
Proposed cross-linking model for carboxymethyl cellulose /starch superabsorbent polymer blend

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Abstract: Superabsorbent polymer (SAP) blend has been synthesized from Carboxymethyl Cellulose (CMC) , starch, and aluminum sulfate octadecahydrate cross-linker. Water Absorption Capacity (WAC), FTIR, SEM, DSC, CHO, Flame Photometer and ignition tests are carried out to determine the used CMC formula, investigate the cross-linking process, and suggest a cross-linking model. Flame Photometer results showed there are two sodium acetate groups in the CMC molecule. This result confirmed by theoretical calculations and CHO test . To investigate which of Al^{3+} and SO_4^{2-} ions causes the cross-linking : the extraction of the cross-linked CMC/starch tested with $BaCl_2$ solution (showed dense white precipitate ; sulfate group not share for blend formation), NaOH solution (showed white precipitate of aluminum hydroxide; Al^{3+} ion present (i.e. Al^{3+} ion share in the blend structure). These results confirmed by flame test for sodium ion, which showed high Na emission energy (5.75); there is an exchange between Al and Na ions. To check that aluminum is a part of the structure, sample of the cross-linked CMC ignited. A white precipitate appear for aluminum oxide ,which confirms the presence of Al. Based on that there are three CMC molecules connected to each Al atom, theoretical calculations about the amount of Al in the cross-linked CMC molecule showed a good agreement with the CHO results (5.613% Vs. 5.739 % respectively). FTIR spectrum of the cross-linked CMC/starch blend showed that there is a reaction between CMC and starch molecules; i.e. the new repeating unit contains three starch molecules. This conclusion confirmed by theoretical calculations and results of EDX, CHO, and ignition tests. Al% in the new mer appeared a good agreement between theoretical calculations (4.32%) and CHO results (4.512%). Ignition test calculations confirmed that the new mer contains three Al atoms. Evidences of the occurrence of the cross-linking process were obtained from FTIR, morphology, DSC and absorbency results. Absence of the primary hydroxyl alcohol band in the CMC/starch blend spectrum, indicates that this site is active and the reaction between starch and CMC molecules occurs through it. Morphologies studies showed that the sample after crosslinking is more compact than before as well as show one piece for after cross-linking comparing with different pieces before cross-linking. Optimum cross-linking ratio appeared to be 2wt% corresponded to WAC equal to 58 g/g.in distilled water and DSC results indicates that CMC/starch is a miscible blend.

Keywords: Superabsorbent Polymer, Cross-Linking, NaCMC

1. Introduction

Superabsorbent polymers (SAPs) are one of the most fascinating materials in modern polymer technology. These polymers are able to absorb up to 1500 g of water per gram of SAP [1]. SAPs containing absorbed liquid are called a hydrogels[2].

The swelling properties of these hydrogels have attracted the attention of researchers and technologists, and have found

wide-spread applications in drug delivery systems, agriculture, separation processes and many other fields [3].

Generally they consist of a network of polymer chains that are cross-linked to avoid dissolution. Usually there are ionic functional groups along the polymer chains to encourage diffusion of water within the network.[4].

2. Crosslinking Process

Cross-links between polymer chains form a three-dimensional network and prevent the polymer swelling to infinity i.e. dissolving. Cross-linking makes SAPs insoluble in water [5].

This is due to the elastic retraction forces of the network, and is accompanied by a decrease in entropy of the chains, as they become stiffer from their originally coiled state[6].

Crosslinks can be formed by covalent, electrostatic, or hydrophobic bonds, or dipole–dipole interactions [7].

Small amounts of cross-linkers play a major role in modifying the properties of superabsorbent polymers. In addition to modifying the swelling and mechanical properties, the cross-linker affects the amount of soluble polymer found during the polymerization. Efficiency of crosslinking will also depend on steric hindrance and reduced mobility at the site of pendant double bonds, the tendency of a given cross-linker to undergo intermolecular addition reactions, and the solubility of the cross-linker in the monomer mixture[8].

The cross-linking agent, is a monomer with two or more double bonds, decrease the molecular freedom by joining polymer chains together through covalent or ionic bonds to form three-dimensional network . It is network allows liquid absorption into the empty spaces between the polymer chains and prevents the polymer to dissolve due to the elastic retraction forces of the network. The degree of cross-linking increases the strength of the network (gel strength) [9].

Covalent crosslinks are formed when the major monomers (e.g., acrylic acid) is copolymerized with a di-,tri-, or tetra – vinyl monomer such as N,N-methylenebis(acrylamide). Ionic cross-links are formed by reacting a polyvalent ion of opposite charge with the charged polymer chains. The crosslink forms as a result of charge association of the unlike charges.

Physical crosslink usually formed by means of hydrogen bonding of segments of one chain with the segments of another chain.

3. Crosslinking Types in Superabsorbent Polymers (SAPs)

There are two main types of cross-linking in most SAPs:

3.1. Bulk or Core Crosslinking

Normally takes place during the polymerization stage of superabsorbent production. In SAP manufacture the most common types of cross-linker are organic molecule that contain two or more polymerizable double bonds. These molecules are incorporated into the backbone of the polymer chains as they grow during the polymerization reaction.

Reactivity ratios are a measure of the affinity for each of the reaction components to react with each other, i.e. does an acrylic acid molecule prefer to react with one like itself or something else like a cross-linker molecule for example [6].

If the cross-linker has a high reactivity ratio then most of it

will be consumed in the early stages of the polymerization and any polymer chains made during the latter stages will be less likely to cross-link and end up as extractable chains.

Cross-linkers with low reactivity ratios have the opposite tendency. The choice of cross-linker or mixture of cross-linkers determines the structure of the final polymer network.

Generally, low molecular weight polymer chains, that are not incorporated into the polymer network are called the soluble or extractable fraction. The degree of soluble polymer is important in determining the optimum cross-linker level and performance of the product. Too little cross-linker and the polymer will have a high swelling capacity, low strength against pressure and a tacky feel due to high extractable, and too much will give low extractable, low tackiness but a low swelling capacity.

3.2. Surface Crosslinking

Improving the absorption against pressure and the swelling rate of a SAP can be achieved by cross-linking the surface of the particles. Post cross-linking is normally performed on the dried, milled and sized SAP as the final stage of the process.

Surface cross-linking of the superabsorbent particles improves the flow significantly. The surface-cross-linked particles maintain their shape during the swelling process, which generates a less densely packed gel bed with air pockets, so the fluid can flow in a less restricted fashion (Figure 1, b). This higher permeability allows for a more efficient use of the gel bed[10].

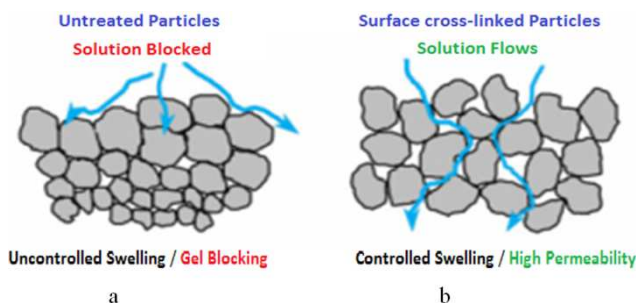


Fig.(1). Schematic representation of the swelling and flow of aqueous solutions through the (a) uncross-linked and (b) surface-cross-linked SAP particles in the gel bed[10]

4. Experimental Part

4.1. Materials

Carboxymethyl Cellulose Sodium Salt NaCMC and corn starch(25% amylose and 75% amylopectin) were obtained from HIMEDIA Laboratories Pvt. Ltd. Company (India) . Pure Aluminum Sulfate Octadecahydrate $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was obtained from REACHIM Company (USA).

4.2. Preparation of the Cross-Linked CMC

An appropriate amount of CMC solution agitated for 1 hour at 70°C . Aluminum sulfate octadecahydratecross-linker was added and allowed to mix for another 30 minutes. The solution was then spread on Teflon baking pans and dried

at 70°C (in a WG 71 Electric Blast Dry Box) until a film is formed. The film was shredded with a blender, then ground into a powder with a mortar and pestle.

4.3. Preparation of the Cross-Linked 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 80°C 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°C. Result paste was dried overnight at 100°C, crushed, and tested.

4.4. Tests

4.4.1. Water Absorption Capacity (WAC)

WAC was measured using tea-bag method according to the following equation :

$$WAC = \frac{W_1 - W_0}{W_0}$$

Where W_0 : dry weight and W_1 wet weight

4.4.2. Structural Analysis

Infrared spectra of the SAPs in KBr pellets (mass ratio of 1:10) were obtained from 4000 – 400 cm^{-1} using IR Affinity-1 SHIMADZU Fourier Transform Infrared Spectrometer Class 1 laser product.

Analytical Scanning Electron Microscope (SEM), model (Tescan VEGA-SB) used to examine the surface morphology of gels, which is first sputtered with gold .

To measure T_g , differential scanning calorimetry (DSC) , type ETTLER TOLEDO (Switzerland), model DSC1 was used with STAR*E software, test conditions (Temperature range: 25-300°C, Heating rate: 10 K/ min, N_2 gas 50 ml/min).

4.4.3. CHO Test

EURO EA Elemental Analyzer, EURO Vector Company, Italy

4.4.4. Jenway PFP7 Flame Photometer

The PFP7 operates with liquefied petroleum gas (LPG) and supplied with Na, K, Ba, Ca and Li filters. Before use, calibration with a series of standard NaCl solutions was done.

5. Results and Discussions

5.1. Water Absorbing Capacity (WAC)

Results shows that this hydrogel belong to the superabsorbent hydrogels, since it absorbs 58 times its original weight.

5.2. FTIR Results

Fig. (2) shows the FTIR spectra for the starting materials (CMC and starch) and the cross-linked CMC/starch blend .

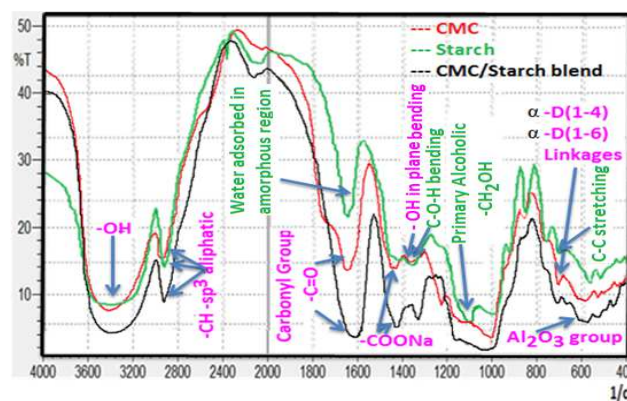


Fig. (2). FTIR spectra of CMC, starch, and CMC/starch blend

The CMC spectrum (Figure 2) proves that the sample is CMC because it has a fingerprint 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 [11]. The band at 1030 cm^{-1} is due to carboxymethyl ether group $> \text{CH O CH}_2-$ stretching .

The presence of strong absorption band at 1605 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 $-\text{C}-\text{O}-\text{C}$ asymmetry bridge stretching [12].

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 $-\text{CH}_2$ and CH_3 groups [13].

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 $-\text{OH}$ group [7].

Starch spectrum shows C-C stretching at 764 cm^{-1} , skeletal mode vibrations of α -1,4, glycosidic linkage (C-O-C) at 930 cm^{-1} , primary alcoholic $-\text{CH}_2\text{OH}$ stretching mode at 1078 cm^{-1} , C-O-H bending at 1094 cm^{-1} , C-O stretching at 1163 cm^{-1} , CH_2 bending at 1415 cm^{-1} , water adsorbed in the amorphous regions of starch at 1642 cm^{-1} , O-H stretching at 3000-3600 cm^{-1} [14].

5.3. Investigation of Cross-Linking

Many evidences of the occurrence of the cross-linking process were obtained through this study. Those evidences provided by FTIR, morphology, and absorbency results.

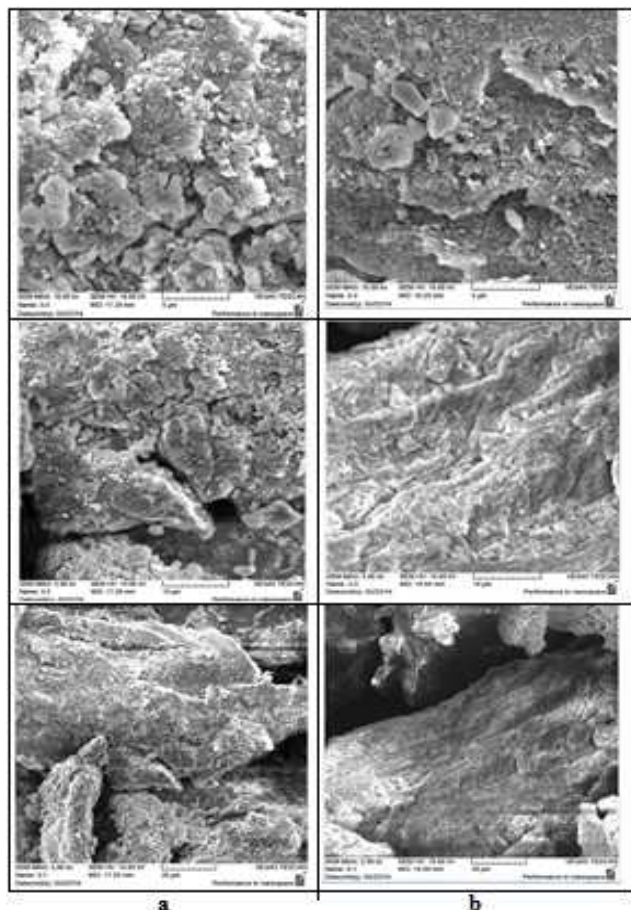


Fig.(3). Surface morphologies of CMC/starch blend with different magnifications (a) before (b) after cross-linking with $Al_2(SO_4)_3 \cdot 18 H_2O$

In the CMC/starch blend spectrum, the absence of the starch primary alcoholic band indicates that this site is active and the reaction between the starch molecule and the CMC molecule occurs through this site [15]. Also, the appearance of the $-COONa$ and $C=O$ groups refer to the efficiency of the blending process. Broadening band at $2900 - 3600\text{ cm}^{-1}$ is due to the huge amount of $-OH$ groups in the blend from both starting materials(CMC and starch).

From morphologies studies, as seen in Figure 3, it seen that there is a different general structures. It is clear the sample after crosslinking is more compact than before as well as show one piece for after cross-linking comparing with different pieces before cross-linking . This is due to binding the CMC molecules by the cross-linker aluminum sulfate octadecahydrate especially there are three CMC molecules connected to one atom of aluminum, so that the space between molecules before cross-linking disappear after that, i.e. more compact molecule.

5.4. Evaluation of Blend Miscibility

Since that differential scanning calorimetry (DSC) used for discrimination between miscible and immiscible polymer blends (where one T_g indicates a miscible system, while two T_g 's indicate an immiscible blend, and the two T_g 's shifted to the direction of their average is typical of partially miscible

systems) [16], it can be concluded from Figure 4 that CMC/starch is a miscible blend.

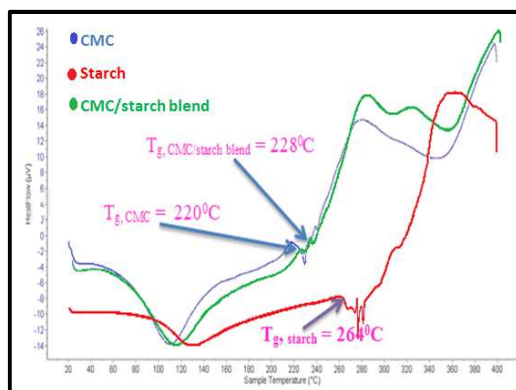


Fig.(4). DSC curves for CMC, starch, and the CMC/starch blend

5.5. Optimum Cross-Linking Ratio

The effect of the amount of aluminum sulfate octadecahydrate, which was used as the cross-linker in the polymerization, was studied and the result was shown in Figure 5. The max. of absorbency (58 g/g in distilled water) was at 2% of aluminum sulfate octadecahydrate. Above and lower this percent the degree of water absorbency decreases .

According to Floy' theory, increasing cross-linker could increase the nodes of network and the cross-linker density, which is favorable to the super-absorbent absorbing and retaining fluid [17].

Low concentration of the cross-linker leads to low degree of cross linking, and it is hard for network structure to form, so the water absorbency is low. However, when it is higher than the best value, there are more cross-linking points and the pores become smaller in the network, which causes the macroscopic decrease of the absorbency[18].

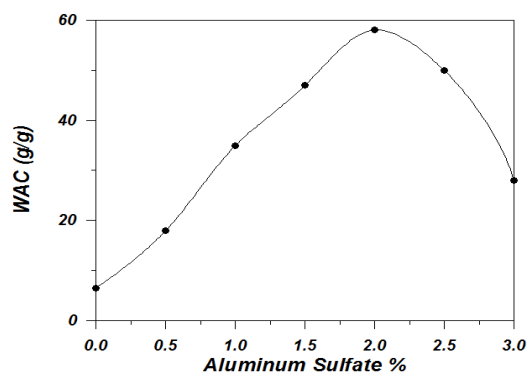


Fig. (5). Optimum percent of aluminum sulfate octedecahydrate cross-linker

It was observed that increasing the concentration of the acidic cross-linking agent (such as the aluminum sulfate octadecahydrate) up to a certain limit enhances the swelling properties of CMC hydrogel. Cross-linker concentration higher than this limit decreases significantly the swelling of the hydrogel. This could be ascribed to decrease flexibility of the chains and the ability of the chains to undergo segmental motion. Diffusion of the hydrolyzing agents (water) into the

polymer network also decreases thereby giving rise to more rigid structure of the polymer Network [7].

5.6. Proposed Cross-Linking Model

In order to suggest a reasonable cross-linking mechanism, some tests and investigations have been done to follow the reactions between the cross-linker and the starting components (CMC and starch).

5.6.1. Determination of Chemical Formula of CMC

By using standard sodium chloride solution, three standard concentrations (37.5, 75, and 150 ppm) of sodium chloride (NaCl) is studied using emission spectrum technology, JENWAY pfp7 Flame Photometer (see Figure 6)

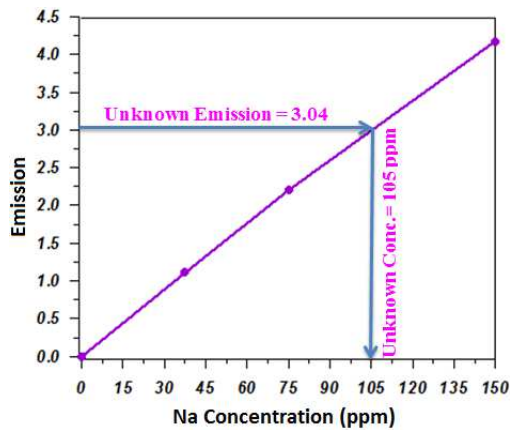


Fig.(6). calibration curve for Na

Unknown solution of 0.1 g CMC in 100ml distilled water used to check the number of sodium acetate group, which 105 ppm of sodium. From this concentration calculation shows the presence of two acetate groups.

Theoretically, the concentration of the sodium in the unknown solution assuming there are two sodium acetate groups in the CMC molecule can be calculated as:

| Weight of CMC/g | Weight of sodium/g |
|-----------------|--------------------|
| 484 | 46 |
| 0.1 | X |

$$X = \frac{0.1 \times 46}{484} = 0.0095 \text{ g Na in } 100 \text{ ml solution} = 95 \text{ ppm}$$

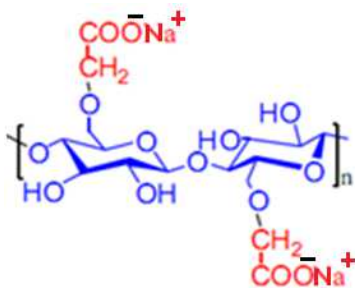


Fig.(7). Chemical structure of the used CMC

Which is in a good agreement with the result obtained practically (105 ppm), thus the used CMC molecule contained two acetate groups with the molecular weight of

484 g/mol, i.e., the structure will be as seen in Figure 7.

To confirm that, a CHO test is carried out (using EURO EA Elemental Analyzer). As shown in Table 1, the CHO results were coincide with the theoretical calculations. The sample may not be completely dry.

Table 1. Elemental chemical analysis of the used CMC

| Element | Theoretically % | Practically % [CHO test] |
|---------|-----------------|--------------------------|
| C | 39.669 | 38.985 |
| H | 4.545 | 4.615 |
| O | 46.282 | 45.900 |
| Na | 9.504 | 10.500* |

* Determined by Flame Photometry method

5.6.2. Investigation of the Active Ion

When aluminum sulfate octadecahydrate $[Al_2(SO_4)_3 \cdot 18H_2O]$ cross-linker dissolve in water, the material dissociates into $2Al^{3+}$ and $3SO_4^{2-}$. It is necessary to investigate which of these ions enters the cross-linking reaction.

To answer the above question, the following procedure have been adopted:

- 1 Pieces of the cross-linked CMC/starch blend immersed in hot water $70^{\circ}C$ for 30 minutes and then filtered. The extraction then divided into two parts.
- 2 The first part is tested for sulfate group using $BaCl_2$ solution, shows dense white precipitate; i.e. that the sulfate group not share for blend formation.
- 3 The second part is tested for Al^{3+} ion using $NaOH$ solution, shows the absence of Al^{3+} ion, which indicates that the Al^{3+} ion share in the blend structure.
- 4 To confirm this conclusion, test was carried out with platinum wire test on sodium flame shows high Na emission energy (5.75 compared with 0.0 to the distilled water), which indicates that there is an exchange between Al and Na ions.
- 5 To check that aluminum is a part of the structure or not, sample (1.5523 g) of the cross-linked CMC ignited to $800^{\circ}C$ for 2 hours in which all hydrocarbons converted to CO_2 and H_2O , while Al changes to oxide if it present. A white precipitate appear (0.1684g) for aluminum oxide (Al_2O_3) and this test confirms the presence of Al.

The amount of Al in this Al_2O_3 precipitate can be calculated as follows:

| Weight of Al_2O_3 /g | Weight of Al /g |
|------------------------|-----------------|
| 102 | 54 |
| 0.1684 | X |

$$X = \frac{0.1684 \times 54}{102} = 0.0891 \text{ g of Al}$$

and from Na platinum wire test shows that the presence of Na ion in the solution of the blend which indicates that Al substitute Na in the blend.

The Al % in this cross-linked CMC structure can be calculated as follows:

$$Al \% = \frac{\text{weight of Al}}{\text{weight of structure}} = \frac{0.0891 \text{ g}}{1.5523 \text{ g}} \times 100\% = 5.739 \%$$

Since that the Al ion is a trivalent, three CMC molecules can connect to this ion to form the cross-linked CMC (molecular weight of the mer is 1443 g/mol for the repeating unit) as shown in Figure 8.

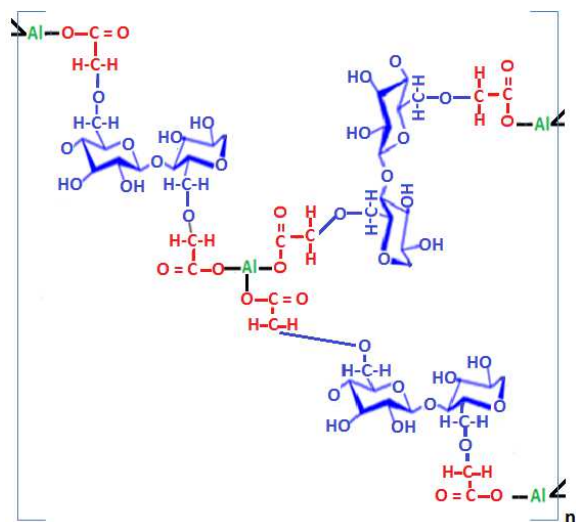


Fig. (8).Proposed cross-linking mechanism between Al ion and CMC molecules

Theoretically, the Al% of this structure can be calculated as follows:

$$Al \% = \frac{\text{AtomicweightofAl}}{\text{Molecularweightofcross-linkedCMC}} \times 100 = \frac{3 \times 27}{1443} \times 100 = 5.613 \%$$

Which is in a good agreement with the practical Al% value; 5.739 % as shown in Table 2.

Table 2. Elemental chemical analysis of the cross-linked CMC

| Element | Theoretically % | Practically % [CHO test] |
|---------|-----------------|--------------------------|
| C | 39.916 | 39.275 |
| H | 4.573 | 4.470 |
| O | 49.898 | 50.516 |
| Al | 5.613 | 5.739* |

* Determined by ignition method

The following calculation confirms that this structure contains three Al atoms:

| | |
|------------------------------|----------------|
| Weight of cross-linked CMC/g | Weight of Al/g |
| 1.5523 | 0.0891 |
| 1443 | X |

$$X = 82.82 \text{ Al} \cdot \text{No. of Al atoms} = \frac{\text{AmountofAl}}{\text{AtomicweightofAl}} = \frac{82.82}{27} = 3.06 \text{ atoms}$$

5.6.3. Cross-Linked CMC/Starch Blend

FTIR spectrum for the cross-linked CMC/starch blend (Figure 3) showed the absence of the hydroxy primary alcoholic group in the starch molecule at 1078 cm⁻¹. This indicates that the link between starch and CMC molecules occurs at this site, which can be attributed to lowest space hindrance at this site. This means the new repeating unit contains three additional starch molecules; the molecular

weight is 1875 g/mol of the mer.(Figure 9)

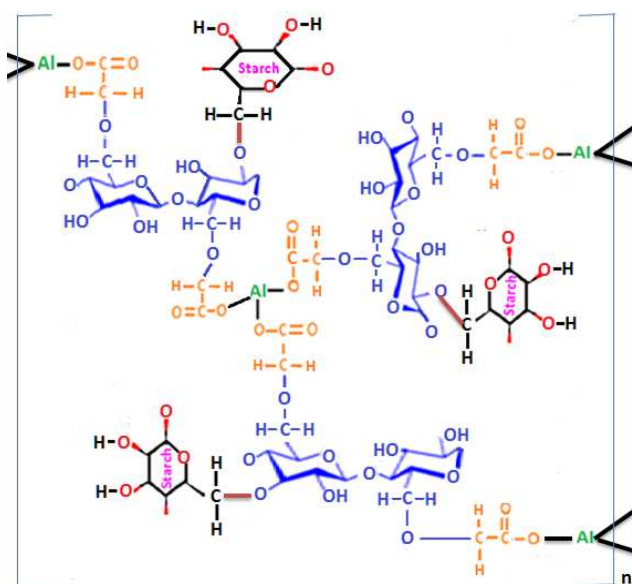


Fig.(9).Proposed cross-linking mechanism model for the Al/ CMC / starch blend

Table 3. EDX test for the cross-linked CMC/starch blend

| Element | AppCo nc. | IntensityCo rr. | Weight % | Weight%Sig ma | Atomic % |
|---------|-----------|-----------------|----------|---------------|----------|
| C K | 27.71 | 0.4154 | 43.06 | 1.93 | 46.5 |
| O K | 31.51 | 0.3664 | 55.50 | 1.91 | 48.86 |
| Al K | 1.79 | 0.7985 | 1.45 | 0.28 | 4.64 |
| Total | | | 100.00 | | |

To confirm this chemical structure, in addition to the EDX results (Table 3 and figure 10), a comparison between the practical CHO test results and their theoretical calculations was done (Table 4) . Therefore, sample (1.921 g) of the cross-linked Al/CMC/ starch blend ignited at 800⁰C for 2 hours. A white precipitate appear (0.1615g) for aluminum oxide (Al₂O₃).

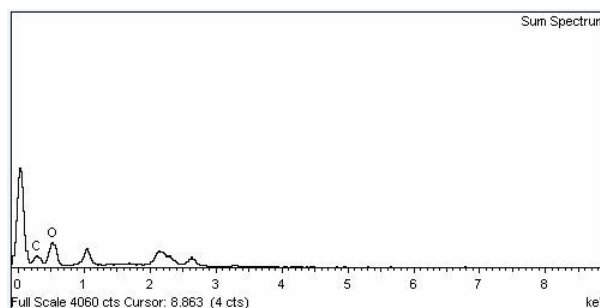


Fig.(10). EDX spectrum for the cross-linked CMC/starch blend

Table 4. Elemental chemical analysis of the cross-linked CMC/ starch blend

| Element | Theoretically % | Practically % [CHO test] |
|---------|-----------------|--------------------------|
| C | 42.240 | 41.635 |
| H | 4.960 | 4.875 |
| O | 48.480 | 48.978 |
| Al | 4.320 | 4.512* |

* Determined by ignition method

Also, the following calculation confirms that this new chemical structure (for the cross-linked CMC/starch blend) contains three Al atoms:

| | |
|--|--------------|
| Weight of Al ₂ O ₃ | Weight of Al |
| 102 | 54 |
| 0.1615 | X |

$$X = \frac{0.1615 \times 54}{102} = 0.0855 \text{ g of Al}$$

| | |
|----------------------------|--------------|
| Weight of CMC/starch blend | Weight of Al |
| 1.921 g | 0.0855 g |
| 1875 | X |

$$X = \frac{0.0855 \times 1875}{1.921} = 83.452 \text{ g/mol of Al}$$

$$\text{No. of Al atoms} = \frac{\text{Amount of Al}}{\text{Atomic weight of Al}} = \frac{83.452}{27} = 3.0908 \text{ atoms}$$

In a very good agreement with three atoms aluminum in the repeating units (mers).

6. Conclusions

The aim of this work is to prepare an organometallic compound from CMC/starch/Alum is proposal to get high porous structure (high water absorbance capacity).

- 1 Tests and theoretical calculations confirm that the start material is disodium carboxymethyl cellulose salt.
- 2 Aluminum ion from Alum (cross-linker) substitutes sodium ion in the starting material.
- 3 Several tests are carried on to confirm the presence of cross-linker compound.
- 4 The prepared cross-linked compound shows high porous character.
- 5 The prepared cross-linked compound shows highly water absorbency capacity reaches 58g water/g sample.

References

- [1] V. Mechtcherine, H-W. Reinhardt "Application of Superabsorbent Polymers (SAP) in Concrete Construction" Springer, New York, 2012.
- [2] C. Nystrand "Feasibility of lignocellulose as feedstock for biological production of superabsorbent polymers" Master Thesis, Linköping University, 2010
- [3] M. Sadeghi, F. Soleimani "Synthesis and Characterization of Superabsorbent Hydrogels for Oral Drug Delivery Systems" International Journal of Chemical Engineering and Applications, Vol.2, No.5, October 2011
- [4] P.K. Chatterjee, B.S. Gupta "Absorbent Technology" Elsevier, USA, 2002
- [5] G. F. John "Towards Improved Application of Super Absorbent Polymers in Agriculture and Hydrology: A Cross-Disciplinary Approach" MSc Thesis, Auburn University, 2011.
- [6] M. Elliot "Superabsorbent Polymers" BASF, 2010.
- [7] M. Hashem, S. Sharaf, M.M. Abd El-Hady, A. Hebeish "Synthesis and characterization of novel carboxymethyl cellulose hydrogels and carboxymethylcellulose-hydrogel-ZnO-nanocomposites" Carbohydrate Polymers 95 (2013) 421–427
- [8] Buchholz and Peppas "Superabsorbent Polymers" ACS Symposium Series, 1994.
- [9] F. L. Buchholz and A. T. Graham "Modern Superabsorbent Polymer Technology" Wiley-VCH, 1997.
- [10] S. Jockusch, N. J. Turro, Y. Mitsukami, M. Matsumoto, T. Iwamura, T. Lindner, A. Flohr, G. Massimo "Photoinduced Surface Cross-linking of Superabsorbent Polymer Particles" Journal of Applied Polymer Science, Vol. 111, 2163-2170, 2009
- [11] P. Mario, D.W. Adinugrada, M. Haryadi, 2005. Synthesis and characterization of sodium carboxymethyl cellulose from Cavendish banana pseudo stem (Musa cavendishii LAMBERT). Carbohydr. Polym., 62: 164-169.
- [12] G. S. Hutomo, D. W. Marseno, S. Anggrahini and Supriyanto "Synthesis and characterization of sodium carboxymethyl cellulose from pod husk of Cacao (*Theobroma cacao* L.)" African Journal of Food Science Vol. 6(6), pp. 180-185, 31 March, 2012.
- [13] J. Wang, P. Somasundaran "Adsorption and conformation of carboxymethyl cellulose at solid-liquid interfaces using spectroscopic, AFM and allied techniques" Journal of Colloid and Interface Science 291 (2005) 75–83.
- [14] R. Kizil, J. Irudayaraj, and K. Seetharaman "Characterization of Irradiated Starches by Using FT-Raman and FTIR Spectroscopy, 2011.
- [15] Jaleel K. Ahmed "Cross-linking Condensation Polymerization of Rayon Fiber" National Journal of Chemistry Vol.26, 2007, pp 270-283.
- [16] Herman F. Mark "Encyclopedia of Polymer Science and Technology" Third edition, 2005.
- [17] A. Pourjavadi, G.R. Mahdavinia, 2006. Superabsorbency, pH-sensitivity and swelling kinetics of partially hydrolyzed chitosan-g-poly (acrylamide) hydrogels. Turk. J. Chem. 30, 595–608.]
- [18] Z. Ma, Q. Li, Q. Yue, B. Gao, X. Xu, Q. Zhong "Synthesis and characterization of a novel super-absorbent based on wheatstraw" Bioresource Technology 102(2011) 2853-2858.