



Preparation and characterization of starch grafted with methacrylamide using ammonium persulphate initiator

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ABSTRACT

In this study, methacrylamide (MAA) was successfully grafted with starch by simple free radical polymerization technique using ammonium persulphate (APS) initiator. Reaction conditions were examined. The highest percentage grafting of 351.60% was found to be best at 1:4 starch:methacrylamide weight ratio, 0.4 g APS and 90 °C reaction temperature. The washed copolymers were characterized by spectroscopic and thermal analyses. Fourier transform infrared spectroscopy results showed the presence of MAA peaks. Thermogravimetric analyses (TGA) revealed that the prepared copolymer has improved thermal stability.

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1. Introduction

Starch is a polysaccharide having large number of repeating units joined by α -D-glycosidic bond. Its biodegradability, biocompatibility, non-toxicity and cost effectiveness have made it a biopolymer with great potentials. Its applications in biomedical fields have been reported [1–3]. Starch was grafted with different vinyl monomers using ceric ammonium nitrate initiator [4–6] and ammonium persulphate/*N,N,N,N*-tetramethylethylenediamine as redox pair initiator. Polystyrene was grafted onto starch [7] and carrageenan grafted with polymethacrylamide using cross linker. Grafting of acrylamide and acrylic acid onto sweet potato starch was reported using potassium persulphate and ammonium persulphate as initiators [8] and ceric ammonium nitrate [1]. Graft copolymerization of acrylamide onto starch was reported by some researchers using different techniques [9–12].

Recently, several vinyl monomers were grafted onto starch using various methods [13–16]. The researchers either used a different monomer or different initiator in the modification of starch. In this research, we report a simple technique to modify

starch by grafting with polymethacrylamide and APS initiator without any crosslinker. The copolymerization has the highest percentage grafting than any other techniques reported in the literature. The copolymer prepared could potentially be used effectively in drug delivery.

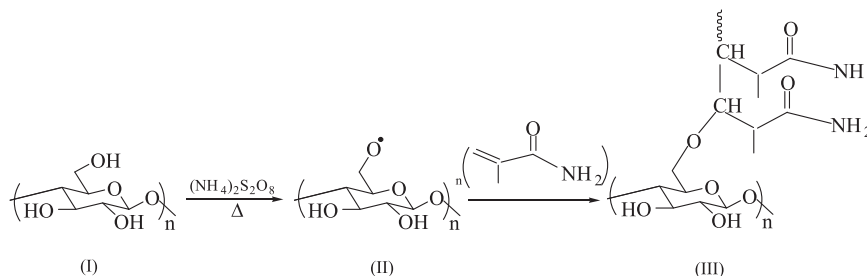
2. Materials and methods

Starch, diethyl ether (analytical grade) and chloroform were purchased from QRèc (Selangor, Malaysia). Methacrylamide (90%) was purchased from Sigma-Aldrich (St. Louis, USA). Potassium bromide was purchased from Merck (Darmstadt, Germany) and ammonium persulphate was purchased from Acros Organics (New Jersey, USA). Methanol (HPLC grade) and tetrahydrofuran (THF) (HPLC grade) were purchased from J. T. Baker Chemical (New Jersey, USA). FTIR analysis was conducted using Perkin Elmer Spectrum One FT-IR Spectrometer (Boston, USA). DSC and TGA analyses were carried-out using Hitachi DSC7000X differential scanning calorimeter (Tokyo, Japan). All the chemicals were used as received.

Graft copolymers were prepared at different reaction conditions. A gelatinized starch pastes were prepared as reported [7]. Starch (1 g) was transferred into three-neck reaction flask. Distilled water (30 mL) was added to the above flask. The reaction

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Scheme 1. (I) Starch, (II) starch-macroradicals, and (III) starch-g-PMAA copolymer.

Table 1

Effects of starch:methacrylamide weight ratio and temperature on the percentage grafting, G(%), percentage yield, Y(%) and percentage efficiency of the graft copolymer, E(%), for the reactions polymerized with APS initiator (0.4 g) and water (80 mL) and 3 h reaction time.

Starch (g)	MAA (g)	Temp (°C)	^a W ₂	^b G (%)	^c Y (%)	^d E (%)
1	3	70	3.217	217.70	73.90	89.34
1	3	80	3.396	239.60	79.86	90.78
1	3	90	3.639	264.90	88.30	95.67
1	3	100	2.229	229.20	76.40	65.85
1	2	90	2.312	131.20	65.60	88.08
1	4	90	4.516	351.60	87.90	97.62
2	1	90	2.121	6.10	12.10	91.66

^aW₂, ^bG(%), ^cY(%) and ^dE(%) represent weight of washed copolymer after Soxhlet extraction, percentage grafting, percentage yield and percentage efficiency, respectively.

mixture was then heated on an oil bath with constant stirring, using a magnetic bar at 60 °C for 40 min to obtain a homogenous solution. Ammonium persulphate (0.1– 0.7 g) was dissolved in 10 mL of water and then added to the above gelatinized starch solution. The reaction flask was fitted with condenser and stirred for another 20 min (pre-interacting time) under nitrogen atmosphere. Methacrylamide solution dissolved in distilled water (40 mL) was added to the system. The reaction mixtures were then heated at temperature range (50–100 °C). The copolymerization was stopped by pouring the reaction mixture into methanol. The precipitate was filtered using sintered glass funnel. The precipitate was dropped into diethyl ether, stirred with glass rod and filtered. The process was repeated using THF. The white precipitated obtained was dried in a vacuum oven at ambient temperature until constant weight. Chloroform was used to wash the crude product (Soxhlet extraction) for 24 h to remove any polymethacrylamide homopolymer present. The extracts were dropped into methanol, filtered and then dried in a vacuum oven to constant weight.

The percentage grafting G(%), yield of graft copolymerization, Y (%) and percentage efficiency, E(%) were evaluated using the equations below [17]:

$$G(\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

$$Y(\%) = \frac{W_2 - W_1}{W_3} \times 100 \quad (2)$$

$$E(\%) = \frac{W_2}{W_4} \times 100 \quad (3)$$

where:

W₁, W₂, W₃ and W₄ represent weights of the starch, copolymer after Soxhlet extraction, methacrylamide monomer, and crude polymer respectively.

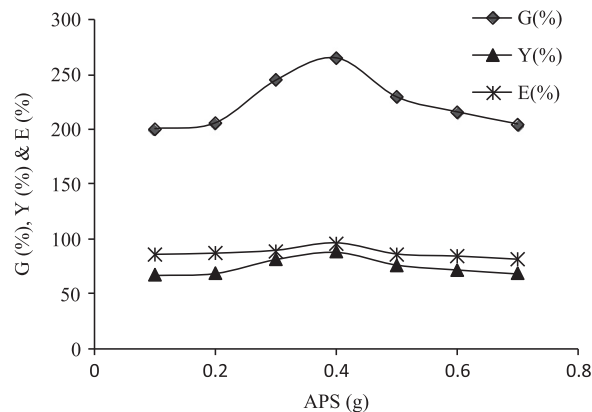


Fig. 1. Effect of initiator content on G(%), Y(%) and E(%) of samples polymerized using 80 mL of water, 0.4 g of APS at 90 °C.

3. Results and discussion

Suspensions of swollen starch particles were obtained in hot water. This could be due to the distortion of semi-crystalline structure of the starch. It is believed that water soluble initiators such as APS dissociates at a favorable temperature, to produce a pair of initiating radicals (SO₄·). Some of these initiating radicals diffuse out of the solvent cage and attack the most easily accessible hydroxyl group (OH) by abstracting the hydrogen atom attached to it. This would create active site(s) on the backbone of the polymer that could in turn, initiate graft copolymerization of some vinyl monomer(s) from the backbone of the cellulose-like polymers as shown in scheme [18,19] (Scheme 1).

Polymerization was conducted at various reaction conditions. At 1:3 starch:methacrylamide weight ratio and 3 h reaction time, the percentage grafting, G(%) and percentage yield, Y(%) were found to increase from 50 to 90 °C and then decreased at temperature above 90 °C (Table 1). This could be attributed to the increase in radical propagation rate, which will lead to more free-radical generation [17,20]. The decrease in G(%) and Y(%) could be due to early termination of the growing radicals at higher temperature [18]. The results also revealed that, the methacrylamide rich system offered the highest G(%) and Y(%).

To determine the initiator content that offers the highest percentage grafting, 1:3 starch:methacrylamide weight ratio was polymerized at 90 °C for 3 h, varying the initiator content (0.1–0.7 g). Both G(%) and Y(%) increased with initiator from 0.1 to 0.4 g, and then decreased at above 0.4 g (Fig. 1). This could be due to increase in concentration of the initiating radicals, which would either be consumed by possible fast alternative side reactions and hence, favor early termination of the growing radicals or result in homopolymer formation [17,18].

The FT-IR analyses indicate the presence of polymethacrylamide peaks with broad IR bands intensities at 3412 cm⁻¹ (N-H stretch, sharp), 2995 cm⁻¹ (C-H stretch (sp³)), 1662 cm⁻¹ (C=O stretching)

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