CMC prepared at 40°C

d) Gel of CMC prepared at 40°C



e) Gel of CMC prepared at 70°C

Fig (8): Thermograms of, a) Cotton linter, b) Cotton linter treated with NaOH ,c) CMC prepared at 40°C, d) Gel of CMC prepared at 40°C and e) Gel of CMC prepared at 70°C.

4. Conclusion

The studies performed confirmed that the crosslinking of CMC with epichlorohydrin resulted in formation of a hydrogel substance with decreased water solubility and improved swelling behavior. Since the degree of swelling of the crosslinked product changes as the pH is varied over a wide range it can be used as a pH responsive polymer for various applications.

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