



Free radical grafting kinetics of acrylamide onto a blend of starch/chitosan/alginate



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ABSTRACT

Grafting of monomer onto polymer backbone is one of the effective and accessible methods for the chemical modification of polysaccharides. Grafting of acrylamide (AAM) onto polysaccharides blend (PsB) composed of starch, chitosan and alginate has been carried out using potassium persulfate (KPS) as an initiator. The kinetics of the grafting polymerization also has been studied. The grafting parameters have been evaluated by changing the initial concentrations of AAM from 8 to 16 g, PsB from 6 to 14 g and KPS from 0.2 to 1 g. Evidence of grafting has been obtained from FTIR, XRD and TGA. The kinetics of the grafting polymerization also has been studied. The grafting rate equation of the produced hydrogel (PsB-g-AAM) hydrogel has been expressed by: $R_g = k[AAM][PsB]^{0.5}[KPS]^{0.5}$. The grafting rate is a first order dependence to [AAM] initial concentration and square root to [PsB] and [KPS] initial concentrations in the used concentrations range.

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1. Introduction

Grafting is a useful method for modifying some properties of natural and synthetic polymers. In grafting process, amount of monomer is attached onto the polysaccharide backbone, the formed product can be provided with a number of new properties such that, it swells in water media with good product yield (El-Sayed et al., 2011; Sadeghi, Heidari, & Montazeri, 2011; Shifeng, Ying, Lucile, & Da-Wen, 2012).

Using a polysaccharide blend in the hydrogel preparation shows better mechanical stability and water retention ability, compared to single polysaccharide. In addition, it gives the opportunity to more field applications.

In view of the limitations encountered using the pure polysaccharides blend in hydrogel preparation, the concept of alginate–chitosan polyelectrolyte complex was introduced. Complexation of alginate with chitosan reduces the porosity of the alginate beads which in addition, chitosan acquires a higher level of mechanical strength with the support of the alginate gel mass (Wong, Chan, Kho, & Heng, 2002).

Considerable work on the graft polymerization of natural and synthetic polymers with the vinyl monomers has been reported

(Jasim, Al-Karawi, & Hussein, 2010; Patel, Patel, Patel, Patel, & Patel, 1986; Saifuddin, Nur, & Abdullah, 2011; Vieira, Cestari, Airoidi, & Loh, 2008). Grafting process was initiated through generation of free radicals along the polysaccharide backbone as well as the monomer. Among the various methods allowing the generation of radicals, redox initiation systems were widely used (Abd-Alla, Mohamed, & Hesham, 2007; Abdel-Halim, 2012; Ifuku, Iwasaki, Morimoto, & Saimoto, 2012; Mino, Koizerman, & Rasmussen, 1959).

There are many comparative work for the grafting single polysaccharides with acrylamide using the traditional conventional methods. Potassium persulfate (KPS) has been used for the grafting of AAM onto starch, SWR obtained was 605 g/g, using [KPS] of 1.5 wt% of starch, St:AAM (weight ratio) of 1:1 and 140 min at 80 °C (Charoen, Toha, Azizon, & Suda, 2010).

Much attention had been paid to the studied of kinetics of radical graft polymerization of monomers onto polysaccharides by Berlin and Kislenco. Their investigation covering grafting efficiency and the study of the interaction kinetics of initiators with polysaccharides promotes the finding of key reactions for the determination of rate of graft copolymerization, and the development of mathematical models of process kinetics.

Grafting rate (R_g) of acrylonitrile (AN) onto starch using KPS and potassium permanganate ($KMnO_4$) initiator, respectively has been studied. The grafting rate equations using two different types of initiators has been achieved (Brydon, Burnett, & Cameron, 1974; Singh, Tiwari, Pandey, & Singh, 2007):

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Graft polymerization of AAm, acrylic acid (AA) and methylmethacrylate (MMA) monomers onto starch using potassium dichromate (PDC) as an initiator has been carried out (Berlin & Kislenco, 1992), Also the grafting of AA and ethyl methacrylate (EMA) monomers onto starch using CAN has been studied (Taghizadeh & Mehrdad, 2007).

The present work is concerned with studying the graft polymerization of acrylamide onto polysaccharides blend (PsB) in aqueous media using potassium persulfate as an initiator and methylene bis-acrylamide (MBA) as a crosslinker for producing a hydrogel. Moreover, the kinetics of free radical graft polymerization of AAm onto a blend of polysaccharides has been examined. The obtained hydrogel integrated platform for the development of hydrogel based functionality compounds.

2. Materials and methods

2.1. Materials

Normal corn starch (Sigma–Aldrich, Germany), chitosan medium molecular weight (Sigma–Aldrich, Germany), alginic acid sodium salt from brown algae “alginate” (Routh, Germany) and acrylamide (Baker Chemical Co., USA) were the basic raw materials used for the hydrogel preparation. Potassium persulfate (KPS) (Merck, Germany) and methylenebisacrylamide (MBA) (Fluka, Germany) have been used as initiator and crosslinker, respectively. Other chemicals include: acetone, acetic acid and ethanol (El Nasr Pharmaceutical Chemicals Co.), and sodium hydroxide pellets (Laboratory chemicals, Modern Lab., Egypt). All experiments have been performed using distilled water (DW).

2.2. Methods

2.2.1. Preparation of the polysaccharides blend (PsB)

Three grams of starch were suspended in 70 ml DW and stirred for 30 min at 80 °C. 1 g of chitosan was dissolved in 70 ml acidified DW containing 1 wt% acetic acid and stirred for five hours at room temperature. 1 g of alginate was dissolved in 70 ml DW and stirred for four hours at room temperature. The three solutions have been mixed and stirred for 10 min giving the polysaccharides blend (PsB).

2.2.2. Grafting of acrylamide onto PsB

A known weight of KPS, AAm and 0.1 g of MBA have been added to PsB. The reaction mixture has been allowed to react in a water bath at 60 °C under nitrogen atmosphere. For a different grafting periods (10, 20, 30, 60, 90 and 120 min) have been conducted.

2.2.3. Graft polymerization for kinetics analysis

2.2.3.1. *Determination of grafted AAm.* The amount of the grafted AAm monomer onto the polysaccharides backbone (%G) has been estimated according to the following equation (Taghizadeh & Mafakhery, 2001):

$$\%G = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

where, W_1 , W_0 , and W_2 denote the weight of grafted product, original PsB and AAm, respectively. All the reaction parameters are presented in Table 1.

2.2.3.2. *Effect of PsB concentration.* The effect of adding different PsB weights (6, 8, 10, 12 and 14 g) using (12 g) acrylamide, (0.6 g) KPS and (0.1 g) MBA at 60 °C has been studied. AAm/PsB weight ratios of (2, 1.5, 1.2, 1 and 0.86 g/g) has been obtained.

Table 1

Experimental conditions for kinetic analysis of graft copolymerization of methyl acrylate and sago starch by ceric ion.

Exp. no.	PsB weight (gm)	Initiator KPS weight (gm)	Acrylamide weight (gm)	MBA weight (gm)
1	6	0.6	12	0.1
2	8	0.6	12	0.1
3	10	0.6	12	0.1
4	12	0.6	12	0.1
5	14	0.6	12	0.1
6	8	0.2	12	0.1
7	8	0.4	12	0.1
8	8	0.6	12	0.1
9	8	0.8	12	0.1
10	8	1	12	0.1
11	8	0.6	8	0.1
12	8	0.6	10	0.1
13	8	0.6	12	0.1
14	8	0.6	14	0.1
15	8	0.6	16	0.1

2.2.3.3. *Effect of initiator concentration.* The effect of adding different initiator weighs (0.2, 0.4, 0.6, 0.8 and 1 g using (8 g) PsB, (12 g) AAm and (0.1 g) MBA has been studied.

2.2.3.4. *Effect of monomer concentration.* The effect of adding different acrylamide weighs (8, 10, 12, 14 and 16 g) using (8 g) PsB, (0.6 g) KPS and (0.1 g) MBA has been studied giving AAm/PsB weight ratio of (1, 1.25, 1.5, 1.75 and 2 g/g).

2.3. Characterization and analysis

The prepared hydrogel has been characterized using the following methods.

2.3.1. Fourier transform infrared spectroscopy (FTIR)

JASCO FTIR-6100, Japan, using the absorbance technique (400–4000 cm^{-1} and resolution 4 cm^{-1}) was used to identify pure manganese octoate crystals.

2.3.2. X-ray diffraction (XRD)

Phillips X-Ray diffraction equipment PW/1710 with Monochrome TOR, Cu-radiation at 40KV, 35 mA and scanning speed of 0.02°/s.

2.3.3. Thermal gravimetric analysis (TGA)

The thermal analysis was done by means of Shimadzu TGA-50H. The temperature of the powdered sample was raised 10 °C/min up to 500 °C.

3. Results and discussion

3.1. Characterization of PsB-g-AAm

3.1.1. Fourier transforms infrared spectroscopy (FTIR)

Grafting of acrylamide onto polysaccharide blend (PsB) has been confirmed by comparing FTIR spectra of pure PsB mixture with the grafted PsB as shown in Fig. 1. For the pure PsB, there are peaks at 1157, 1080, 1016, and 927 cm^{-1} due to the C=O stretching, a peak at 3390 cm^{-1} (O–H stretching) and a band at 2926 cm^{-1} (C–H stretching), the characteristic peaks of chitosan are 1600 cm^{-1} (N–H bend), 1327 cm^{-1} (C–N stretch), 1155 cm^{-1} (bridge O stretch), two peaks at 1618 and 1440 cm^{-1} (–COO– stretching) and the characteristic peak of alginate appeared at 819 cm^{-1} (Na–O). For the grafted PsB, some new absorption peaks appeared; N–H and O–H stretching absorption are merged to a strong peak around 3428 cm^{-1} . Amide (I) and Amide (II) bands are seen as one strong sharp peak at 1450 cm^{-1} while, C–H stretching vibrations are

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