

## Preparation and Characterization of a Cotton-Based Nanocomposite Hydrogel

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### Article history:

Received 15/3/2013

Accepted 22/5/2013

Published online 1/6/2013

### Keywords:

Nanocomposite

Hydrogel

Acrylic acid

Cotton fabric

Silver

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### Abstract

In this work, hydrogel nanocomposites were synthesized by solution polymerization of acrylic acid (AA) and itaconic acid (IA) in the presence of cotton fabric. Ammonium persulfate (APS) was used as the polymerization initiator in the presence of a crosslinker, methylene bisacrylamide (MBA). Insertion of Ag followed by reduction of Ag<sup>+</sup> cations results in a hydrogel nanocomposite. The structure and morphology of the resulting Ag nanoparticle-loaded grafted fabric was characterized by fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD). The influence of both APS and MBA concentration on the swelling capacity of nanocomposites was also studied.

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## 1. Introduction

Over the past few decades, nanomaterials have received increasing attention due to their exceptional properties different from their corresponding bulk counterparts [1, 2]. Inorganic nanoparticles, whose structures exhibit significantly novel properties due to their nanoscale size, have proved much interest [3]. Among inorganic agents, silver has been employed most extensively [4]. Due to a wide range of properties such as flexibility, elasticity, and strength, textile materials have invaded many industrial fields [5]. Metalized textile is a kind of

new composite material that has attracted the attention of scientists and engineers due to its special properties such as heat radiation resistance, oil repellence, soil repellence, and antimicrobial and electrical conductivity [6-9].

Nanoparticles treated fabrics have some functional behaviors including antibacterial activity, UV-protection, self-cleaning etc. These properties increased in the modified fabrics by eco-friendly polymer modifications like polysaccharides. These types of textile materials are needed in the increasingly demanding human society with environmental safety [10-12].

Hydrogels or water-containing gels are cross-linked polymeric structures produced by the reaction of one or more monomers and characterized by hydrophilicity and insolubility in water. In water, they swell to an equilibrium volume, but preserve their shape [13, 14].

Because of their excellent characteristics, hydrogels have been extensively studied and widely used in many applications such as disposable diapers, feminine napkins, drug delivery systems, and soil for agriculture and horticulture. They have aroused considerable interest and been the subject of much research [15-20]. Herein, we report the results of our study using the graft copolymerization to modify cotton fabric with the hydrogel-nanostructured silver nanocomposite in order to impart the cotton.

## 2. Experimental procedure

### 2.1. Materials

Acrylic acid, itaconic acid, methylene bisacrylamide, ammonium persulfate, and silver nitrate were obtained from Merck and sodium borohydride salts were obtained from Sigma-Aldrich Company. Cotton fabric was obtained from a local textile mill.

### 2.2. Preparation of the fabric

The fabric was soaked in a detergent solution for 60 min, followed by extensive washing with tap water until it was free from any detergent. The clean fabric was then washed with distilled water, squeezed, and allowed to dry in an air oven at 60 °C, and finally stored in a vacuum desiccator ready for use.

### 2.3. Preparation of silver nanoparticle-loaded fabric

In brief, in order to prepare poly (AA-co-IA)-grafted fabric, the appropriate amount of fabric was placed in a test tube. One mL AA, 0.3 g IA and 0.005 g crosslinker MBA were dissolved in water and the final volume, 10mL was made. Then, 0.1 g APS was dissolved and the whole reaction mixture was transferred in the test tube and kept in a water bath at 60 °C for a period of 2 h. The grafted fabric was washed thoroughly with distilled water, and then extracted with hot water for 5 h in order to dissolve any homopolymer which may have adhered to the surface of the fabric. The fabric was equilibrated in the ethanol for a period of 24 h to remove water. The grafted samples were then allowed to dry in an air oven at 60 °C.

The swollen fabric was put in an aqueous solution of Ag nitrate prepared by dissolving 20 mg of AgNO<sub>3</sub> in 30 mL of double-distilled water for 24 h. Next the Ag ions present in the fabric were reduced to Ag nanoparticles by putting the fabric in 0.62 mM potassium borohydride solution at 30 °C for 24 h. Finally the fabric was rinsed with distilled water and put in a dust free chamber at 50.

### 2.4. Characterization

The Fourier transformation infrared (FT-IR) spectra of silver nanoparticle-loaded fabric sample were recorded on a FTIR spectrophotometer using KBr .

The surface morphology of the nanocomposite hydrogel was examined using scanning electron microscopy (SEM). After Soxhlet extraction with methanol for 24 h and drying in an oven, superabsorbent powder was coated with a thin layer of gold and imaged in a SEM instrument (Leo, 1455 VP).

### 3. Results and discussion

#### 3.1. Mechanism of nanocomposite formation

A general reaction mechanism for the cotton-g-poly(AA-co-IA) formation is shown in Scheme 1. At the first step, the copolymer was formed via a simple free radical copolymerization. The sulfate anion-radical produced from thermally decomposition of ammonium persulfate radically initiates copolymerization of acrylic acid and itaconic acid monomers led to a copolymer so called cotton-g-poly(AA-co-IA). Since a crosslinking agent, e.g. MBA, is presented in the system, the copolymer comprises a crosslinked structure. A fully swollen hydrogel was then put in the aqueous  $\text{AgNO}_3$  solution. After equilibrium is attained, the hydrogel is transferred into  $\text{KBH}_4$  solution. The resulted mixture was finally reduced to produce a cotton-based nanocomposite hydrogel.

#### 3.2. Spectral characterization

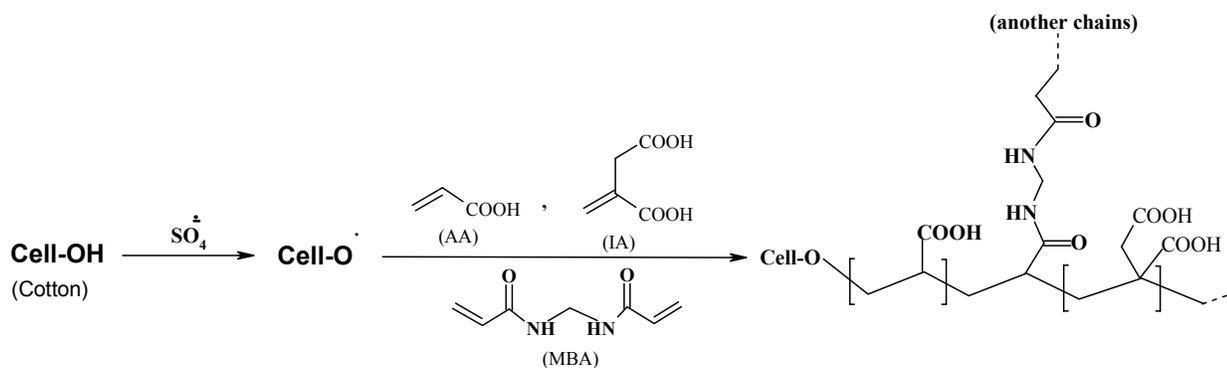
##### 3.2.1 FTIR analysis

The grafting vinyl monomers onto cotton using ammonium persulfate as oxidizing initiator was

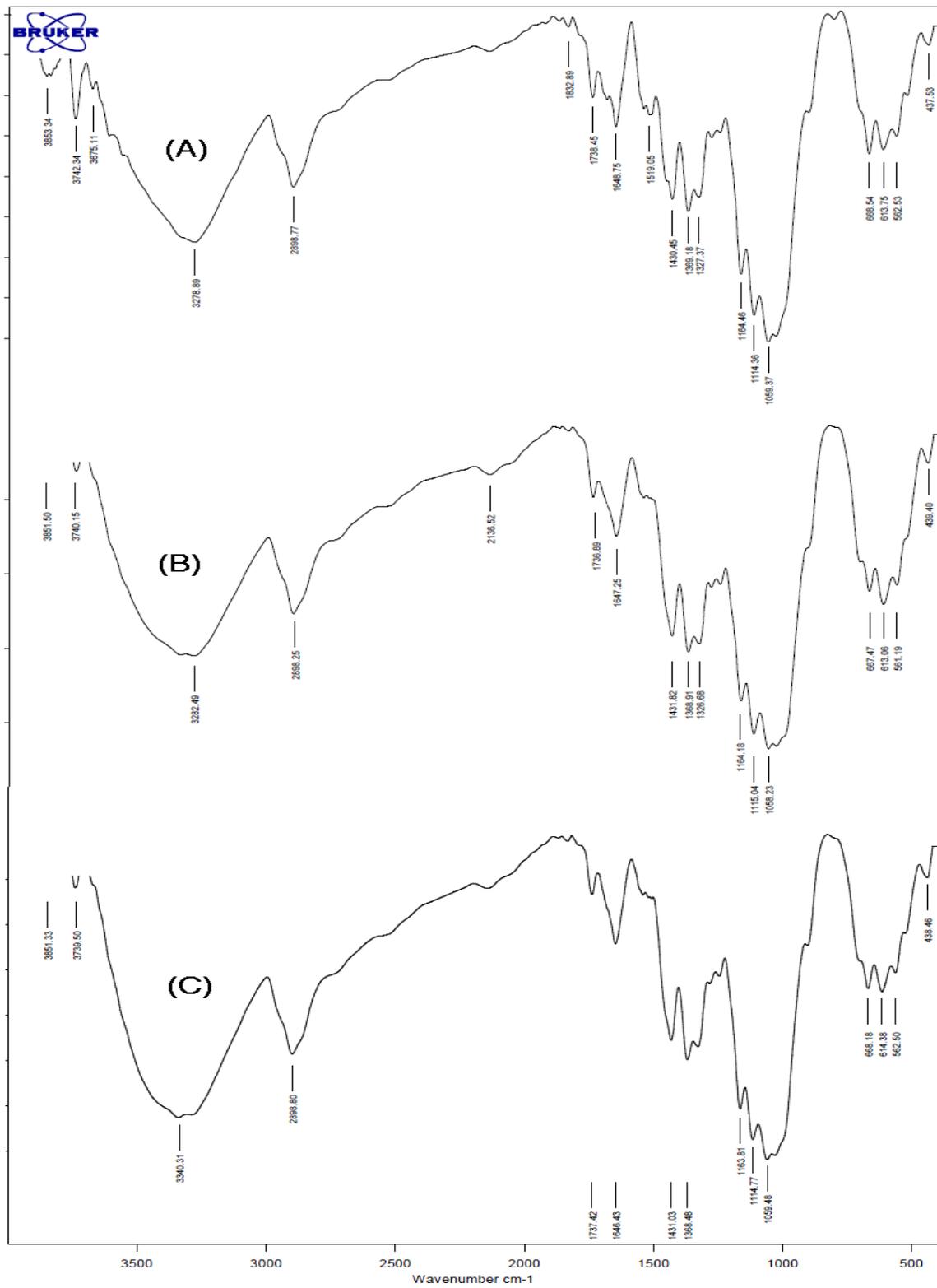
proved using FTIR. Figure 1 shows the FTIR spectra of cotton, poly (AA-co-IA)-grafted cotton, and Ag-loaded grafted cotton fabric. A broad peak at  $3200\text{--}3600\text{ cm}^{-1}$  is due to the presence of both carboxylic groups of IA and AA and also corresponding to the  $-\text{OH}$  hydroxyl group of cotton fabric. In the spectrum of Ag-loaded fabric, the peak at  $3340\text{ cm}^{-1}$ , corresponding to carboxyl groups' functionalities, indicates the binding of an Ag with oxygen in carboxyl groups [21].

##### 3.2.2. SEM analysis

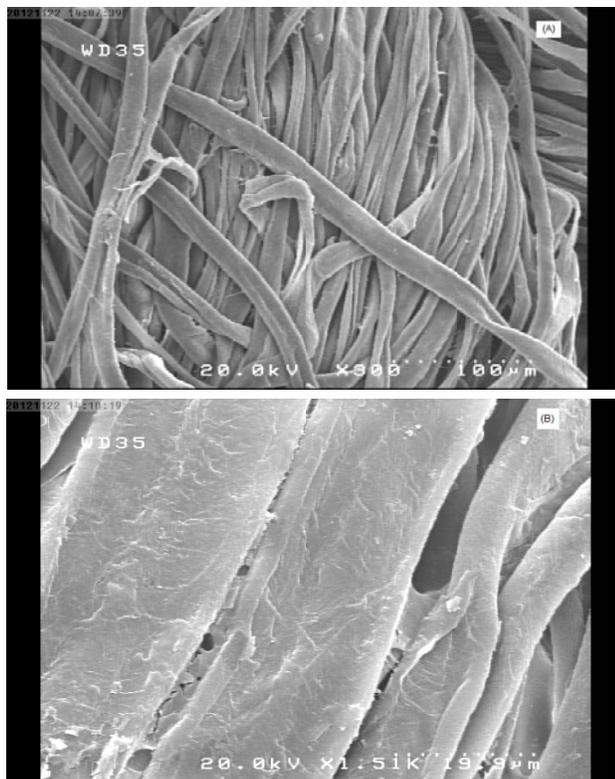
One of the most important properties that must be considered is hydrogel microstructure morphologies. Figure 2 shows the scanning electron microscope (SEM) photograph of the surface area of the cotton fabric (A) and grafted cotton fabric hydrogel (B). It can be seen that grafted cotton fabric has thin layer of poly(AA-co-IA) on surface. This phenomenon might be attributed to the hydrogen bonds between cotton fabric and grafted chains.



**Scheme 1.** Proposed mechanistic pathway for synthesis of fabric-g-poly(AA-co-IA).



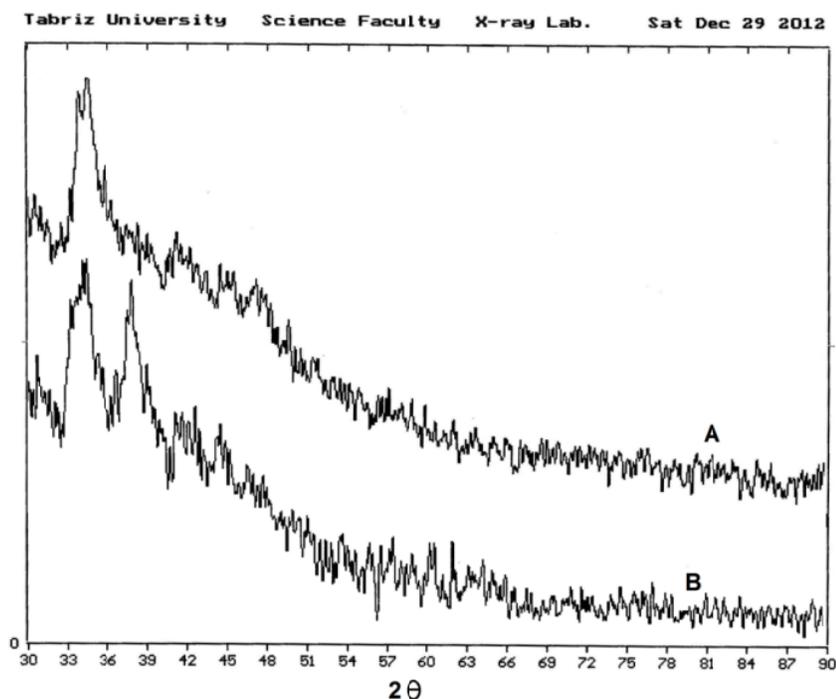
**Fig. 1.** FTIR spectra of cotton (A), cotton-g-poly(AA-co-IA) (B), and cotton-g-poly(AA-co-IA)/Ag nanoparticle (C).



**Fig. 2.** SEM photograph of the cotton fabric (A) and the grafted cotton fabric (B).

### 3.2.3 XRD Analysis

As known, X-ray diffraction pattern of amorphous polymer will not show any sharp and highly intensified peaks whereas the nanocomposites of amorphous polymer show these peaks. This is due to the development of crystallinity in the amorphous polymer. Therefore, structural information of silver nanoparticles was obtained by X-ray diffraction (Fig. 3). The peak exhibited at  $37.8^\circ$  is assigned to reflection through (111) plane of the face centered cubic (fcc) of silver nanoparticles, respectively. However, cotton-g-poly(AA-co-IA) did not show any such peak. Therefore, it is very clear that hydrogel nanocomposite consists of silver nanoparticles.

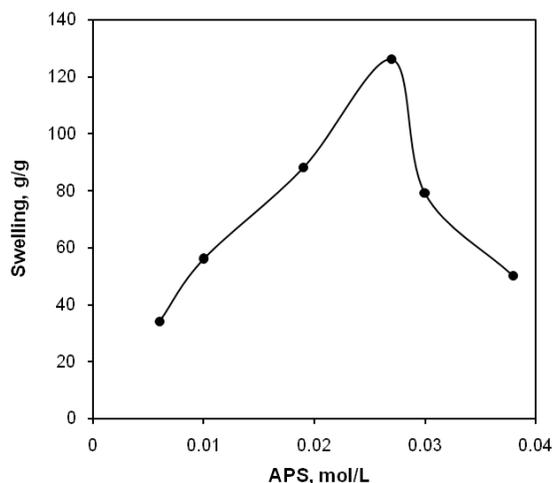


**Fig. 3.** XRD of the grafted cotton fabric (A) and the grafted cotton fabric/Ag nanoparticle (B).

### 3.3 Effect of APS on Water Absorbency

The effect of the initiator concentration on the water absorbency of the superabsorbent was studied (Fig. 4). The increase of water absorbency with increasing initiator concentration up to 0.027 mol/L may be ascribed to the increase of the active sites on the backbone of the cotton arising from the attack of sulfate anion-radical. An additional reason, according to Flory [22], is imperfection of the polymer networks obtained from high-initiator polymerization systems .

The decrease of water absorbency with initiator concentration beyond 0.027 mol/L may be due to (a) increased number of produced radicals leading to terminating step via bimolecular collision, (b) predominance of homopolymerization over grafting, (c) molecular weight loss of the synthetic part of the polymer network [17], and (d) free radical degradation of cotton substrate.

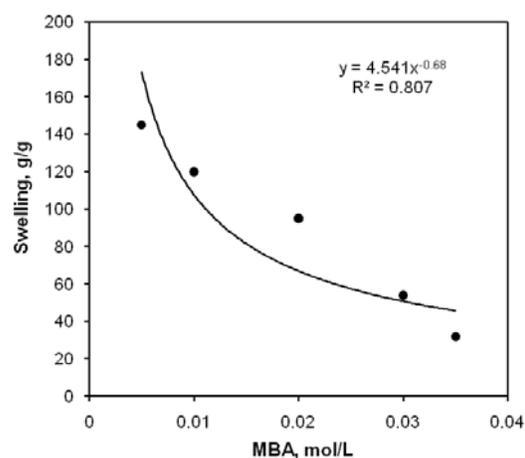


**Fig. 4.** Effect of initiator concentration on swelling capacity.

### 3.4. Effect of MBA on Water Absorbency

Crosslinks is necessary to form a superabsorbent in order to prevent dissolution

of the hydrophilic polymer chains in an aqueous environment. The effect of MBA concentration on the water absorbency of the hydrogel was studied by varying the concentration of MBA from 0.005 to 0.035 mol/L (Fig. 5). As the concentration of MBA was increased, the water absorbency of the superabsorbent decreased. This is due to a decrease in the space between the polymer chains as the cross-linker concentration is increased.



**Fig. 5.** Effect of cross-linker concentration on swelling capacity.

## 4. Conclusion

In summary, silver nanoparticles have been successfully prepared via ammonium persulfate induced graft co-polymerization of acrylic monomers onto cotton fabric in an aqueous medium. The grafted cotton fabric was loaded with Ag nanoparticles by entrapment of Ag<sup>+</sup> ions into a grafted polymer network followed by borohydride reduction. After structure characterization using FTIR and SEM, the synthesis of nanocomposites was optimized by varying the reaction parameters affecting the ultimate swelling capacity of the final product. As an extension of this work, the nanocomposite

is being subjected to further investigation for its antibacterial activity to various bacteria.

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