



ORIGINAL ARTICLE

Synthesis of Natural graft Copolymerization based on Acrylic acid and Alginate

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ABSTRACT

The polysaccharide, alginate, has been chemically modified by graft copolymerization of acrylic acid (AcA) in an aqueous medium using ammonium persulfate (APS) as an initiator under argon atmosphere. A plausible reaction mechanism of grafting has been suggested. Evidence of grafting was obtained by comparison of FTIR spectra of alginate and homopolymer-free alginate-g-poly (acrylic acid) as well as solubility characteristics and gravimetric analysis of the products.

Keywords: polymerization, alginate, acrylic acid, grafting.

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INTRODUCTION

Graft copolymerization of hydrophilic and hydrophobic vinyl monomers is a well-known technique employed by polymer chemists for significantly modifying the chemical and physical properties of the synthetic or natural starting materials with minimum degradation of the original properties. Graft copolymers are prepared by first generating free radicals on the polysaccharide backbone and then allowing these radicals to serve as macroinitiators for the vinyl monomers[1]. These biodegradable and low cost graft copolymers, with new properties can be used in many applications such as textiles, paper industry, agriculture, medical treatment, in petroleum industry as flocculants and thickening agents and also development of selective permeable membranes, sorption agents, and in fabrication of drug delivery systems[2]. Though much work has been reported on the grafting of acrylic acid onto various polysaccharides, but a literature survey reveals that no paper has been reported in the case of acrylic acid grafting onto alginate. Therefore, the present investigation deals with the optimization of graft copolymer synthesized based on alginate.

MATERIALS AND METHODS

Experimental

Materials

Sodium alginate (chemical grade, MW 50000), ammonium persulfate (APS, from Fluka), acrylic acid (AcA, from Merck), were used without further purification. All other chemicals were also analytical grade. Double distilled water was used for the hydrogel preparation and swelling measurements.

Procedure to Graft Copolymerization:

Synthesis of the graft copolymer, alginate-g-poly (acrylic acid), was carried out using APS as an initiator in an aqueous medium. A general procedure for graft copolymerization of acrylic acid onto alginate was conducted as follows. Alginate (0.50-1.20 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm), including 40 mL doubly distilled water. The reactor was immersed in a thermostated water bath preset at desired temperature (30-75 °C). After complete dissolution of alginate, various amounts of the initiator solution (0.01-0.40 g APS in 5 mL H₂O) were added to the mixture. After stirring for 10 min, certain amounts of monomer (2.0-

6.5 mL) were added to the reaction mixture. After 60 min, the produced copolymer was poured to excess non-solvent ethanol (200 mL) and remained for 3 h to dewater. Finally, the filtered composite is dried in oven at 60 °C for 10 h.

Homopolymer extraction

The graft copolymer, alginate-g-poly (acrylic acid), was freed from poly (acrylic acid) homopolymer, by pouring 0.50 g of the product in 50 mL of ethanol-aceton. The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymer by filtration of the alginate-g-poly (AcA), copolymer, the product was washed with ethanol and dried in oven at 50 °C to reach a constant weight.

Grafting parameters

The grafting parameters, i.e. grafting ratio (Gr %), add-on value (Ad %), and homopolymer content (Hp %), used to characterize the nature of the copolymer are defined and calculated using the following equations [6] :

$$\text{Gr \%} = 100 (W_2 - W_0) / W_0 \quad (1)$$

$$\text{Ad \%} = 100 (W_2 - W_0) / W_2 \quad (2)$$

$$\text{Hp \%} = 100 (W_1 - W_2) / W_1 \quad (3)$$

Where W_0 , W_1 , and W_2 are the weight of the initial substrate, total product (copolymer and homopolymer), and pure graft copolymer (after ethanol-aceton extraction), respectively.

Infrared analysis

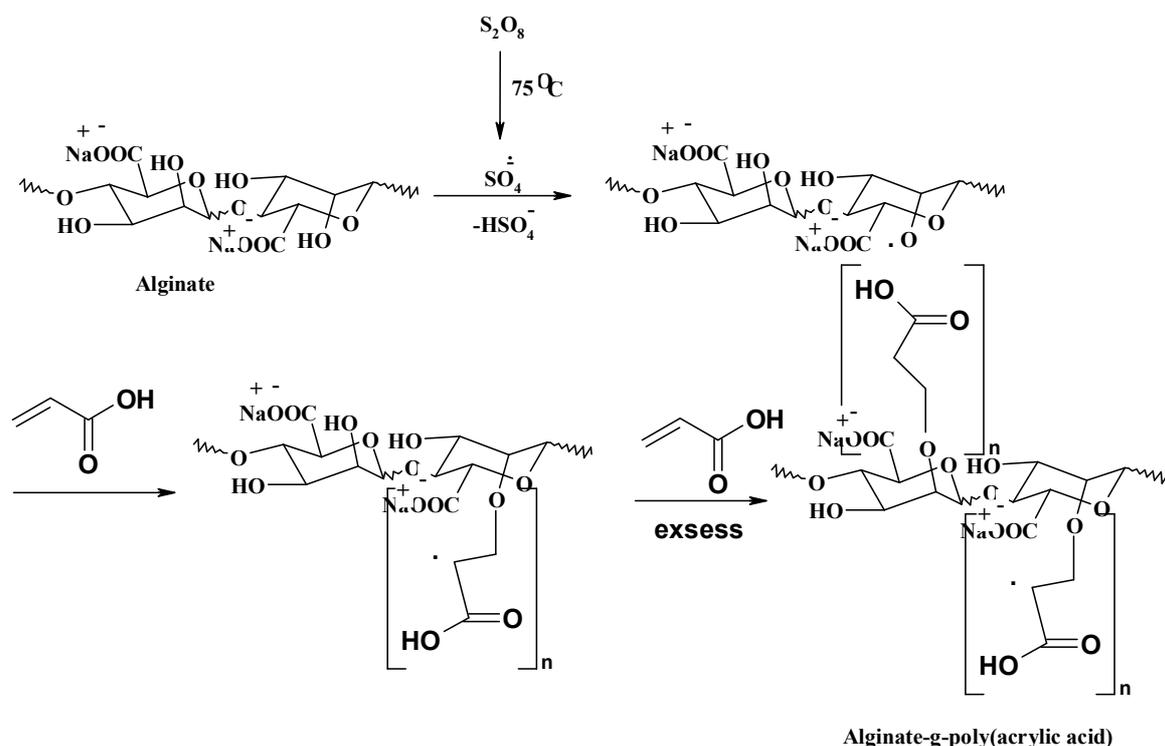
The samples were crushed with KBr to make pellets. Spectra were taken on an ABB Bomem MB-100 FTIR spectrophotometer.

Thermal analysis

Thermo gravimetric analyses were performed on a Universal V4.1D TA Instruments (SDT Q600) with 8–10 mg samples on a platinum pan under nitrogen atmosphere. Experiments were performed at a heating rate of 10 °C/min until 600 °C.

RESULTS AND DISCUSSION

A general reaction mechanism for crosslinking graft copolymerization of acrylic acid monomer onto alginate backbones in the presence of initiator is shown in Scheme 1. The sulfate anion-radical produced from thermal decomposition of APS, abstracts hydrogen from one of the functional groups in side chains (i.e. COOH, SH, OH, and NH₂) of the substrate to form corresponding radical [3-4]. Then the resulted macro radicals radically initiate graft copolymerization of acrylic acid monomer led to a graft copolymer so called alginate-g-poly (acrylic acid).



Scheme 1. Proposed mechanistic pathway for synthesis of alginate-based copolymer.

Evidence for grafting

FTIR analysis

Structural changes of alginate and its graft copolymer were confirmed by FTIR spectroscopy. Figure 1 shows the FTIR spectra of non-modified alginate and alginate-*g*-PolyAcA. The broad band at 3200-3400 cm^{-1} is due to stretching of -OH groups of alginate. The IR spectrum of the alginate-*g*-Polyacrylic acid (Fig. 1(b)) shows a new characteristic absorption band at 1707 cm^{-1} verifying the formation of alginate-*g*-PACA. This peak attributed to C=O stretching in carboxylic acid functional groups of PACA. In the spectra of the copolymer the characteristic band at 1542 cm^{-1} was attributed to C=O asymmetric stretching in the carboxylate anion. This was confirmed by another peak at 1402 cm^{-1} which is related to the symmetric stretching mode of the carboxylate groups. The broad band at 3200-3400 cm^{-1} is due to stretching of -OH groups of alginate.

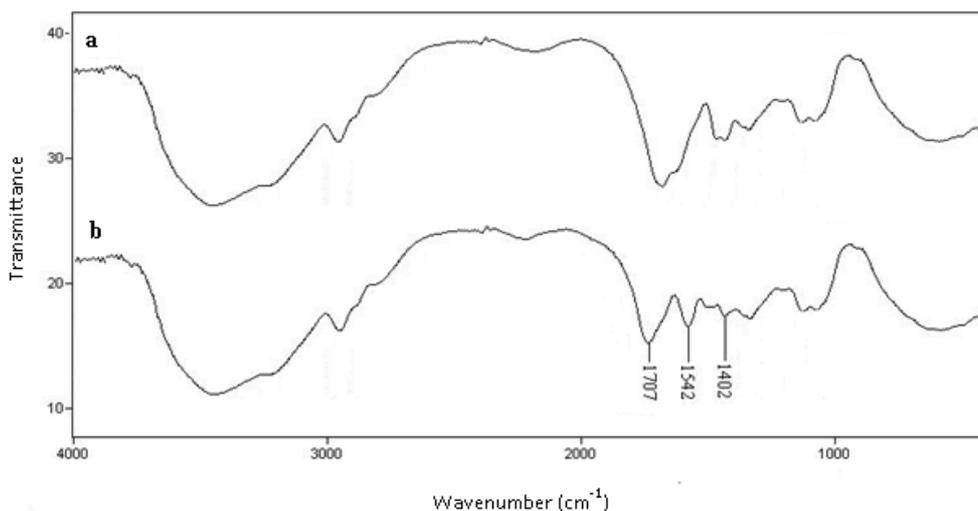


Figure 1. FTIR spectra of (a) alginate and (b) graft copolymer, alginate-*g*-PACA.

Thermogravimetric behavior

TGA of alginate shows a weight loss in two distinct stages (Fig. 2a). The first stage ranges between 30 and 120 °C and shows about 5% loss in weight. This may correspond to the loss of adsorbed and bound water. No such inflexion was observed in the TGA curve of alginate-*g*-PACA. This indicated that the grafted copolymers were resistant to moisture absorption. The second stage of weight loss starts at 290 °C and continues up to 510 °C during which there was 63% weight loss due to the degradation of alginate. Grafted samples, however, show almost different behavior of weight loss between 30 and 550 °C (Fig. 2b). The first stage of weight loss starts at 205 °C and continues up to 330 °C due to the degradation of alginate. The second stage from 370 to 570 °C may contribute to the decomposition of different structure of the graft copolymer. The appearance of these stages indicates the structure of alginate chains has been changed, which might be due to the grafting of PACA chains. In general, the copolymer had lower weight loss than alginate. This means that the grafting of alginate increases the thermal stability of alginate in some extent [7-9].

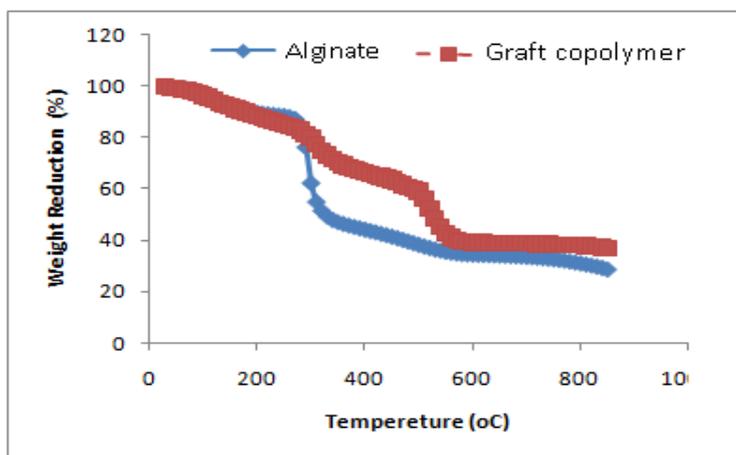


Figure 2. TGA curves of (a) alginate and (b) alginate-*g*-PACA.

Solubility test

To obtain an additional evidence of grafting, solubility difference between the grafted and the non-grafted polymer was used. Alginate-g-PAcA and poly (acrylic acid) are soluble in water and ethanol-aceton, respectively. When a reaction product was extracted with ethanol-aceton and alternatively with water for 24 h, an insoluble solid still remained [10-12]. A physical mixture of alginate and poly (acrylic acid) was treated in the same way and was found to dissolve completely. Therefore, it is obvious that the resulted graft copolymer was not a simple physical mixture, but some chemical bonds must exist between the alginate substrate and poly (acrylic acid) macromolecules. In addition to the formation of graft copolymers, crosslinking between the chains of alginate may also take place [13]. This was evident by the reaction between alginate and the initiator, in the absence of monomers, giving a product with reduced solubility (unpublished data).

Gravimetric analysis

The graft copolymerization reaction was monitored gravimetrically. Increase in the mass of alginate, after extraction of homopolymer, was taken as evidence for grafting. This weight gain in alginate forms the basis for the determination of the grafting parameters [14-15].

CONCLUSIONS

Graft copolymerization was employed as an important technique to obtain a chemically modified natural polysaccharide, sodium alginate (NaAlg). The grafting of acrylic acid onto NaAlg was carried out using ammonium persulfate (APS) as an initiator in aqueous medium. The characteristic absorbing peaks in the FTIR spectra, TGA analysis and gravimetric analysis have proven that sodium alginate participates in graft copolymerization with acrylic acid monomers.

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