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Research Article

CELLULOSIC SUPERABSORBENT PRODUCTION WITH CITRIC ACID CROSS-LINKING METHOD

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ABSTRACT

In this study, it was aimed to determine water and liquid salt solution absorption capacity of cellulosic superabsorbents that were produced by using citric acid crosslinking method. Cellulosic superabsorbents were prepared with mixing cellulose and carboxymethylcellulose at different ratio. The highest water absorption capacity in water was determined 2616% at pH:7 for cellulosic superabsorbent which was produced with cellulose (10%) and carboxymethylcelulose (90%). Absorption capacity of cellulosic superaborbent in salt solution was calculated 984% for NH4Cl2 liquid salt solution. It was concluded that carboxymethylcellulose had an affirmative effect on water absorption capacity of cellulosic superabsorbents.

Keywords: Superabsorbent, absorption, cellulose, carboxymethylcellulose, citric acid.

1. INTRODUCTION

Superabsorbent polymers (SAPs) are one of the most fascinating materials in modern polymer technology. Thesepolymers are able to absorb up to 1500 g of water per gram of SAP .SAPs containing absorbed liquid are called a hydrogel. The swelling properties of these hydrogels have attracted the attention of researchers and technologists, and have found wide-spread applications in biomedical, drug delivery systems, agriculture, separation processes and many other fields. 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 [1].

Most of the practically applied superabsorbents (acrylate-based gels being the most widely used) are non-biodegradable. Therefore, producing gels with high water uptake using renewable and biodegradable materials is of great practical importance. Such renewable source is cellulose, the most abundant renewable material on earth, which can also be easily functionalized due to its hydroxyl groups [2].

Pure cellulose is also capable of forming gels, however, in order to produce hydrogels it requires the Use of special solvents, such as alkali-urea , DMAc-LiAc or ionic liquid systems.

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Difficulties of such solvents' application suggest using a different way to get cellulose based hydrogels: proper gel stability and high water uptake can be achieved by developing inter- and intramolecular crosslinks in colloidal aqueous solution of cellulose derivatives. Substitution of the hydroxyl groups with methyl, ethyl, carboxymethyl, hydroxyethyl, etc. groups on the cellulose backbone significantly changes the cellulose properties, including increased swelling in water up to solubility [3].

Carboxymethyl cellulose (CMC) is an anionic and water-soluble natural polymer derivative that is widely used in detergents, in oil exploration, and in the food, paper, and textile industries because of its viscosity-increasing properties. CMC, similar to other natural cellulosic polymers, is a degradable polymer under irradiation but can be crosslinked to form a hydrogel under suitable conditions [4]. Adding cross-links between polymer chains affect the physical properties of the polymer depending upon the degree of cross linking and presence and absence of crystallinity. Cross linking results in e*lasticity, decrease in* the viscosity, insolubility of the polymer, increased Tg and increase strength and toughness, lower melting point, transformation of therrmoplasts into thermosets [5].

In general, literature review shows that carboxymethyl cellulose (CMC), methyl cellulose (MC), hydroxyethyl cellulose (HEC) and hydroxypropyl cellulose (HPC) are used in the synthesis of superabsorbents [3]. However, CMC is the most preferred among these because of its easy solubility in water, easy bonding with water and reactivity. Due to these properties, CMC has yielded very good results in superabsorbent synthesis with both cross-linking and grafting method [6,7]. However, the most important disadvantage of the superabsorbents obtained from CMC is the low gelation resistance (dispersion of the structure as a result of swelling and swelling) [8,9,10].

Dissolving pulp and citric acid were used in this study to overcome this disadvantage of CMC. In this study, the effects of cellulose and citric acid used in the production of (cel-SAP) hydrogel on properties of SAP were investigated.

2. EXPERIMENTAL

2.1. Materials

Spruce dissolving pulp was used as cellulose resource (Borregaard). Alpha cellulose content, Kappa no and DP of spruce dissolving pulp were determined 95.2%, ≤1 and 1406, respectively. Carboxymethylcellulose (CMC) was purchased by Sigma Aldrich (Mw: 700000). Citric acid (CA) were obtained as analytical-grade.

2.2. Preparation of Cel-SAP

Hydrogel samples were obtained reacting, in water, CMC-Na and dissolving pulp with CA as a crosslinking agent according the following procedure. First, a total polymer concentration of 2% by weight of water, using a mixture of CMC-Na and dissolving pulp was dissolved in distilled water by stirring gently at room temperature until viscose solution was obtained. Afterwards, superabsorbent synthesis was completed by keeping it at 80 ° C for 24 hours in order to complete the esterification reaction.The conditions of cel-SAP preparation are presented in Table 1.

Table 1. Conditions of cel-SAP production

Cellulose (%)	CMC (%)	Suspension (ml)	Citric acid (%)
10	90	200	5
30	70	200	5
50	50	200	5

2.3. Determination of Absorption Capacity (AC)

The synthesized cel-SAPs were immersed in water at constant room temperature (25 ° C) for 12 h. Water absorption capacity (WAC) and swelling in acidic, alkaline and neutral conditions of cel-SAPs was determined by adjusting the water to pH 2, 7 and 10. Cel-SAPs were filtrated to remove excess distilled water. NaCl, KCl, $MgCl_2$ and NH_4Cl_2 were used for the detetermination of liquid salt solution absorption capacity (LSSAC). Absorption capacity (AC) was calculated by the following eqution:

$$AC = (M_2-M_1) / M_1 \qquad (1)$$

Where, M_1 and M_2 are the mass of the dried and swollen sample, respectively. The AC value was calculated as grams of water per gram of sample.

2.4. SEM Analysis

Surface properties of superabsorbents were investigated by scanning electron microscopy images (Jeol JSM-6060- Zeiss Evo LS-10). Cel-SAP sample were coated with Au before SEM observation.

3. RESULTS AND DISCUSSION

3.1. Water Absorption Capacity of Cel-SAPs

Wüstenberg (2015) was determined that water absorption capacity of cel-SAPs increased evidently with an increase CMC content in cel-SAPs. CMC has highly hydrophilic carboxyl group. These groups could absorb to enhance WAC of cel-SAPs [11]. CMC is a polyelectrolyte, which shows sensitivity to pH and ionic strength variations. Indeed the presence of CMC in a cellulose-based hydrogel provides the hydrogel itself with electrostatic charges anchored to the network, which have a double effect on the swelling capability. On one side, the electrostatic repulsion established between charges of the same sign forces the polymer chains to a more elongated state than that found in a neutral network, thus increasing the swelling. On the other, the counterions that are present in the gel to ensure macroscopic electrical neutrality induce more water to enter the network [12].

Cel-SAPs were prepared dissolving pulp cellulose and CMC at different ratios (10/90, 30/70 and 50/50) by using citric acid crosslinking method, as can be seen in Table 1. HCl (pH:2) and NaOH (pH:10) were used for acidic and basic adjustment, before water absorption capacity determination. The results of water absorption capacity in distilled water at 25 °C for cel-SAPs which were prepared with dissolving pulp cellulose (C) and CMC mixture are presented in Figure 1.

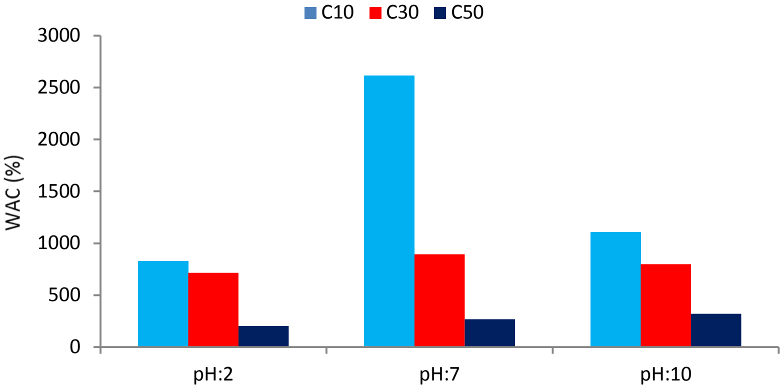


Figure 1. Water Absorption Capacity of Cel-SAPs which were prepared Dissolving pulp cellulose and CMC mixture with citric acid crosslinking method

The WAC value of the superabsorbent produced using 10% cellulose and 90% CMC, and EPH crosslinker was determined as 2000% for pH 7 and 2500% for pH 12 [13].

Water absorbency of the hydrogel depended on the crosslinking degree: lower crosslinking degrees could not retain water molecules inside the gel, whereas a higher degree of crosslinking suppressed the expan- sion of the gel structure. In addition, increase in the degree of crosslinking of the hydrogels was shown to lead to a decrease in biodegradability, similar to those of other cellulose derivatives. It was also shown to lead to an increase in physical strength of the hydrogels [14].

In this study, . NaCl, KCl, $MgCl_2$ and NH_4Cl_2 were used for the detetermination of liquid salt solution absorption capacity (LSSAC). It was found that LSSAC sorted out following: NH_4Cl_2, KCl, NaCl and $MgCl_2$. Liquid absorption capacity and swelling values of cellulosic SAP control samples in different salt solutions were presented in Figure 2.

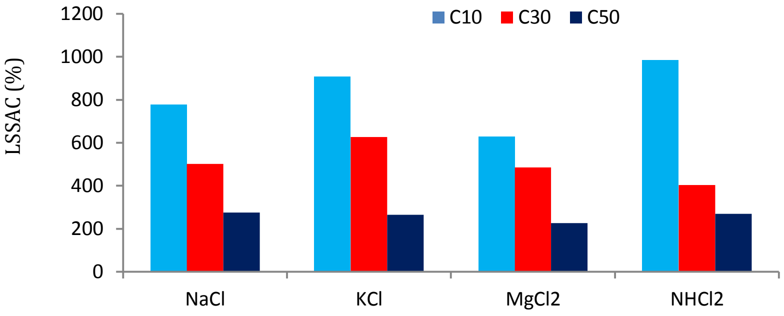
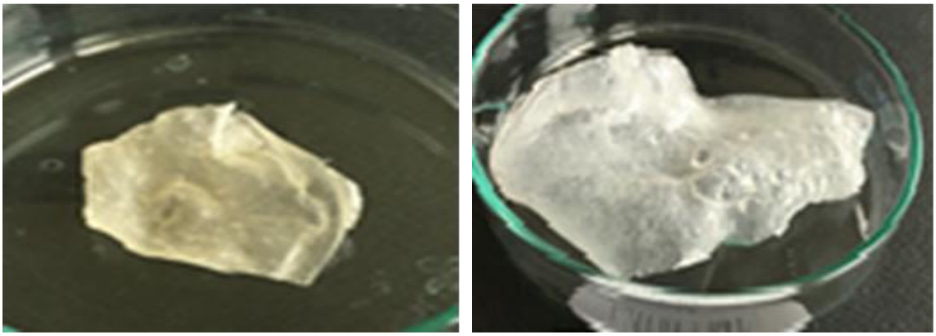


Figure 2. Liquid absorption capacity and swelling values of cellulosic SAP control samples in different salt solutions

Alam et al. (2019) were determined that equilibrium swelling capacity Ws of the gel in the presence of monovalent cations decreased in the following descending order: $NH_4+ > K+ > Na+$. This can be explained by the fact that the charge screening effect of these cations on the Ws values decreased in the same order. In the presence of salts with different cationic charges, the absorption capacity of the hydrogel declined in the order monovalent > divalent >trivalent cations [15].

The photos of cellulosic superabsorbent produced in this study are submitted as dry sheet and water uptake form in Figure 3.

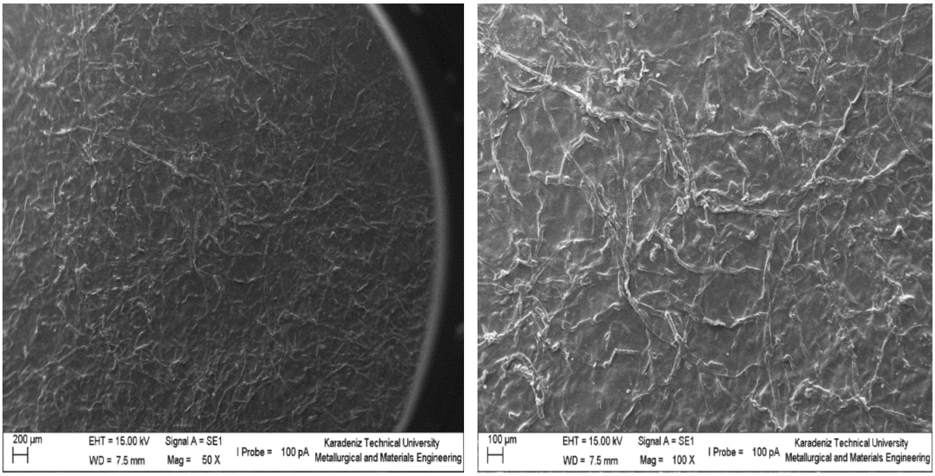


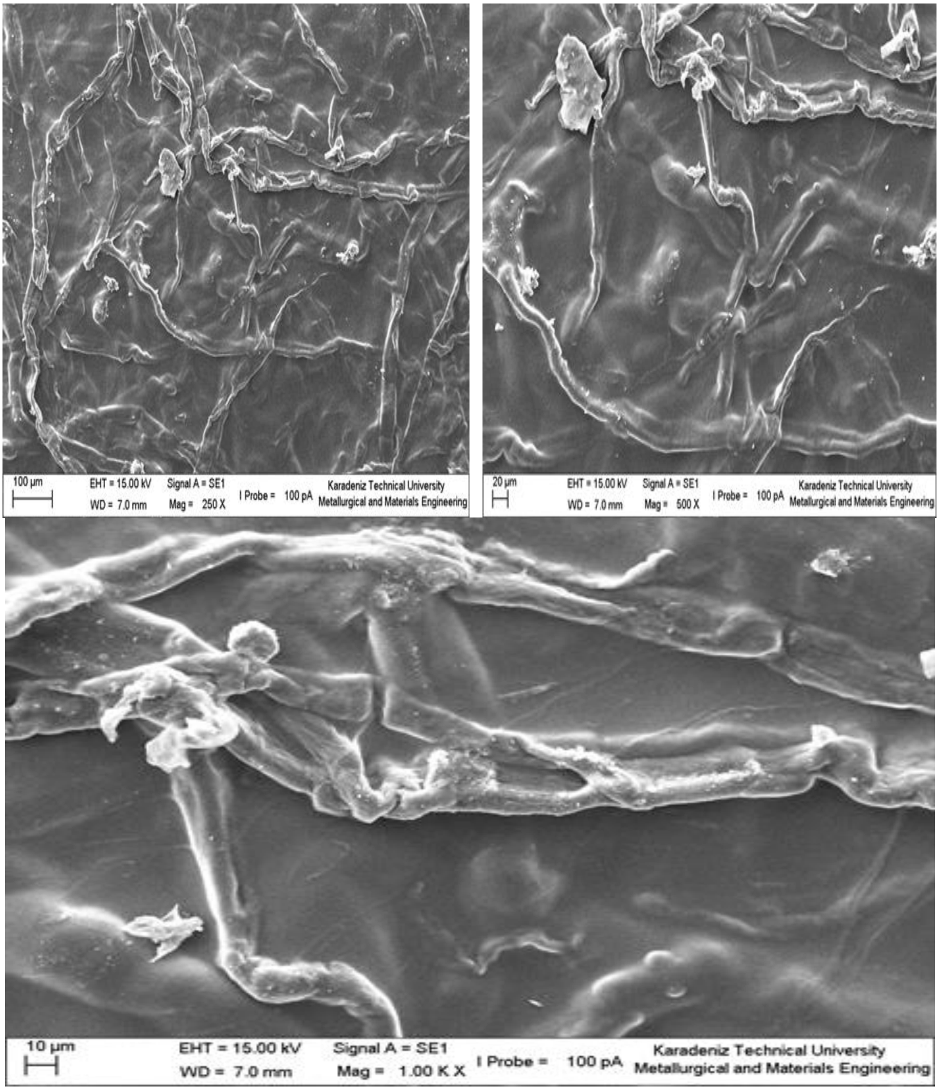
(A) **(B)**

Figure 3. Photos of cellulosic superabsorbent. (A) Dry sheet form, (B) After water uptake.

3.2. SEM Analysis

SEM photos of cellulosic superabsorbents are presented in Figure 3. SEM photos show dissolving pulp fibres form the skeleton structure of the cellulosic superebsorbent. CMC contributed to the transparent image of superabsorbent.





3. CONCLUSION

It was concluded that dissolving pulp cellulose contributed to the skeletal structure of hydrogel. However, as the rate of dissolving pulp cellulose in the superabsorbent increased, it was determined that water absorption capacity of cellulosic superabsorbent (hydrogel) decreased. It was concluded that LSSAC sorted out following: NH_4Cl_2, KCl, NaCl and $MgCl_2$.

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