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Hydrogel prepared from biomaterials specifically from Carboxylmethyl cellulose and its blend with starch for metal removal from water

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Abstract: Hydrogel is a crosslinked polymeric network which is water swelling produced by the simple reaction of monomers. This polymeric material exhibits the ability to swell and retain a significant fraction of water within its structure, but will not dissolve in water. A hydrogel is a network of polymer chains that are hydrophilic, as a colloidal gel in which water is the dispersion medium. Hydrogels are highly absorbent and they can contain over 90% water. Hydrogels also possess a degree of flexibility very similar to natural tissue, due to their significant water content. A study on hydrogels for various applications with a sustainable and environmental friendly pure biomaterial is conducted. Sodium salt of carboxy methyl cellulose was used as the base material, which is the biomaterial for hydrogel preparation with optimum crosslinking. It is also studied the CMC/ starch blend with crosslinking. The Hydrogels were characterized with FTIR and physical properties. Thermal analysis was also conducted using TGA and DSC. Metal adsorption was confirmed with the help of UV absorbance.

Introduction:

Cellulose is tone of the most abundant renewable material in the world. It is insoluble in water [1] make it suitable for hydrogel formation. Introducing various substituent in the cellulose structure decreases the number of the strong hydrogen bonds between the hydroxyl groups, thus water solubility can be reached relatively easily. Common groups are alkyl, hydroxyalkyl and carboxymethyl functional groups are used to modify cellulose [2, 3]. For gelation purposes, carboxymethylcellulose (CMC) is in the base material, but significant amount of research works in literature is available for other cellulose derivatives also.

Carboxymethylcellulose-based Hydrogels are prepared from aqueous solutions with several crosslinking methods. Crosslinking agents like polycarboxylic acids, epichlorohydrin and *N*, *N′*-methylene-bisacrylamide (MBA) are commonly used, but the gelation can also be achieved with multivalent cations like Fe^{3+} as well [4]. For the initiation of the crosslinking reaction in pure CMC high energy irradiation (both electron beam and gamma irradiation) is frequently applied [5]. A great advantage of irradiation is that gel formation occurs even without crosslinking agents. The presence of crosslinkers greatly improves the gelation process, resulting in better gelation and milder required synthesis conditions. The gelation process is affected by several parameters, such as chemical structure and molecular mass of the polymer, solute concentration, absorbed dose and atmosphere [6, 7].

Starch is also a very cheap renewable resource, which is mostly used as a copolymer in synthetic polymer based hydrogels. Homogeneous structure of starch is obtained by starch pregelatinized with heat treatment before the copolymerization [8, 9]. Crosslinking of Hydrogels can be achieved by initiator system or by high energy irradiation which give free radical crosslinking and are having very high swelling capabilities. The properties of hydrogels are influenced by the starch source and different amylopectin/amylose ratio [10, 11].

Starch based hydrogels combined with other renewable materials like starch/chitosan hydrogels, which gives hydrogels have poor water uptake. Carboxymethylcellulose is mostly applied in copolymers with other cellulose derivatives and blends with other low cost, renewable materials [12-14]. Cellulose and its water soluble derivatives were used mostly for the preparation of various composite films with gelatinized starch. Hydrogels were synthesized with carboxymethyl starch and carboxymethylcellulose in the presence of MBA crosslinker [15].

The goal of this work is to prepare pure crosslinked CMC and CMC/starch hydrogels with improved superabsorbent properties as compared to pure CMC based gels. Starch/CMC blend is prepared by taking starch and CMC in different ratio. Citric acid is used as catalyst. Properties were studied. The effect of the starch content on the gel properties at various synthesis conditions was examined. Characterisation was done by FTIR, and thermal studies by DSC and TGA. Swelling studies were conducted under various conditions.

Experimental:

Materials required

CMCNa (MW 700 kDa, DS 0.9 ,viscosity 1%aqueous solution at 20^0 c, pH of 2% solution-6.0-8.0) , Citric acid (Merck Life Science Pvt Ltd) (M=211.14 g/mol) by Nice chemicals Pvt Ltd. Potato starch (25% amylose and 75% amylopectin) by CTCRI Trivandrum.

Preparation of the Crosslinked CMC

An appropriate amount of CMC solution was agitated for 1 hour at 70 degree Celsius.1 percentage citric acid solution was added as crosslinker and allowed to mix for another 30 minutes. The solution was then dried at 70°C until a film is formed. The film was shredded with a blender, and then ground into a powder with a mortar and pestle.

Preparation of the Crosslinked CMC/Starch Blend

The cross-linked CMC/ starch blend prepared as follows: An appropriate amount of starch dissolved in distilled water (DW) in water bath 800C for 45 minute. Dried film of the cross-linked CMC was crushed and dissolved in DW. Using magnetic hot plate, gelatinized starch (step1) mixed with the solution obtained from step 2 for 30 minute at 70^0C. Result paste was dried overnight at100^0C, crushed, and tested.

Starch/CMC blend was prepared by mixing 50% starch and 50% CMC crosslinked with 1% citric acid. Different ratios of Starch/CMC blend was prepared by mixing Starch and CMC in different ratio and their properties were studied. Then 75%Starch and 25%CMC was blended. Finally 25% Starch and 75% CMC was blended and their properties were studied. The effect of the starch content on the gel properties at various synthesis conditions was examined.

Characterization

1. Water Absorption Capacity (WAC): Pre weighed amount of hydrogel was placed in water for 24 hours in room temperature. The weight changed happened to hydrogel was calculated in percentage.

2 Thermograviametric analyses (TGA): TGA is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature or as a function of time. Micro thermo balance measures any changes in the mass of the sample, whether due to adsorption of oxygen ,thermal degradation, oxidation or other heterogeneous reactions.TGA was determined using the instrument Q50 at 600 ^{0} C at 10 ^{0} C per minute.

3 Differential scanning calorimetry (DSC): Thermal property of films was determined using a differential scanning calorimetry. The instrument model Q20 at the temperature range -20 to 300 at 10 ^{0} C per minute was used to study DSC.

4 UV analysis: The instrument used to study UV was Rigol ultra 3600 in the temperature range from 800-200 ^{0} C.

5 FTIR analyses: Fourier transform infrared spectroscopy (FTIR) has traditionally been used in material analysis within the chemical industry; however, more recently, it has been applied to biological and biomedical analyses.

Results and Discussion

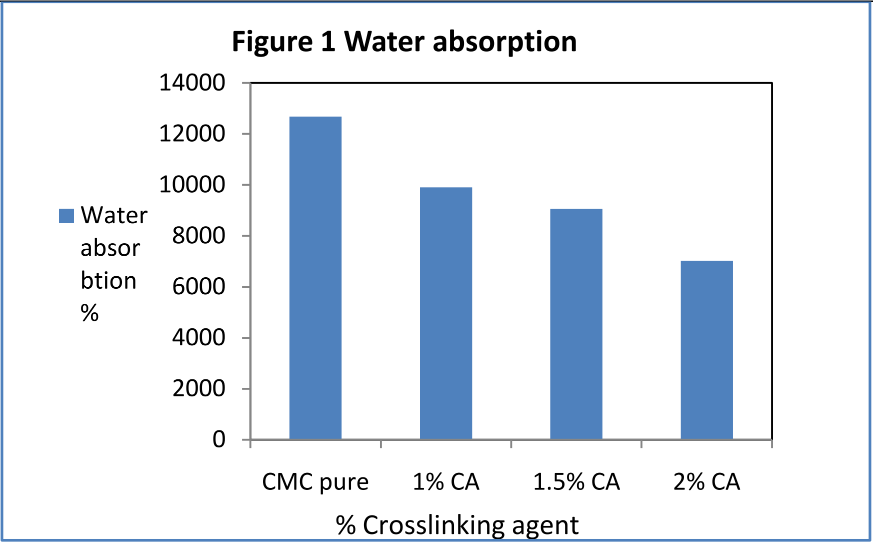
1. Physical Properties

Table: 1Physical properties of hydrogels

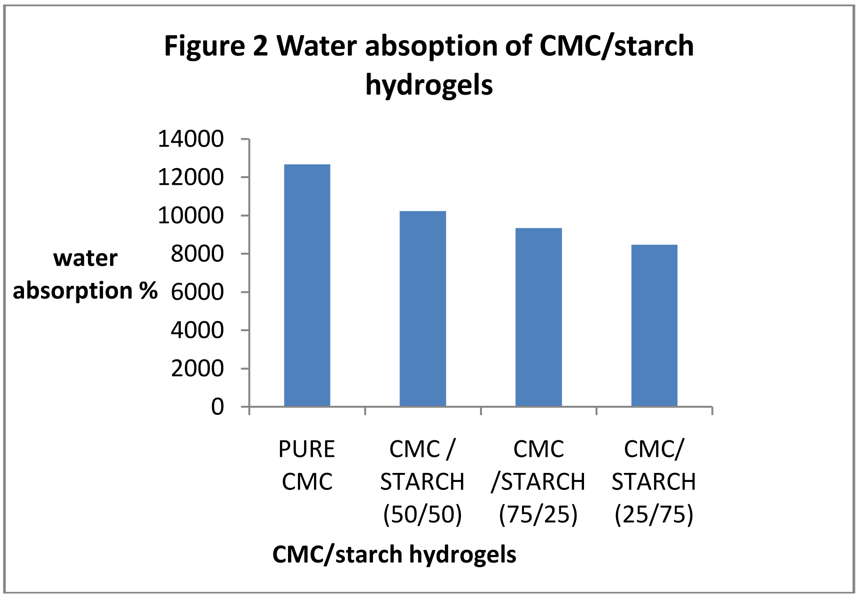
SL NO	Film	Thickness (mm)	Density(g/cm^3)
1	*CMC pure*	0.05	0.013
2	*1% CA*	0.049	0.015
3	*1.5% CA*	0.0485	0.014
4	*2% CA*	0.0484	0.010
5	CMC / STARCH (50/50)	0.045mm	0.014
6	CMC /STARCH (75/25)	0.0415mm	0.19
7	CMC/ STARCH (25/75)	0.0325mm	.032

Table 1 shows the physical properties of CMC /citric acid hydrogel based films. CMC/1% CA shows greater thickness and density compare with others.

Figure 1 shows the water absorption behavior with changing crosslink agents. Results shows that this hydrogel belong to the superabsorbent hydrogels, since it absorbs more than 58 times its original weight. Greater water absorption is shown by CMC 1% citric acid as crosslinking agent when compared with 1.5% and 2%.Citric acid is used as crosslinking agent. As the amount of crosslinking agent increases it is very clear that water intake decreases which is the general tendency of super absorbing hydrogels.



Water absorption of starch/CMC blend hydrogels crosslinked with citric acid, of different ratios was examined. Water absorption values of these hydrogels are shown in the given figure 2. It is evident that the 50/50 ratio of starch and CMC gave maximum water absorption. All the hydrogels are qualified for supersbsobant characteristics as the water absorption is very high.



2. UV Analysis

UV absorption of the CMC/Citric acid film was analyzed. The graph (Figure 3) shows the absorbance of UV for Cr $^{2+}$ ions by the hydrogels. It is found that absorbance decreases as the time increases reaches a minimum, and becomes steady state or in equilibrium. The absorbance of crosslinked hydrogels are also estimated, which shows as crosslinking increases amount of Cr $^{2+}$ ion increases. The trends in all hydrogels are found to be same.

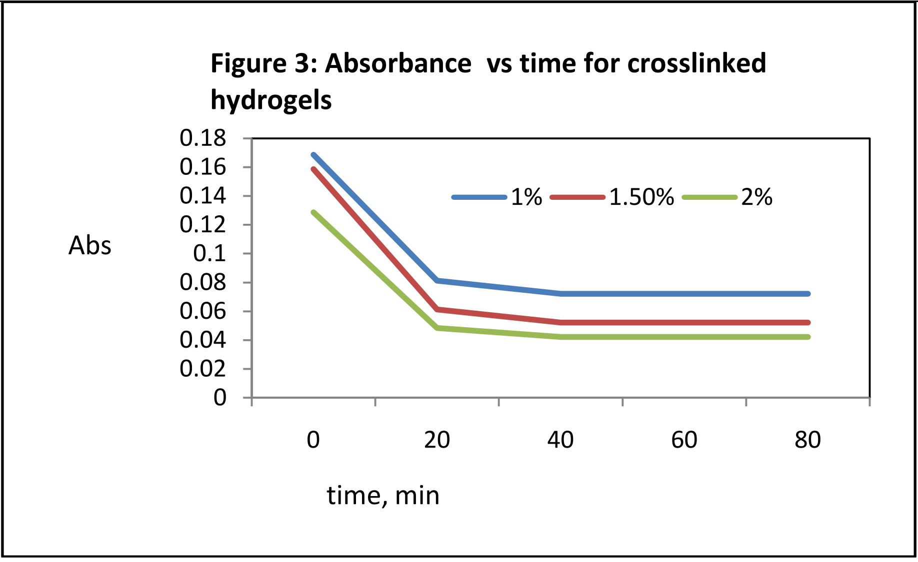
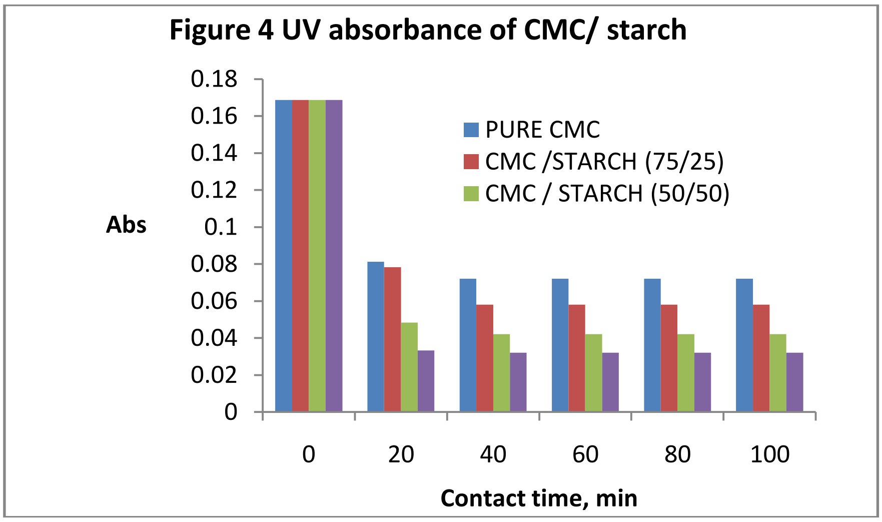


Figure 4 shows the UV absorbance ratios of the CMC/starch blend crosslinked with citric acid. UV absorption of the CMC/Citric acid film was analyzed. The graph shows the absorbance of UV for Cr $^{2+}$ ions by the hydrogels. It is found that absorbance decreases as the time increases reaches a minimum, and becomes steady state or in equilibrium. The absorbance of crosslinked hydrogels are also estimated, which shows as crosslinking increases amount of Cr $^{2+}$ ion increases. The trends in all hydrogels are found to be same. According to the water absorbance and retention this material confirmed to be a super absorbing hydrogel.



3. TGA

Thermo gravimetric analysis of the CMC/CA (1%) film was analysed. Figure 5 shows the TGA thermogram of CMC/ citric acid hydrogel with 1 % crosslinking agent present. TGA curve and its derivative TGA curve of CMC sample is presented in Figure. 5. TGA curves show that the thermal stability of the sample and the degradation is completed in two steps. These steps are distinguishable in the diagram of mass loss (TGA %) during heating as well as more clearly in the diagram of derivative mass loss (TGA). The weight of the sample is plotted against temperature or time to illustrate thermal transitions in the material such as loss of solvent and plasticizers in polymers, water of hydration in inorganic materials and decomposition of the material.

The sample shows a small (5–15%) mass loss for the first decomposition step and more significant mass loss (39–75%) for the second step. All volatiles and easily degradable organic materials got removed in this temperature. The lower values of percentage mass loss in the first decomposition step may be due to the evaporation of bound water [1]. The higher values of the mass loss in the second decomposition step may be attributed to the degradation of side chain and the loss of CO_2 in the case of CMC. Derivative TGA curves show two broad temperature peaks corresponding to the first and second decomposition. Degradation is maximum at 267 ^{0}C.

Figure 6 shows the TGA thermogram of CMC/ starch hydrogel. TGA curves and their derivative TGA of CMC/starch blend sample are presented in Figure 6. The sample shows a small (12%) mass loss for the first decomposition step and more significant mass loss (42%) for the second step. Degradation is maximum at 267 ^{0} C. All volatiles and easily degradable organic materials got removed in this temperature. Starch/CMC blend shows transitions at 122.19 ^{0} C, at 283.27 ^{0} C and at 372.88 ^{0} C.

Figure 5 TGA of CMC/ 1 % citric acid

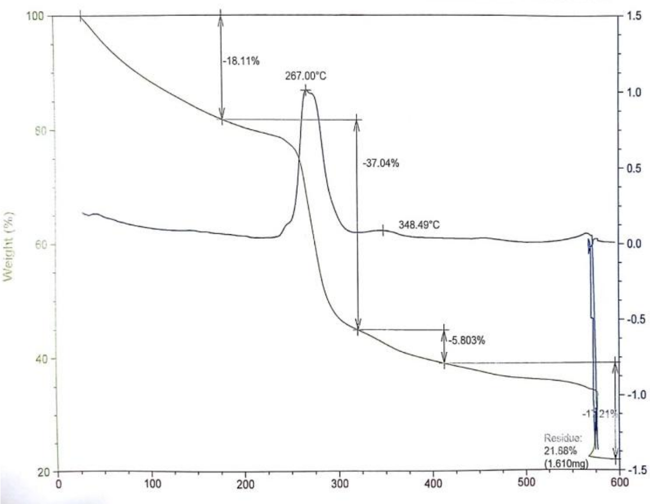


Figure 5: TGA of CMC crosslinked with CA

Figure 6 TGA graph of CMC/Starch hydrogel (50/50)

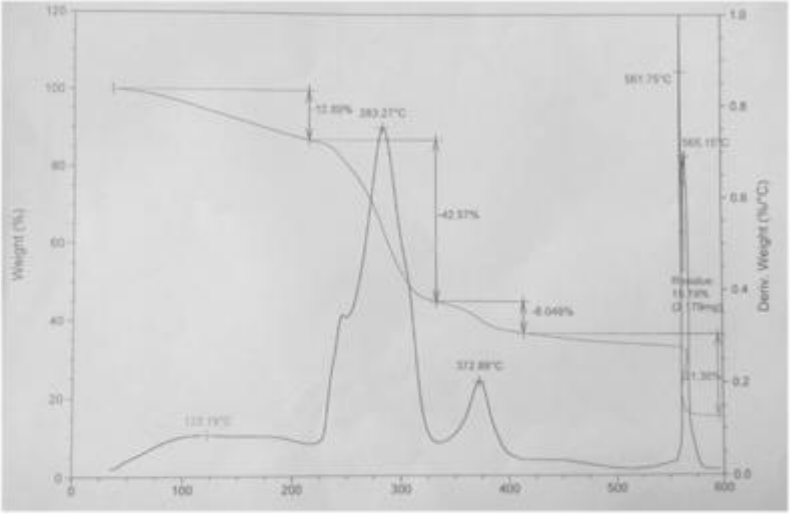


Figure 6: TGA of CMC blend Starch

DSC

DSC analysis of the CMC/CA- 1%film was done which is shown in figure 7. Differential Scanning Calorimetry (DSC) is a thermal analysis technique used to measure changes in heat flows associated with material transitions. DSC measurements provide both qualitative and quantitative data on endothermic (heat absorbing) and exothermic (heat evolving) processes. DSC is commonly used to determine the glass transition temperature and crystalline melting point of polymeric materials. This technique can also be used to determine the percent crystallinity of a polymers, oxidative induction time (OIT) of a material, heat of reaction, and normal boiling point. The figure shows the major transition at 127.84 ^{0} C.

DSC is capable of revealing first and second order thermal transitions like melting(Tm), crystallization (Tc) and glass transition (Tg) phenomena. Figure 7 shows the heating run of CMC samples upto 300 ^{0}C. The heat required for melting of 100% crystalline CMC is 138.6 J/g [2]. The relatively weak and broadened glass transitions can be ascribed to the semicrystalline nature of the material. The values of Tg and Tm are in agreement with those in previous reports [3, 4, 5, and 6]. DSC thermogram of CMC shows peaks which are relatively broad and glass transition around 75 ^{0} C and exothermic crystalline transition at 278 ^{0} C.

Figure 7 DSC of CMC/citric acid

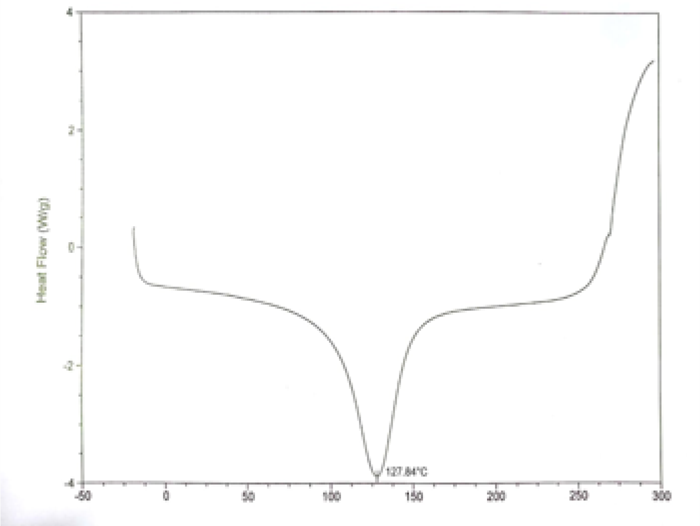


Figure 7: DSC of CMC crosslinked with CA

Figure 8 shows DSC of CMC /starch blend heating run of CMC samples upto 300 ^{0}C. The heat required for melting of 100% crystalline CMC is 138.6 J/g [6]. The relatively weak and broadened glass transitions can be ascribed to the semicrystalline nature of the material. The values of Tg and Tm are in agreement with those in previous reports [7, 8, 9,]. DSC thermogram of CMC shows are relatively broad end other m glass transition around 75 ^{0} C and exothermic crystalline transition at 278 ^{0} C. The figure shows the major transition at 109.81 ^{0} C. Starch does not have any melting point , as it is blended with CMC it shows the melting transition at 109.81^{0} C , which is an endothermic peak due the thermoplastic nature of the blend.

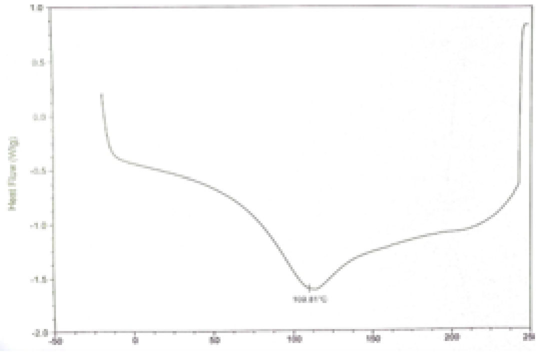


Figure 8: DSC of CMC /starch blends

5. FTIR

The goal of any absorption spectroscopy (FTIR, ultraviolet-visible ("UV-Vis") spectroscopy, etc.) is to measure how well a sample absorbs light at each wavelength. The most useful technique is to shine a monochromatic light beam at a sample, measure how much of the light is absorbed, and repeat for each different wavelength. Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state or lowest frequency, and several excited states or higher frequencies. One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the ground state and the first excited state. Figure 9 FTIR of CMC/ citric acid hydrogel

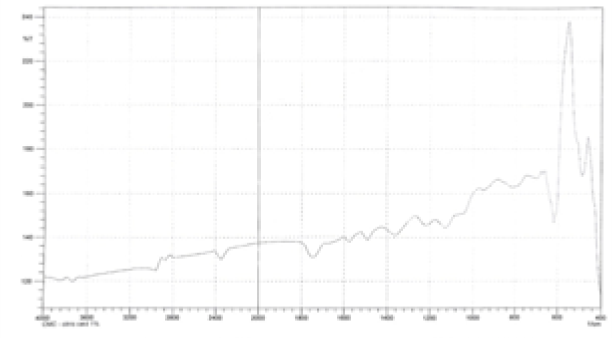


Figure 9: FTIR of CMC crosslinked with CA

IR spectroscopic analysis was used to illustrate the nature of the bond formation in the hydrogen and crosslinking moieties in the anhydroglucose units. The FT-IR spectra of CMC hydrogel is shown in Figure 9. Pure CMC had absorption bands related to O–H stretching at 3462.22 cm^{-1} as well as intra-molecular and intermolecular hydrogen bonds in cellulose, $-CH_2-$stretching on anhydroglucose. 2926.01 cm^{-1}, C=O carbonyl stretching in the anhydroglucose unit of the cellulose at 1583.56 cm^{-1}, C–OH in the in-plane bend at 1419.61 cm^{-1}, and ring stretching at 904.61 cm^{-1}. These values were consistent with those reported by Rimdusit et al. [7] and Wang et al. [8] as shown in Figure 9 the characteristic absorption bands of CMC at 1062.78 and 1112.93 cm^{-1} were obviously weakened after the reaction in the CMC hydrogel. The bands at 3664.75–2409.09 cm^{-1} (O–H stretching, usually very broad, strongly H-bonded) overlaps the $-CH_2-$ stretching of CMC. Therefore FTIR spectrum in Figure 9 proves that the sample is CMC because it has a fingerprint region for CMC bands. Weak bands at around 770 cm^{-1} are due to ring stretching and ring deformation of α-D-(1–4) and α-D-(1–6) linkages respectively. The band around 1320 cm^{-1} is assigned to OH bending vibration. Broad absorption band at 3200 - 3600 cm^{-1}, due to the stretching frequency of the –OH group [9].

Mario *et al.*, have found the carboxyl groups and its salts appear at wave numbers of 1600-1640 cm^{-1} and 1400-1450 cm^{-1} respectively[10].The band at 1030 cm^{-1} is due to carboxymethyl ether group > CH O CH_2- stretching . The presence of strong absorption band at 1605 $\text{cm}^{-\ 1}$confirms the presence of C=O group (indicated CMC), where absorption band associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that model. Band at 1111 cm^{-1} belong to the –C-O-C asymmetry bridge stretching [11]. The band at 2924 cm^{-1} is due to C–H stretching of the $-CH_2$ and CH_3 groups [12].

FTIR CMC/starch (50/50) blend crosslinked with citric acid was examined. Figure 10 shows the FTIR spectra for the cross-linked CMC/starch blend. Figure proves that the sample is CMC because it has a confirmed region for CMC bands. Mario et al., have found the carboxyl groups and its salts appear at wave numbers of 1600-1640 cm^{-1} and 1400-1450 cm^{-1} respectively [1]. The band at 1030 cm^{-1} is due to carboxymethyl ether group > CH O CH_2- stretching. The presence of strong absorption band at 1605 cm-^{1} confirms the presence of C=O group in CMC, where absorption band associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that model. Band at 1111 cm^{-1} belong to the –C-O-C asymmetry bridge stretching [2]. Weak bands at around 770 cm^{-1} are due to ring stretching and ring deformation of α-D-(1–4) and α-D-(1–6) linkages respectively. The band at 2924 cm^{-1} is due to C–H stretching of the $-CH_2$ and CH_3 groups [3]. The band around 1320 cm^{-1} is assigned to OH bending vibration. Broad absorption band at 3200 - 3600 cm^{-1}, due to the stretching frequency of –OH group [4]. Starch spectrum shows C-C stretching at 764 cm^{-1}, vibrations of α-1,4,glycosidic linkage (C-O-C) at 930 cm^{-1}, primary alcoholic $-CH_2OH$ stretching mode at 1078 cm^{-1},C-O-H bending at 1094cm^{-1},C-O stretching at 1163cm^{-1}, CH_2 bending at 1415 cm^{-1} , water adsorbed in the amorphous regions of starch at 1642cm^{-1},O-H stretching at 3000-3600cm^{-1}[5].

Figure 10 FTIR of CMC/ starch hydrogel

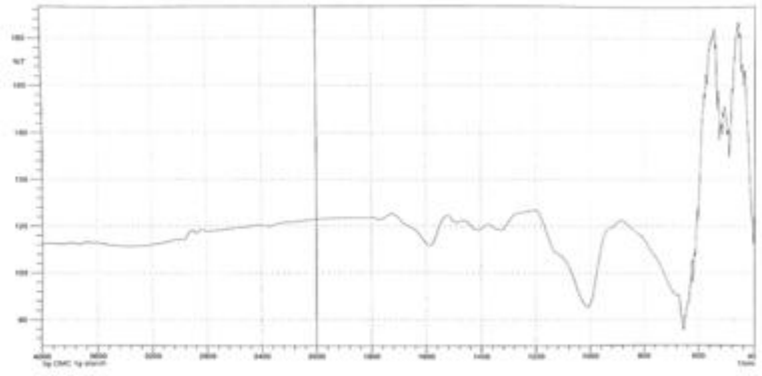


Figure 10 FTIR of CMC /starch blend

Conclusions:

Sodium salt of carboxy methyl cellulose based hydrogels were prepared with optimum crosslinking. The CMC/ starch blend with crosslinking also prepared. The Hydrogels were characterized with FTIR and physical properties. Thermal analysis was also conducted using TGA and DSC. Dissolved heavy metal adsorption from contaminated water was confirmed with the help of UV absorbance. It is found that the Hydrogels are effective in absorbing heavy metals and purification of water. These Hydrogels are giving better scope for adsorption and separation of heavy metals from water and other effluents, without dissolving in it and easily separated from water after usages. Thus the techniques give immense scope for purification processes.

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