

SYNTHESIS AND SWELLING BEHAVIOUR OF COLLAGEN-*g*-POLY(MAA)/KAOLIN SUPERABSORBENT HYDROGEL COMPOSITES

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Abstract

In this work, a novel superabsorbent hydrogel composite based on collagen have been prepared via graft copolymerization of methacrylic acid (MAA) in the presence of kaolin powder by using methylenebisacrylamide (MBA) as a crosslinking agent and ammonium persulphate (APS) as an initiator. A proposed mechanism for hydrogel formation was suggested and the structure of the composite was established by using FTIR spectroscopy and gravimetric analysis of the products. A new absorption band at 1728cm^{-1} in the composite spectrum confirmed kaolin-organic polymer linkage. The effect of kaolin amount and MBA concentration showed that with increasing of these parameters, the water absorbency of the superabsorbent composite was decreased.

1. Introduction

Vinyl graft copolymerization onto polysaccharide backbones is a well-known method for synthesis of natural-based superabsorbent hydrogels

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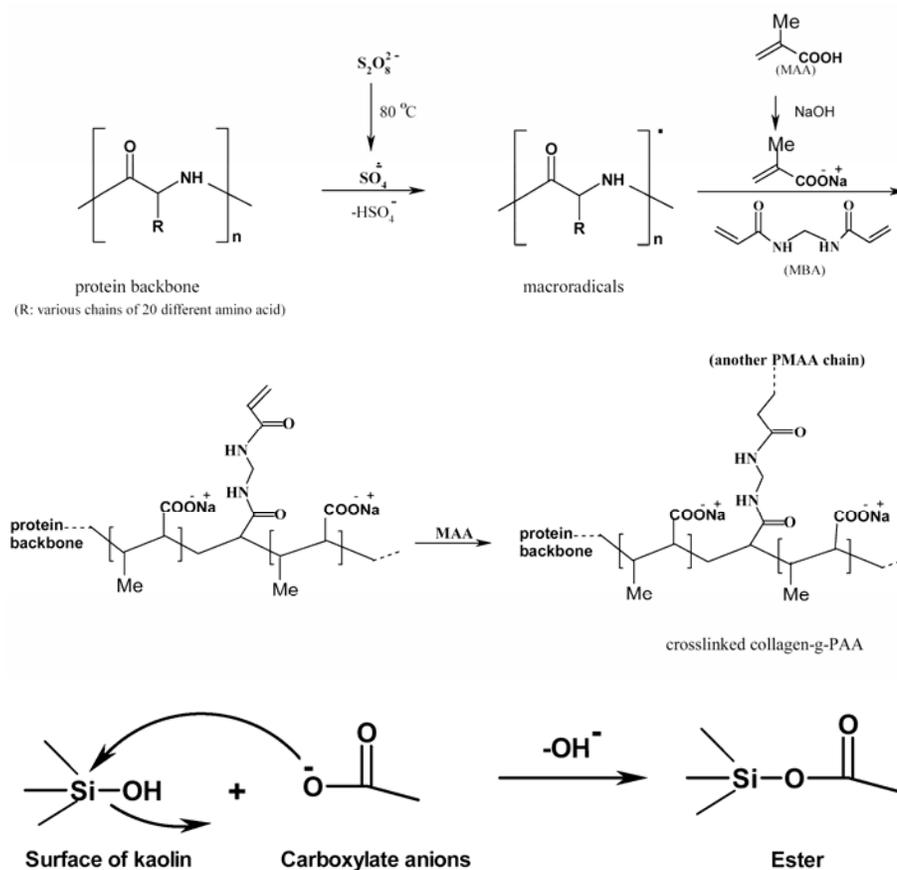
[2, 4]. The first industrial superabsorbent hydrogel, hydrolyzed starch-graft-polyacrylonitrile, was synthesized by using this method. These biopolymer materials are crosslinked hydrophilic polymers, capable of absorbing large quantities of water, saline or physiological solutions [6]. They are widely used in many fields, such as hygienic, cosmetics, and agriculture. More ever, proteins are widely distributed in nature and are synthesized mainly in animals, i.e., collagen, keratin, gelatin, ant, etc., and in a few plants such as soya. In general, proteins are high molecular weight polymers and their solubility in aqueous solutions is difficult. Two efficient methods for preparation of aqueous soluble proteins are alkaline and enzymatic hydrolysis [6]. Only a few studies have been reported in the case of protein-based SAPs. In the present report, to modify the hydrolyzed collagen, the grafting of methacrylic acid (MAA) onto collagen chains in the presence of a crosslinking agent and kaolin was performed in a homogeneous system.

2. Experimental

2.1. Synthesis and spectral characterization of superabsorbent composite

Synthesis of the superabsorbent hydrogel composite was carried out by using KPS as an initiator and MBA as a crosslinker in an aqueous medium. A general procedure for chemically crosslinking graft copolymerization of MAA onto collagen backbones was conducted as follows. Hydrolyzed collagen (0.75g) was dissolved in 50mL distilled water and filtered to remove its insoluble salt. Then, the solution was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300rpm). The reactor was immersed in a thermostated water bath preset at a desired temperature (70°C). After complete dissolution of collagen, various amounts of kaolin powder (2.50-0.25g) were added to the solution and allowed to stir for 10 min. Then, the initiator solutions (0.017, 0.043, 0.087, 0.17, 0.35, and – 0.52g KPS in 5mL H₂O) were added to the mixture. After stirring for 15 min, certain amounts of 70% neutralized MAA (1.5, 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0g in

5mL H₂O) and MBA (0.13, 0.16, 0.21, 0.24, and 0.27g in 5mL H₂O) were simultaneously added to the reaction mixture. After 90 min, the produced hydrogel was poured to excess non solvent ethanol (200mL) and remained for 6h to dewater. Then ethanol was decanted and the product scissored to small pieces (diameter ~ 5mm). Again, 250mL fresh ethanol was added and the hydrogel was remained for 24h. Finally, the filtered hydrogel is dried in oven at 60°C for 5h. After grinding, the powdered superabsorbent was stored away from moisture, heat, and light. Mechanism of hydrogel composite formation can be shown as follows:



Scheme 1. Proposed mechanistic pathway for synthesis of the partially neutralized collagen-g-PMAA/kaolin hydrogel composite.

FTIR spectroscopy was used for identification of the hydrogel composite. The FTIR spectra of initial substrates and composite graft copolymer are depicted in Figure 1. Figure 1(a) represents the spectrum of the physical mixture of kaolin and collagen substrates. In the layer silicate structure, -OH groups show absorption bands at $3628\text{-}3675\text{cm}^{-1}$. The carboxylate groups of the grafted poly(methacrylic acid) can be react with the -OH groups on the kaolin surface. The replacement of -OH groups in the surface of kaolin by carboxylate anions results in the ester formation [8].

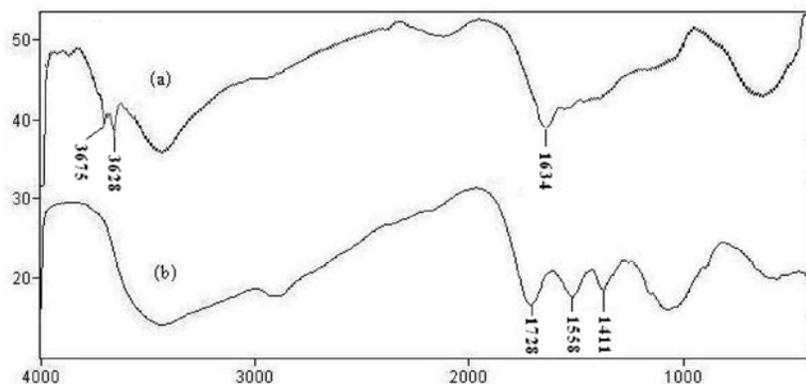


Figure 1. FTIR spectra of physical mixture of kaolin and collagen (a) and the synthesized hydrogel composite (b).

The band observed at 1634cm^{-1} can be attributed to $\text{C}=\text{O}$ stretching in carboxamide functional groups of substrate backbone. In the spectrum of the composite (Figure 1(b)), two new absorption peaks at 1558 and 1728cm^{-1} are appeared. The characteristic band at 1558cm^{-1} is due to $\text{C}=\text{O}$ asymmetric stretching in carboxylate anion that is reconfirmed by another peak at 1411cm^{-1} , which is related to the symmetric stretching mode of the carboxylate groups [10, 11]. The absorption band at 1728cm^{-1} can be corresponding to the ester groups that can be formed

during the graft polymerization reaction. As shown in this figure, the absorption bands of $-OH$ of kaolin at $3628-3674\text{cm}^{-1}$ are disappeared.

2.2. Thermal analysis

Thermogravimetric analysis (TGA) was employed to thermally characterize the hydrogel in comparison with the intact collagen (Figure 2). The thermal stability of the grafted collagen is improved as is obvious from the TGA curve. TGA of collagen (Figure 2(a)) shows a weight loss in two distinct stages. The first stage ranges between 10 and 130°C and shows about 17% loss in weight. This may correspond to the loss of adsorbed and bound water. No such inflexion was observed in the TGA curve of collagen-g-poly(MAA)/kaolin hydrogel (Figure 2(b)).

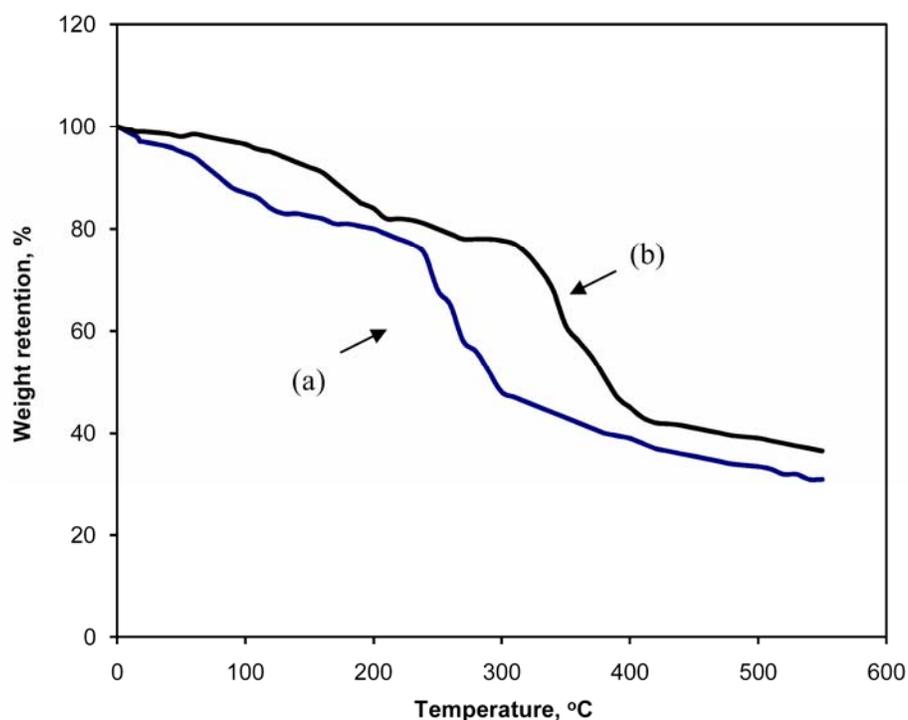


Figure 2. TGA of collagen (a) and collagen-g-poly(MAA)/kaolin hydrogel composite (b).

This indicated that the grafted copolymers were resistant to moisture absorption. The second stage of weight loss starts at 230°C and continues up to 300°C during which, there was 52% weight loss due to the degradation of collagen. In general, degradation of native collagen is faster than that of grafted collagen. About 60% weight loss takes place in the temperature range of 220-370°C for collagen. In the collagen-g-poly (MAA)/kaolin sample, a residual weight of 77% was observed at 310°C. The appearance of these stages indicates the structure of collagen backbones has been changed, which might be due to the grafting of poly(MAA) chains. In general, the copolymer had lower weight loss than collagen. This means that the grafting of collagen increases the thermal stability of collagen in some extent [1].

2.3. Swelling measurements using tea bag method

The tea bag (i.e., a 100 mesh nylon screen) containing an accurately weighted powdered sample ($0.5 \pm 0.001\text{g}$) was immersed entirely in 200mL distilled water and allowed to soak for 3h at room temperature. The sample particle sizes were 40 to 60 meshes (250-350 μm). The tea bag was hung up for 15 min in order to remove the excess solution. The equilibrium swelling (ES) was calculated according to following equation [7]:

$$ES(g/g) = \frac{\text{Weight of swollen gel} - \text{Weight of dried gel}}{\text{Weight of dried gel}}. \quad (1)$$

The accuracy of the measurements was $\pm 3\%$.

3. Results and Discussion

3.1. Optimization of the grafting variables

In this work, the main factors affecting on the grafting conditions and different variables affecting the ultimate swelling capacity (i.e., concentration of MBA, kaolin/collagen, and APS) were optimized to achieve superabsorbents with maximum water absorbency.

3.2. Effect of MBA concentration on swelling

The effect of crosslinker concentration (C_c) on swelling capacity of crosslinked collagen-*g*-poly(MAA)/kaolin hydrogel was investigated. As shown in Figure 3, more values of absorbency are obtained by lower C_c . Such a well-known behaviour reported by pioneering scientists [13]. In fact, higher C_c decrease the free space between the copolymer chains and consequently, the resulted highly crosslinked rigid structure can not be expanded and hold a large quantity of water.

This power law behaviour between swelling capacity and MBA concentration (Equation 2) was conducted from Figure 3.

$$\text{Swelling capacity} \approx K[\text{MBA}]^{-n}. \quad (2)$$

The K and n in Equation 2 are constant values for an individual superabsorbent. The n value represents the extent of the sensitivity of the hydrogel to the crosslinker content, while the K value gives an amount useful for comparing the extent of swelling versus fixed crosslinker content. The $K = 11.65$ and $n = 0.92$ is obtained from the curve fitted with Equation 2.

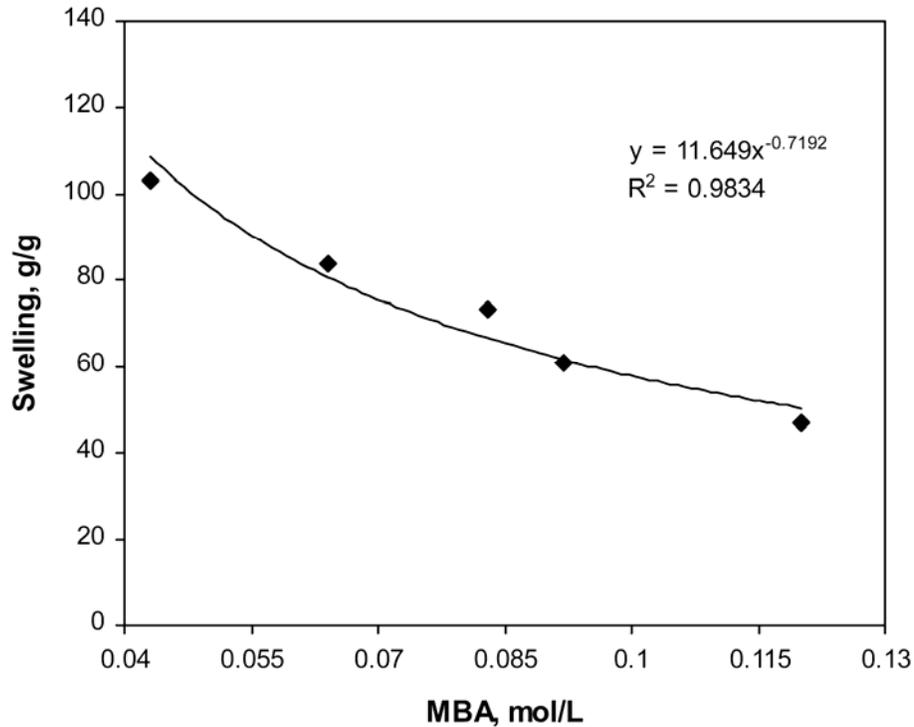


Figure 3. Effect of the crosslinker concentration on water absorbency of the superabsorbent composite.

3.3. Effect of APS concentration on swelling

The influence of initiator concentration on final swelling capacity of the hydrogel has been studied by varying the APS concentration from 0.004 to 0.04 mol/L (Figure 4). Maximum swelling (205 g/g) was obtained at 0.026 mol/L of initiator concentration. More or less than this concentration gives hydrogel with decreased swelling capacity. The number of active free radicals on the gelatin backbone is decreased at lower concentrations than 0.026 mol/L which, in turn, resulting in lower graft polymerization extent and consequently lower final water absorbency [9].

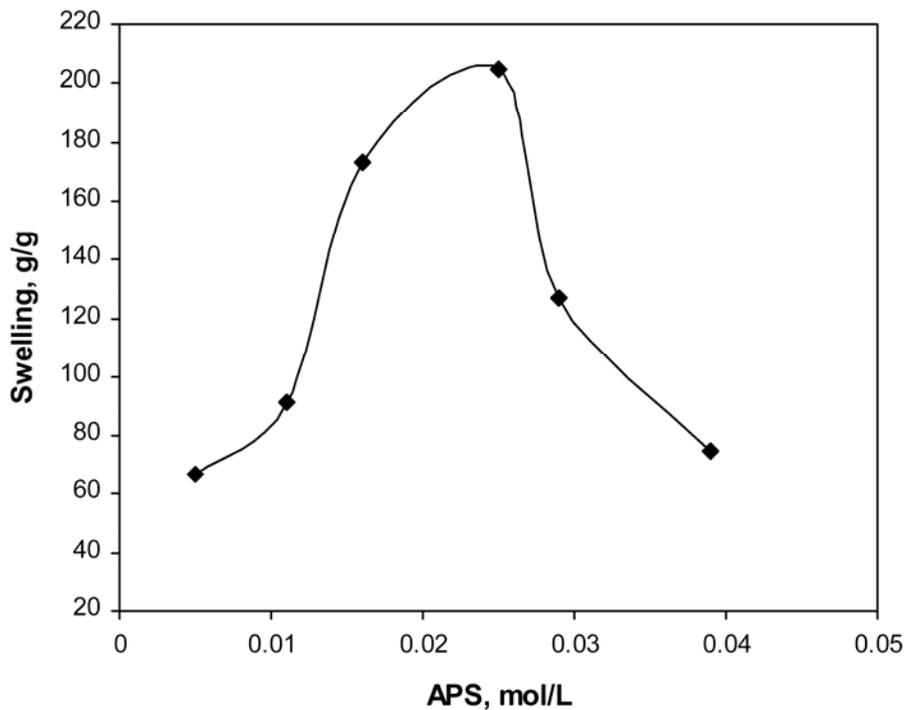


Figure 4. Effect of initiator concentration on water absorbency of the superabsorbent composite.

Subsequent swelling loss can be explained on the basis of (a) an increase in terminating step reaction via bimolecular collision, which is referred to as 'selfcrosslinking' by Chen and Zhao [3] and (b) the decrease in molecular weight (MW) of grafted polyacrylic acid of the hydrogel causes to decrease swelling value. The latter reason is due to the inverse relationship between MW and initiator concentration [3]. Also, the free radical degradation of collagen backbones by sulphate radical-anions is an additional reason for swelling-loss at higher APS concentration. The proposed mechanism for this possibility is reported in the previous work [5]. A similar oxidative degradation of chitosan chains by potassium persulphate is recently reported by Hsu et al. [5].

3.4. Effect of kaolin amount on swelling

The effect of kaolin content on the water absorbency of the composite was studied (Figure 5). The kaolin/collagen weight ratio was varied from 0.25 to 2.50g, while other reaction variables were constant. The effect of kaolin amount on water absorbency is similar to MBA influence on absorbency [12].

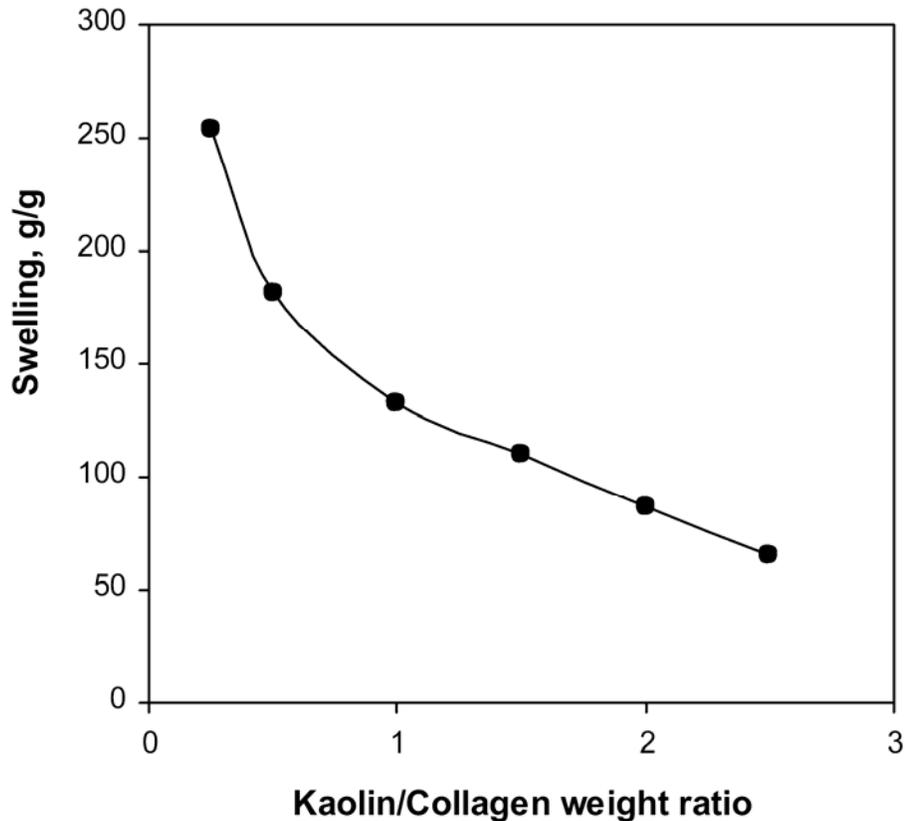


Figure 5. Effect of kaolin/collagen weight ratio on water absorbency of the hydrogel composite.

Figure 5 indicates that the water absorbency of the superabsorbent is decreased with increasing the kaolin amount incorporated in the composite structure. The clay in the polymerization reaction may be acts via two ways: (a) kaolin particles acts as a crosslinking agent (it means

that carboxylate groups of sodium poly(acrylate) chains react with kaolin as obviously proved by FTIR spectra (Figure 1)), and (b) kaolin particles prevent the growing polymer chains through a chain transfer mechanism [12].

4. Conclusion

In the present study, we prepared a novel superabsorbent hydrogel composite by crosslinking graft copolymerization of poly(methacrylic acid) onto a hydrolyzed collagen. The optimum reaction conditions was achieved at MBA 0.043mol/L, initial, APS 0.026mol/L, collagen 0.025, and kaolin 0.01wt%. The effect of the kaolin amount and MBA concentration showed that with increasing of these parameters, the water absorbency of the superabsorbent composite are decreased. The hydrogel composites will most probably posses higher biodegradability (due to the collagen part) and higher swollen gel strength (due to the inorganic parts). The latter properties are of the subjects under consideration in our laboratory.

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