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RESEARCH ARTICLE

DEVELOPMENT OF A NOVEL CONDUCTIVE CMC\POLYANILINE HYDROGEL

Sharaf, S., Abd El-Hady, M. M. and *Farouk, A.

Department of Preparation and Finishing of Cellulosic Fibers, National Research Centre, Textile Division, Textile Chemistry and Technology, Scopus affiliation ID 60014618, 33EL Bohouthst.-Dokki-Giza, Cairo, P.O. Box 12622, Giza, Egypt

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ABSTRACT

This study reports the development of Novel electrically conductinghydrogel polymerthat is shown to combine both electro-properties and hydrogel characteristics. First carboxymethylcellulose (CMC) hydrogel with excellent swelling behavior was prepared by using succinic acid (0.5%), then (CMC\polyaniline) conducting hydrogel was fabricated by in situ polymerization of aniline within the matrix of CMC hydrogel. The influence of initiator as well as aniline monomer concentration on the conductivity of hydrogel was investigated. Morphology of the developed hydrogelwas evaluated by scanning electron microscopy analysis. To consider the potential of electrically conductive hydrogel in biomedical applications, biocidail activity of the aforementioned conductive hydrogelas well as gram positive, gram negative bacteria were studied.

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INTRODUCTION

Many researches focus on the superabsorbent polymer for developing new applications, such as, conducting materials, sensors and release materials, biomaterials, wave-absorbing materials (Bajpai *et al*., 2011; Abdul Barik *et al*., 2012; Ali Hebeish *et al*., 2013; Kim, 2010; Chang *et al*., 2010; Ilieva *et al*., 2008). Superabsorbents prepared with natural material, such as cellulose and its derivatives because of their abundant resources, low productioncostand biodegradability, have attracted great attention (Ito *et al*., 2003; Truelstrup Hansen, 2000). Carboxymethylcellulose (CMC) is a representative cellulose derivative with carboxymethylgroups (–CH2–COONa) bonded to some of the hydroxyl groupson cellulose backbone. It can be easily synthesized by the alkalicatalyzedreaction of cellulose with chloroacetic acid and has beenwidely used as a thickening agent and stabilizing agent. The polar carboxyl groups render the cellulose soluble, chemically reactiveand strongly hydrophilic, and so the application of CMC in superabsorbent fields becomes attractive and promising (Hashem *et al*., 2013; Wan and Li, 2003). A combination of a polymeric hydrogel and a conducting polymer allows obtaining materials that exhibit the properties characteristic for both component (MarcinKarbarz *et al*., 2011). Composite systems comprising a conducting polymer, such as polyaniline (PANI), distributed within a polymer gel represent novel materials that have recently been prepared and investigated (Natalia *et al*., 2009). Polyaniline (PANI) is an electrically conducting polymer (ECP) having a spatially extended p-bonding system, which accounts for its intrinsicSemiconducting nature. It is one of the most promising conducting polymers due to a good combination of properties, stability, price and ease of synthesis by different routes, and uncountable application (Qunwei Tang *et al*., 2008; Rahman *et al*., 2008; Siddhantaa and Gangopadhyay, 2005).

In this paper, an electrically conductive hydrogel is newly developed which has both electro-properties and hydrogel characteristics, CMC-PANI hydrogel is formed by in situ polymerization of aniline within the matrix of CMC hydrogel using ammonium persulfate (APS) as an oxidant. We studied the optimum conditions for the electrical conductivity of the prepared hydrogel. Morphology of the developed hydrogel was evaluated by scanning electron microscopy analysis. The antibacterial properties of the aforementioned conductive hydrogel were also evaluated.

****Corresponding author: Farouk, A.*** *Department of Preparation and Finishing of Cellulosic Fibers, National Research Centre, Textile Division, Textile Chemistry and Technology, Scopus affiliation ID 60014618, 33EL Bohouthst.-Dokki-Giza, Cairo, P.O. Box 12622, Giza, Egypt*

MATERIALS AND METHODS

Materials

Carboxymethyl cellulose (CMC) having high molecular weight (Mw = 10,000 Dalton) was used. Aniline was purchased from Aldrich. Succinic acid, sodium hypophosphite, ammonium persulphate (APS), and hydrochloric acid were of laboratory grade chemicals.

Methods

Preparation of CMC/succinic acid hydrogel

Definite amount of CMC was dissolved in an aqueous solution with continuous mechanical stirring until a homogeneous viscous mixture was obtained. Then definite amount of sodium hypophosphite and0.5 % of succinic acid were added separately drop wise to CMC solution with continuous stirring. The formed paste, was transferred to Petri dish, dried in an oven at 80°C for 5 min then cured for 3 min at temperature 130ºC.

Impregnation of PANI into hydrogel matrix

The impregnation of PANI into the hydrogel matrix was carried out through the polymerization technique. Predetermined solution of aniline was prepared, (dissolved in 1 M HCL), under vigorous agitation, the prepared hydrogel was dipped into predetermined amount of aqueous solution of aniline(0.01-0.06 mole) which resulted in the absorption of aniline monomer inside of the network and the formation of a swollen sample. After that aqueous solution of (0.01-0.06 M) APS was added drop wise. The temperature was maintained at 0-5 ^{o}C and keeping under stirring for 4 hr. As the polymerization proceeds, the semitransparent gel turns green color which is the color of PANI, Hereunder schematic diagram for the polymerization of aniline inside the CMC hydrogel matrix, Figure1.

Characterization and analysis

FTIR Spectroscopy

FTIR analysis was recorded on a Perkin Elmer FTIR Spectrophotometer, using the potassium bromide disk technique, in the range of 4000 - 400 cm-1. The disk was prepared from grinded samples (2 mg) and KBr (45 mg) using 400 kg/cm2 pressure for 10 min.

Scanning Electron Microscopy (SEM)

Surface morphology of the hydrogel was examined on a JEAOL JXA-840 scanning electron microscope (SEM). The hydrogel samples were coated with a thin layer of palladium gold alloy after mounting on a double sided carbon tape.

Antibacterial activity

Antimicrobial activity of the prepared hydrogel was evaluated using agar diffusion test according to AATCC Standard Test Method 147-1988.

Electrical conductivity of the hydrogel

The chemical oxidative polymerization of aniline on the surface of CMC hydrogel was monitored by electrical conductivity of the CMC/succinic acid / PANI hydrogel. The electrical conductivity of formed hydrogel was measured using pocket conductivity meter.

RESULTS AND DISCUSSION

Proposed mechanism

As shown in Figure 2, CMC hydrogel was formed via crosslinking using polycarboxylic acid i.e. succinic acid this was illustrated in our previous work (Wada *et al*., 2004)

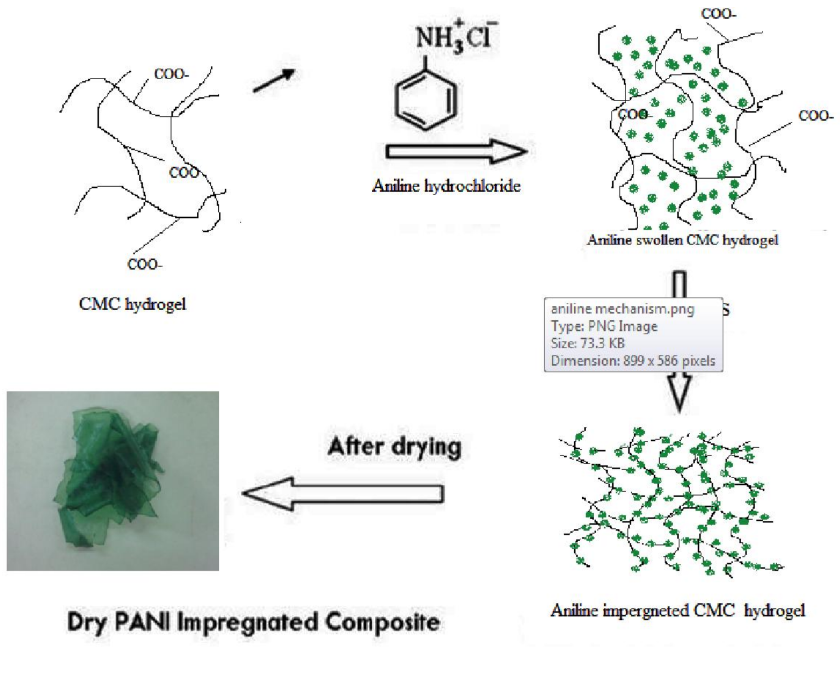


Figure 1. Schematic diagram for the polymerization of aniline inside the CMC hydrogel matrix

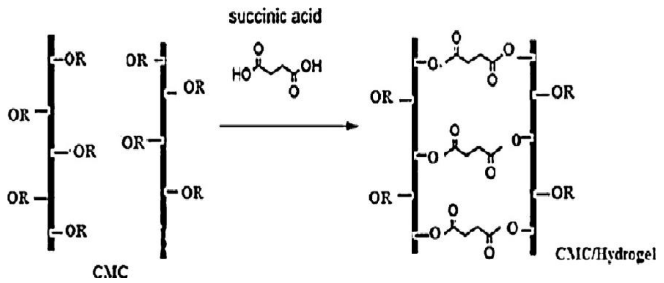


Figure 2. Schematic illustration of hydrogel fabrication

Figure 3 schematically represents the polymerization mechanism of aniline inside the CMC hydrogel matrix. Synthesis of PANI is commonly performed by chemical oxidative polymerization of aniline in a protonic acid aqueous solution (WenboWanga 2010; Wu *et al*., 2006). According to the generally accepted mechanism of conducting PANI formation, the salt of aniline monomer and protonic acid was produced before the oxidative polymerization reaction occurred (Wu *et al*., 2006).

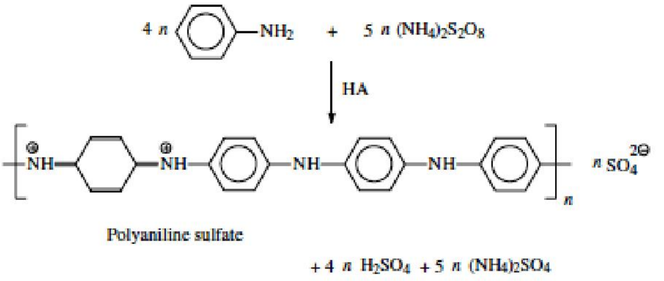


Figure 3a. The oxidation of aniline with ammonium peroxydisulfate in acidic aqueous medium yields protonated polyaniline (emeraldine)

As shown in Figure 3a,b during electrochemical synthesis of PANI, large numberof positive charges are generated on nitrogen atoms inthe polymeric chains. The negative charges of CMC moietiesinteract with positively charge PANI backbone viaelectrostatic interactions (Wu *et al*., 2003).

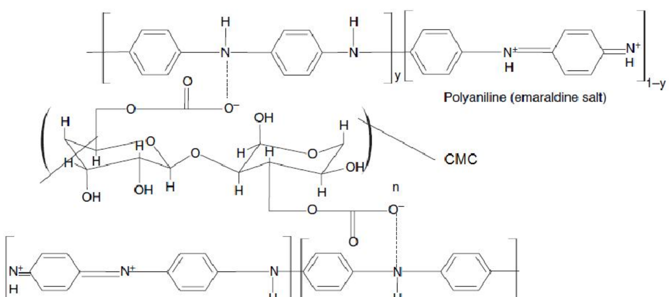


Figure 3b. Proposed mechanism of PANI–CMC hydrogel during polymerization

IR spectrum of PANI–CMC conductinghydrogel

The PANI–CMCconducting polymer was characterized by FT-IRspectrum.

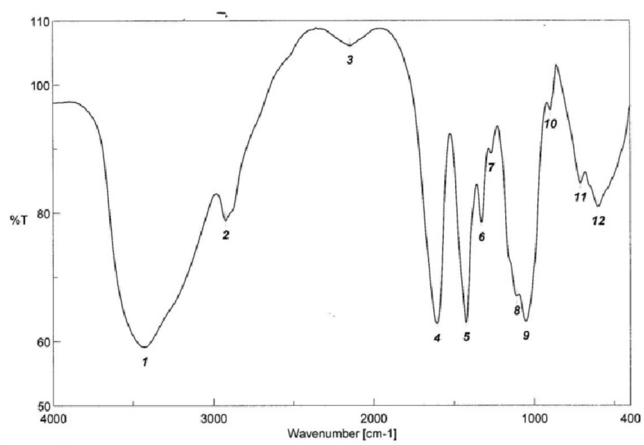


Figure 4a. FTIR of Carboxymethylcellulose

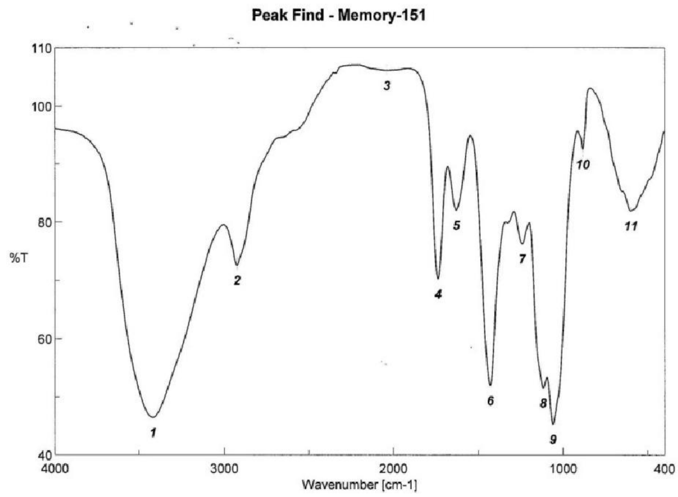


Figure 4b. FTIR of CMC –PANI Hydrogel

Figure 4a,b show FTIR spectra of CMC as well as figure4, FTIR spectra of CMC/PAN hydrogel. In figure 4a exhibit all the bands corresponding to the functional groups available on CMC. The peak 3427 cm^{-1} due to O–H stretching vibration mode of the –OH group and a band at 2923 cm^{-1} is attributed to C–H stretching vibration. The IR band at 1605 cm^{-1} is assigned to COOH group due to ring stretching of glucose. The bands seen around 1425 and 1327 cm^{-1} are assigned to C–H scissoring and –OH bending vibration modes in CH_2 and COH groups, respectively. The band at 1053 cm^{-1} is assigned to C–O stretching vibration modes due to primary alcoholic $–CH_2OH$ stretching mode. The weak band at around 710 cm−1 is due to ring stretching and ring deformation of _-D-(1–4) and _-D-(1–6) linkages.

The presence of newbandsat 2037 and 1735 $cm^{-1}$and the aforementioned band seen at 1425, 1605,1110 and 1053 cm^{-1} shifts to higher frequency region1429,1628, 1118,1060 cm^{-1}in the IR spectra of CMC-PANI hydrogel in figure4b due to interaction between PANI and CMC that revealing the formation of the conductive hydrogel moreover presence of a sharp band at 830 cm^{-1} indicates that the amount of linear chain structure corresponding to the 1,4-para-disubstitution mode in PANI–CMC is dominant.

Factors affecting the conductivity

Conductivity is the most important property of PANI polymer.Its electrical conductive nature is explained by the ability to form polarons, cationradicals. The electrical conductivity of the prepared hydrogel is influenced by several factors. Hereundersuch factors were investigated.

Influence of aniline concentration on the conductivity of hydrogel

The concentration of aniline affects polymerization reaction inside the CMC network and the conductivity of hydrogel. From figure5 it can be seen that as increase aniline concentration from 0.01 moles to 0.04 mole cause an increase in conductivity from 30.6 X10^5 to 41.3 X10^5 this could be attributed to that lower aniline concentration causes a slower velocity for the polymerization reaction between aniline monomers, a lower polyaniline yield, and a lower conductivity. On the other hand, due to the osmosis character of aniline monomer and CMC network, increase aniline concentration increase part aniline monomers penetrate into CMC network and polymerize to form more polyaniline inside the network increasing conductivity of the hydrogel. Under a higher aniline concentration, mostly aniline monomers and oligomer exist outside of CMC network, and are washed out in the preparation process. Consequently, higher aniline concentrations do not produce a higher polyaniline chain density in the network of CMC and higher conductivity chain IR aniline.

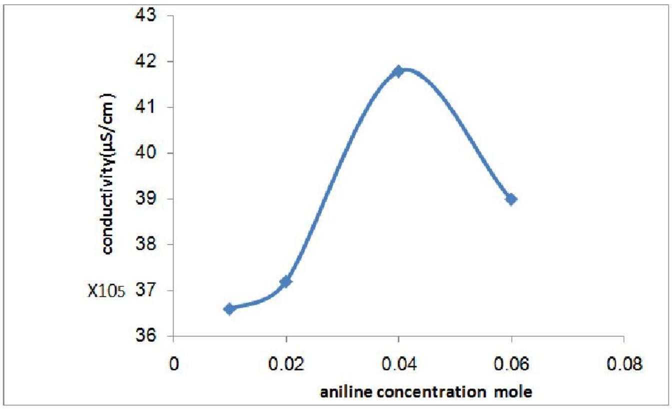


Fig. 5. Effect of aniline concentration on the conductivity of CMC/PANIHydrogel

Influence of the amount of initiator on the conductivity of hydrogel

The electrical conductivity of the hydrogel depends on PANI chains, and the formation of the PANI chains is initiated by APS, so the amount of initiator APS affects the conductivity of the hydrogel. It is seen in Figure 6, the electrical conductivity of the hydrogel increases with the increase of the concentration of APS.a lower amount of APS does not produce enoughcross link points to construct PANI chains and conducting channels, which results in the decline of the electrical conductivity of the hydrogel. On the other hand, KPS is not only an initiator, but also an oxidizer, excessive APS causes a side reaction for oxidizing PANI, which leads to the devastation of the PANI chain in some extent, a conducting channel cannot run through the hydrogel effectively, therefore, the conductivity of the hydrogel decreases.

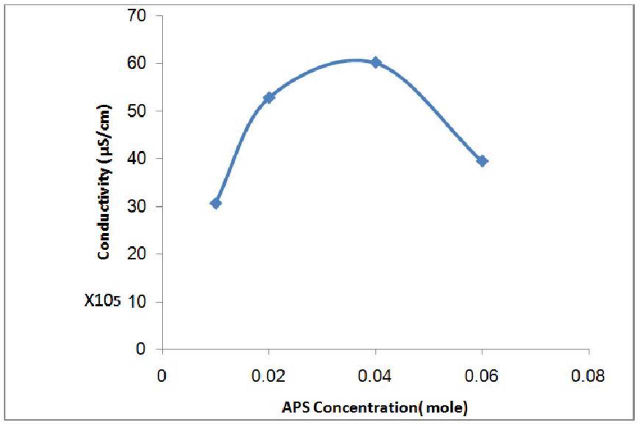


Figure 6. Effect of initiator concentration on the conductivity of PANI/CMC Hydrogel

SEM

From SEM images, it's found pore structure the dried CMC/succsinc hydrogel matrix (Figure 7a), but heterogeneousstructure develops in the matrix on impregnation of PANI into the polymer matrix. From Figure 7b, it can be implied that impregnated PANI molecules from clusters within the matrix. The PANI molecules are hydrophobic in nature, whereas the polymer matrix is hydrophilic. The formation of PANI clusters is probably due to hydrophobic dispersion forces of PANI molecules.

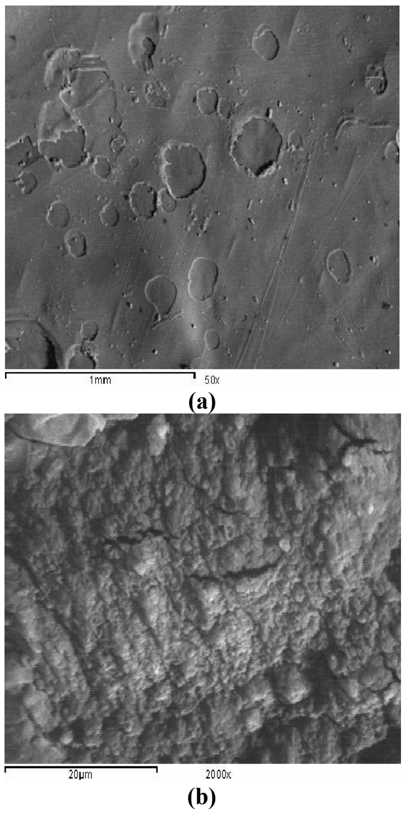
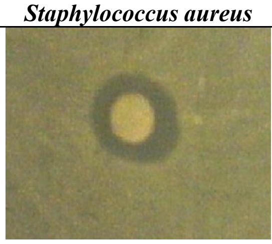
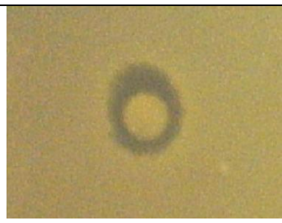


Fig. 7. SEM morphology of (a) CMC/succinic acid hydrogel and (b) PANI impregnated hydrogel

Table 1. Antibacterial properties of the CMC/succinic acid/PANI hydrogel

Sample	Inhibition zone (cm)		
	Staphylococcus aureus	***Escherichia coli***	***Candida albicance***
CMC / succinic acid / PANI	 15	 14	 10

Antibacterial effect

Table 1 illustrates the results on antibacterial properties of the CMC/ succinic acid / PANI hydrogel. All the samples containing PANI exhibited a higher degree of bacterial suppression, which was a result of amide formation from the condensation of the carboxylic acid groups of CMC/ succinic with the amino groups of PANI. The stronger antibacterial activity of CMC/ succinic acid / PANI hydrogel may be a result of electrostatic interactions between the highly positively charged molecule and the negatively charged cell surface (Cao *et al*., 1989). Bacterial strains such as E. coli, with an extracellular capsule, carry less negative charge and are less prone to adsorption by the positively charged surface of CMC/ succinic acid / PANI

Conclusion

(CMC\polyaniline) conducting hydrogel was fabricated by in situ polymerization of aniline within the matrix of CMC hydrogel the polymerization reaction was monitored by the electrical conductivity of CMC/PAN hydrogel. The prepared hydrogels are characterized using swelling behavior, FTIR and SEM. The conductive hydrogel exhibited high antibacterial activity against Gram positive and Gram negative bacteria.

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