Graft copolymerization of itaconic acid onto sodium alginate using benzoyl peroxide

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ABSTRACT

Graft copolymers of sodium alginate (NaAlg) with itaconic acid (IA) were prepared in aqueous solution using benzoyl peroxide (BPO) as the initiator. Grafted copolymers (NaAlg-*g*-PIA) were characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, scanning electron microscopy and thermogravimetric analysis. The grafting parameters, including the graft yield (GY%) of the graft copolymer and the grafting efficiency (GE%) of the reaction were evaluated comparatively. The effects of the reaction variables such as the reaction time, temperature, percentage of sodium alginate, monomer and initiator concentrations on these parameters were studied. It was observed that GY and GE first increased and then decreased with increasing polymerization temperature, concentrations of IA, and BPO. The optimum grafting conditions for maximum graft yield were obtained with reaction time of 1 h, reaction temperature of 85 °C, IA concentration of 1.38 M, BPO concentration of 1.82×10^{-2} M and percentage of NaAlg 1.5 g/dL.

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1. Introduction

Natural polymers, mainly polysaccharides, are biodegradable, cheap, fairly shear stable and easily available from renewable agricultural resources. The biodegradability reduces their shelf-life and needs to be controlled (Da Silva, De Paula, & Feitosa, 2007). Recently, the modification of natural polymers has received much attention for production of new biomaterials with specific properties. Graft copolymerization is one of the techniques employed for modifying the chemical properties of these polymers. In the last decade, many studies have been made of the synthesis, and characterization of graft copolymers of natural polymers such as starch, chitosan, alginate and cellulose (Duan, Chen, Jiang, & Li, 2008; Gupta & Khandekar, 2003; Krishnamoorthi, Mal, & Singh, 2007; Qudsieh et al., 2004; Singh, Tiwari, Singh, Kumari, & Tiwari, 2008; Tripathy & Singh, 2001).

Among such natural polymers, alginates, which are obtained mainly from brown algae belonging to the Phaeophyceae, are composed of two monomeric units, β-ᴅ-mannuronic acid and α-ʟ-guluronic acid (Almeida & Almeida, 2004). Alginate salts are used in a wide range of food, leather, pharmaceutical and industrial applications. They are important hydrocolloids that are capable of both thickening and gelling water (Liu, Yang, Li, & Shi, 2005). However, they are prone to enzymatic degradation and suffer from limitations in fabrication, which limits its application in some fields, for example, in controlled-release technology.

To overcome this problem, efforts have been made to develop chemically modified matrices by grafting. Grafting is a well-established and powerful method for the development of natural-synthetic polymer hybrid materials. Graft copolymerization of vinyl monomers onto alginate can introduce desired properties and enlarge the field of potential application of it by choosing various types of side chains. The grafting of vinyl monomers such as methyl acrylate (Patel, Patel, & Trivedi, 1999), acrylamide (Tripathy, Pandey, Karmakar, Bhagat, & Singh, 1999) and acrylonitrile (Pourjavadi & Zohuriaan-Mehr, 2002) onto alginate has gained considerable attention and proved of value in preparing new polymeric materials with special properties and enlarging the range of its utilization. However, grafting hydrophilic itaconic acid onto NaAlg has not been studied up to now.

Itaconic acid is one of the monomers, which is readily available at low cost. It is obtained from renewable resources by fermentation with *Aspergillus terrus* using carbohydrate materials as molasses and hydrolyzed starch (Kalagasidis Krusic, Dzunuzovic, Trifunovic, & Filipovic, 2004; Mahdavian, Abdollahi, Mokhtabad, Bijanzadeh, & Ziaee, 2006). PIA is interesting as a polyelectrolyte having two ionizable groups, with different p*K*a values, which can form H-bonds. These groups bring additional capability of chelate formation under certain cases. The grafting of IA onto polypropylene (Pesetskii, Jurkowski, & Makarenko, 2002), low density polyethylene (Krivoguz, Pesetskii, & Jurkowski, 2003) and chitin (Mostafa, Naguib, Sabaa, & Mokhtar, 2005) have been studied. It was therefore decided to graft IA onto NaAlg.

In the previous study (Işıklan, İnal, & Yiğitoğlu, 2008), *N*-vinyl-2-pyrrolidone was grafted onto sodium alginate using azobisisobu-

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tyronitrile (AIBN) as initiator and beads of these copolymers were prepared for controlled-release study of indomethacin. In the present work, we carried out the grafting of IA onto NaAlg with BPO to use the product obtained in the controlled drug delivery systems. We also evaluated optimized reaction conditions for grafting using the free radical polymerization method. When the redox initiator such as cerium ammonium nitrate was used in the synthesis, crosslinked and water insoluble copolymer was obtained. Hence, BPO was chosen over the redox initiator in order to obtain water soluble graft copolymer. The initiator was produced by the thermal cleavage of the benzoyl peroxide. The effects of the reaction time, temperature, percentage of sodium alginate, monomer and initiator concentrations on the grafting parameters were investigated. The graft copolymer was also characterized with Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (^{13}C NMR), scanning electron microscopy (SEM) and thermogravimetric analysis (TG/DTG).

2. Materials and methods

2.1. Materials

Sodium alginate with a viscosity of 3500 cps (2% solution, 25 °C) was purchased from Sigma Chemical Co (Louis, USA). IA and BPO were supplied from Fluka Chemie AG (Buchs, Switzerland). Other reagents were Merck products and used as supplied.

2.2. Graft copolymerization

The grafting reactions were carried out under a nitrogen atmosphere in a 250 mL three-necked flask equipped with a reflux condenser, a stirrer, and a gas inlet system, immersed in a constant temperature bath. In a typical reaction, NaAlg (0.5–2.5 g) was dissolved in distilled water (50 mL) at room temperature with constant stirring. The solution was immediately placed into the water bath adjusted to the polymerization temperature. The required amount of IA was dissolved in 10 mL of distilled water. After that, this solution was mixed with NaAlg solution and stirred a slow stream of nitrogen for 30 min. Then BPO at the required concentration in acetone was added slowly to the reaction mixture and the total volume of the reaction mixture was made up to 100 mL with distilled water. A continuous supply of nitrogen was maintained throughout the reaction period. The grafting reactions were carried out for various time (0.5–6 h) and temperature (60–90 °C). At the end of the predetermined polymerization time, the reaction was terminated by adding a saturated solution of hydroquinone. The products were precipitated in an excess of acetone, separated by filtration, and then extracted with methyl alcohol to remove the homopolymer (PIA) for 24 h. After the complete removal of PIA, the pure graft copolymer was dried at 40 °C under vacuum to a constant weight. The grafting parameters, including graft yield (GY) and grafting efficiency (GE), were calculated as follows:

$$GY(\%) = [(w_g - w_o)/w_o] \times 100 \tag{1}$$

$$GE(\%) = [(w_g - w_o)/(w_g - w_o) + w_h] \times 100 \tag{2}$$

where w_o, w_g and w_h denote the weights of the original (ungrafted) NaAlg, grafted NaAlg and homopolymer, respectively.

The rate of grafting (R_g) was calculated with the formula as follows:

$$R_g = [(w_g - w_o) \times 1000]/[M \times t \times V] \tag{3}$$

where M is the molar weight of the monomer; t is the polymerization time (s); and V is the volume (mL) of the overall reaction medium.

2.3. Fourier transform infrared measurements

Fourier transform infrared spectra of NaAlg and NaAlg-g-PIA were taken in the wavelength region between 400 and 4000 cm^{-1} at the ambient temperature, using a Jasco FTIR-480 Plus spectrophotometer (Japan) with KBr discs.

2.4. Nuclear magnetic resonance (^{13}C NMR) spectroscopy

^{13}C NMR spectra of NaAlg and NaAlg-g-PIA were measured using a solid-state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectrometer (DPX-300, Bruker-BioSpin AG, Fällanden, Switzerland) with a spin rate of 5 kHz.

2.5. Thermal analysis

Thermogravimetric analysis was carried out with Setaram Instrument (SETSYS-1750 Simultaneous TG/DTA). Analyses were performed with 8–10 mg samples on a platinum pan under a nitrogen atmosphere at a heating rate of 10 °C/min until 900 °C.

2.6. Scanning electron microscopy

SEM photographs were taken with JSM 5600 Scanning Microscope (Japan) to examine the morphology and surface structure of NaAlg and IA grafted NaAlg at the required magnification at room temperature. The polymers were deposited on a brass holder and sputtered with a thin coat of gold under vacuum. The acceleration voltage was 20 kV with the secondary electron image as a detector.

3. Results and discussion

3.1. Characterization of the graft copolymers of NaAlg with IA

The FTIR spectra of NaAlg and its graft copolymer are shown in Fig. 1a. Grafted and ungrafted NaAlg showed a broad band between 3000 and 3800 cm^{-1}, which was attributed to O–H stretching vibrations. The spectrum of NaAlg showed the peaks at around 2930, 1606, 1417 and 1033 cm^{-1}, indicating the stretching vibrations of aliphatic C–H, COO$^-$ (asymmetric), COO$^-$ (symmetric), and C–O, respectively, which are characteristics of the polysaccharide (Patel et al., 1999). As the similar, the spectrum of the NaAlg-g-PIA showed the peaks at around 2935, 1625, 1423 and 1033 cm^{-1}, indicating the stretching of aliphatic C–H, COO$^-$ (asymmetric), COO$^-$ (symmetric), and C–O, respectively. Moreover, a new strong band compared to NaAlg spectrum at around 1740 cm^{-1} were assigned to carboxylic carbonyl group of itaconic acid, which confirmed the grafting of the monomer. This is in good agreement with the results reported in the literature (Işıklan et al., 2008; Naguib, 2002; Singh et al., 2008; Tripathy & Singh, 2001).

Another evidence of the grafting is ^{13}C NMR spectra of the NaAlg and NaAlg-g-PIA as reflected Fig. 1b. The ^{13}C nuclear magnetic resonance spectrum of the NaAlg is very similar to that obtained by Tripathy and Singh (2001). The absorption peak at δ = 170 ppm was assigned to the carboxyl carbon atom of –COO$^-$Na$^+$ group. Anomeric carbon resonance was observed at δ = 100 ppm. The peaks at δ = 65–85 ppm was for carbon atoms connected by –OH groups of the pyranose ring. In the ^{13}C NMR spectrum of the graft copolymer, peaks related to the NaAlg can be observed. It is also seen that grafted NaAlg showed additional peak at around δ = 42 ppm due to CH$_2$ carbon of poly(itaconic acid) which occurred opening of vinyl group, confirm the grafting. Moreover, it has overlapping peaks at 25–50 ppm and at 165–180 ppm were assigned to the carbons connected to carbonyl groups and
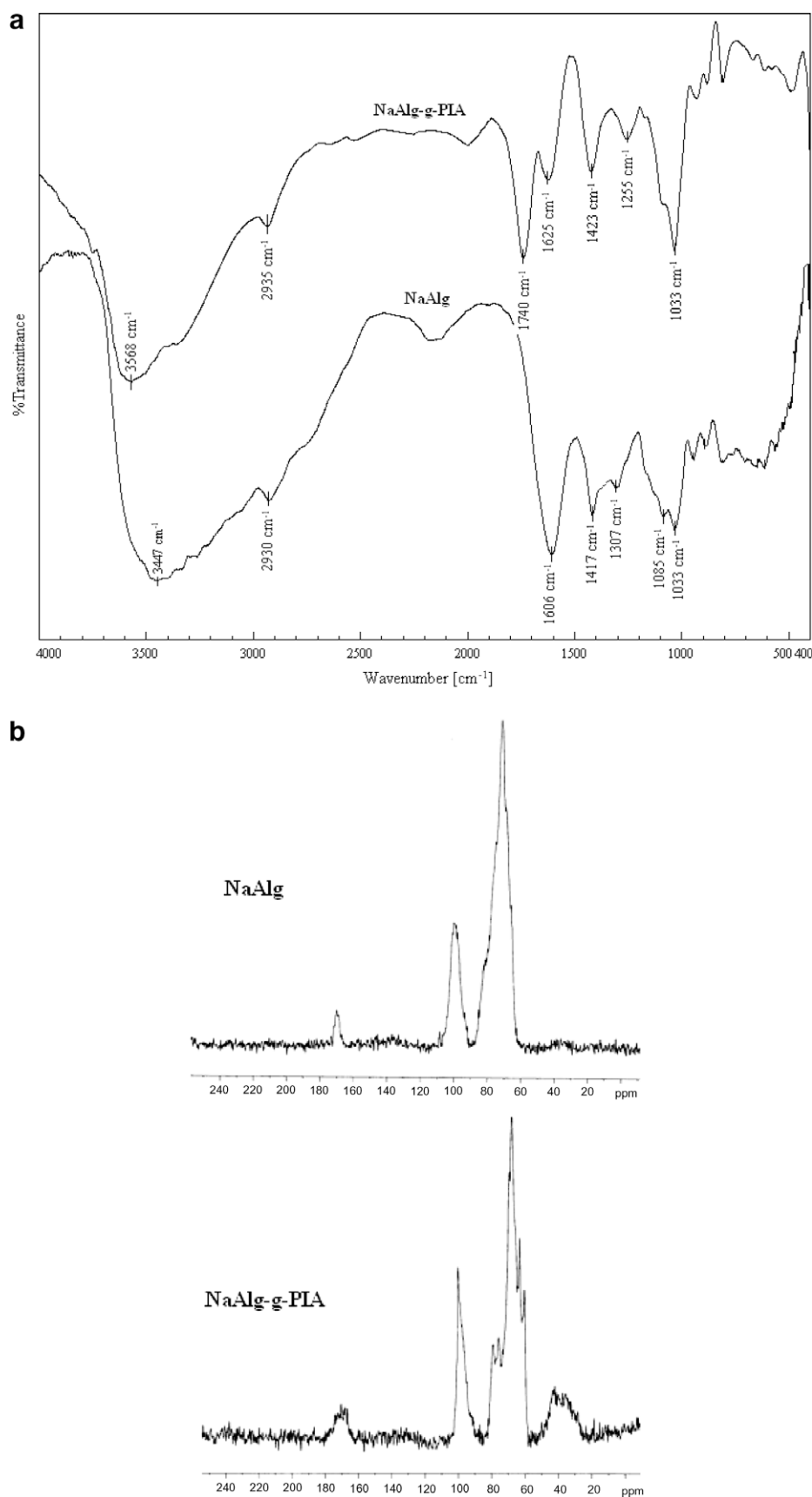
Fig. 1. FTIR spectra of NaAlg and NaAlg-*g*-PIA (a), and solid-state ^{13}C NMR spectra of the NaAlg and NaAlg-*g*-PIA (b).

carbonyl groups of poly(itaconic acid), respectively, as reported by Da Silva et al. (2007).

Thermogravimetric curves of NaAlg and NaAlg-*g*-PIA in a nitrogen atmosphere are displayed in Fig. 2. The thermogram of sodium

alginate exhibited two distinct stages. One in the range of 30–160 °C with a maximum decomposition rate at 104 °C was assigned to elimination of water adsorbed to the hydrophilic polymer. The other in the range of 210–310 °C with a maximum decomposition rate at 248 °C was ascribed to a complex process including dehydration of the saccharide rings, depolymerization with the formation of water,

CO_2 and CH_4 (Zhang, Yuan, Shen, & Lin, 2003). Temperature of 50% weight loss was found to be 340 °C for NaAlg. The differential thermogravimetric curve of the grafted NaAlg also showed two degradation steps. The first in the range of 30–140 °C with a maximum decomposition rate at 87 °C was attributed to elimination of water adsorbed to the NaAlg-*g*-PIA structure. The second in the range of
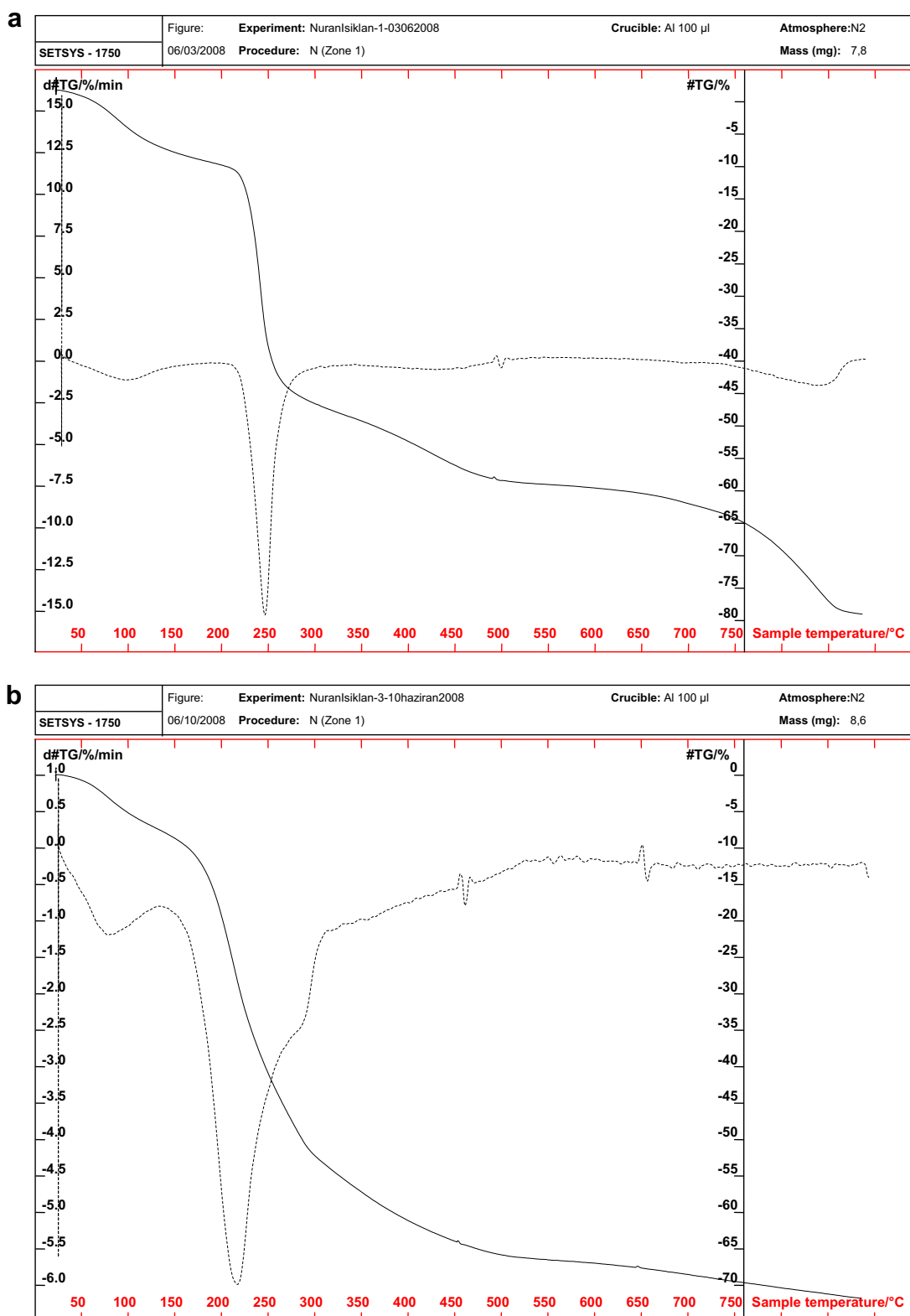

Fig. 2. TG/DTG termogram of NaAlg (a) and NaAlg-*g*-PIA (b).

140–500 °C with a maximum decomposition rate at 222 °C was assigned to depolymerization with the formation of water, CO_2, and CH_4. Temperature of 50% weight loss was also found to be 288 °C for grafted NaAlg. From the DTG curves, it can be concluded that the thermal stability of the polysaccharide decreases with the grafting of PIA chains onto the polysaccharide backbone. This may be attributed to the low thermal stability of poly(itaconic acid) as a result of decarboxylation reaction observed second degradation step. This phenomenon has been also reported by Naguib (2002). He has indicated that thermal stability of the polymer reduced with the grafting of IA onto sisal fiber.

The scanning electron micrographs of ungrafted and IA grafted NaAlg (with 6.54% GY) are shown in Fig. 3. By comparing the surface morphology of the grafted NaAlg (Fig. 3d–f) with ungrafted NaAlg (Fig. 3a–c) we found that the grafted chains drastically changed to the morphology of NaAlg. As shown in the figure, the surface of the NaAlg-g-PIA copolymer was more spongy structure than that of NaAlg which may be attributed to the polarity difference between NaAlg and PIA.

3.2. Effect of the reaction time

The reaction time plays an important role in the graft copolymerization. Grafting of NaAlg was carried out at various polymerization times, with the temperature, monomer and initiator concentrations kept constant, and the results are shown in Fig. 4. As can be seen from the figure, graft yield and grafting efficiency increased with the increase in polymerization time up to 1 h then beyond this value, grafting parameters slightly decreased. The increase in the grafting parameters up to 1 h could be attributed to the increase in the number of grafting sites on the NaAlg backbone and the addition of monomer molecules to the growing grafted chains. The following trend in the GY% and GE% may be due to the decrease in monomer and initiator concentrations as well as the reduction in the number of active sites on the NaAlg backbone. Similar results have found for the graft copolymerization of methyl acrylate onto carboxymethylated NaAlg using cerium (IV) ammonium nitrate (CAN) by Patel and coworkers (1999). They have ob-
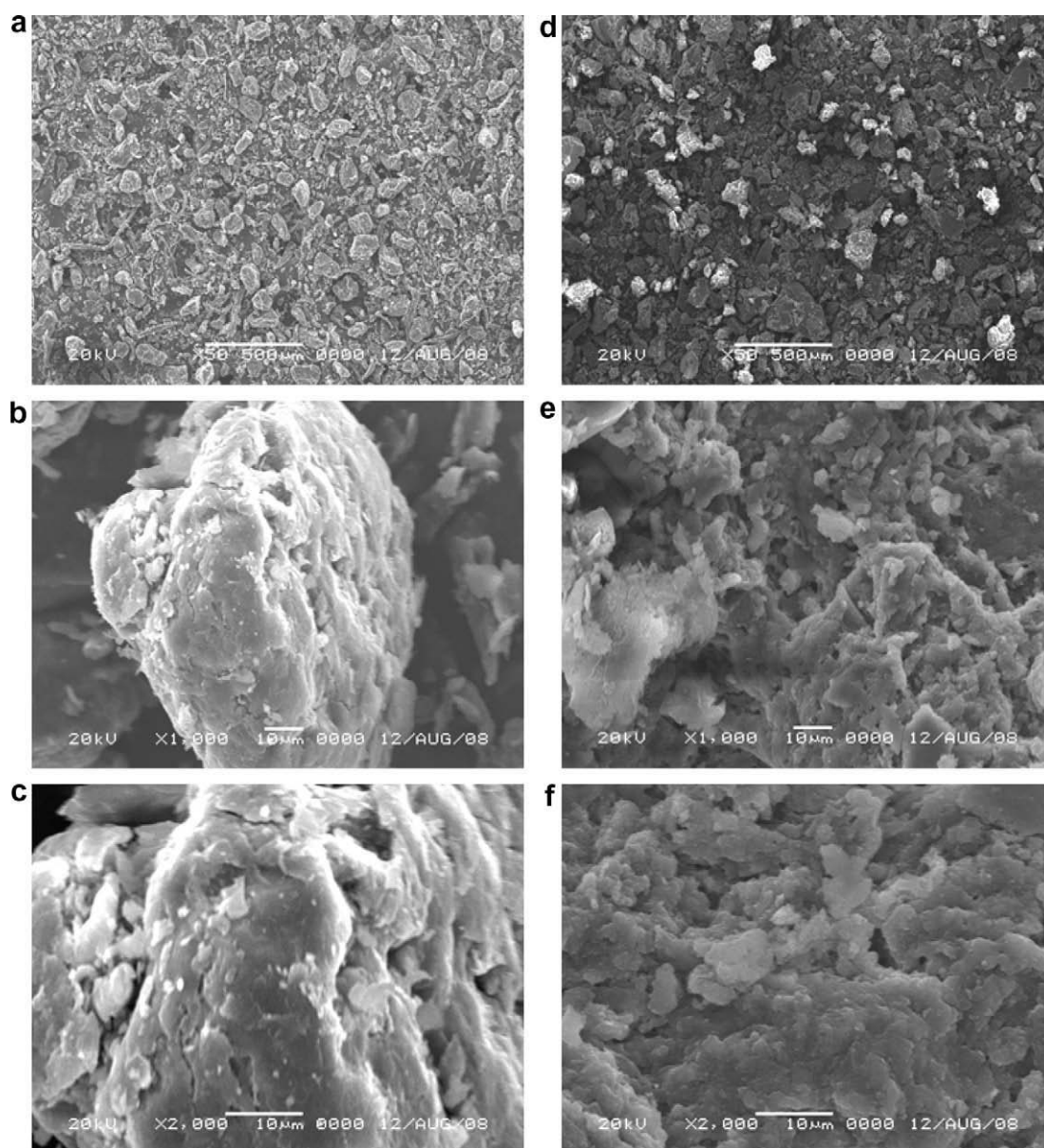

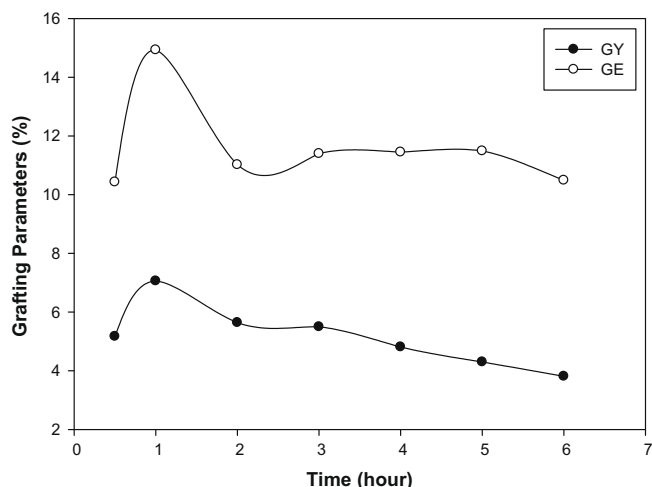**Fig. 3.** SEM micrographs of ungrafted (a–c) and IA grafted NaAlg(d–f).

Fig. 4. Variation of the graft yield (●) and grafting efficiency (○) with reaction time. Reaction conditions: percentage of NaAlg (%) = 1.0; [IA] = 0.46 M; [BPO] = 9.12 × 10^{-3} M; T = 70 °C.

tained the same trend in the effect of the reaction time on the grafting parameters.

Pulat and Babayiğit (2001), have also grafted of acrylamide and itaconic acid onto polyurethane using BPO as the initiator. The optimum reaction time for acrylamide and itaconic acid in their research have reported to be 1 and 2 h, respectively.

Thaker and Trivedi (2005), have studied grafting of methyl acrylate onto another polysaccharide sodium salt of carboxymethylated guar gum. They have reported the same trend in the effect of the reaction time and found to be 3 h for the optimum reaction time.

3.3. Effect of the temperature

To investigate the effect of the temperature on the graft copolymerization of IA onto NaAlg was studied by the variation of the temperature between 60–90 °C, and the results are presented in Fig. 5a. As it is seen from the figure, the graft yield increased slowly with increasing temperature from 60 to 85 °C on a further increase in the temperature, this decreased sharply. On the other hand, grafting efficiency increased very rapidly in the beginning and then it decreased with a further increase in the temperature. The highest graft yield and grafting efficiency values were obtained to be 7.36% and 18.97%, respectively, at 85 °C. The enhancement in the grafting with the rising the polymerization temperature could be ascribed to a higher rate of reaction between the BPO and NaAlg. The increase in the reaction temperature also enhances the mobility of the NaAlg backbone, monomer and initiator molecules. Hence, the diffusion of monomer and initiator into the NaAlg backbone increase with the increasing temperature. Therefore, rates of grafting increased. However, the lowering of grafting parameters by an increase in the temperature above 85 °C could be due to the favored chain termination reactions, chain transfer reactions, and an increase in the formation of homopolymer, as reflected from the grafting efficiency curve in Fig. 5a. Similar results have been obtained by many workers who have studied graft copolymerization (Gupta & Khandekar, 2003; Makhlouf, Marais, & Roudesli, 2007; Mostafa et al., 2005; Pulat & Babayiğit, 2001; Qudsieh et al., 2004; Yiğitoğlu, Işıklan, & Özmen, 2007).

Makhlouf and coworkers (2007), studied the graft copolymerization of acrylic acid onto polyamide fibers using benzoyl peroxide and reported that the grafting parameters increased with an increase in the temperature up to 85 °C and then decreased up to 95 °C.
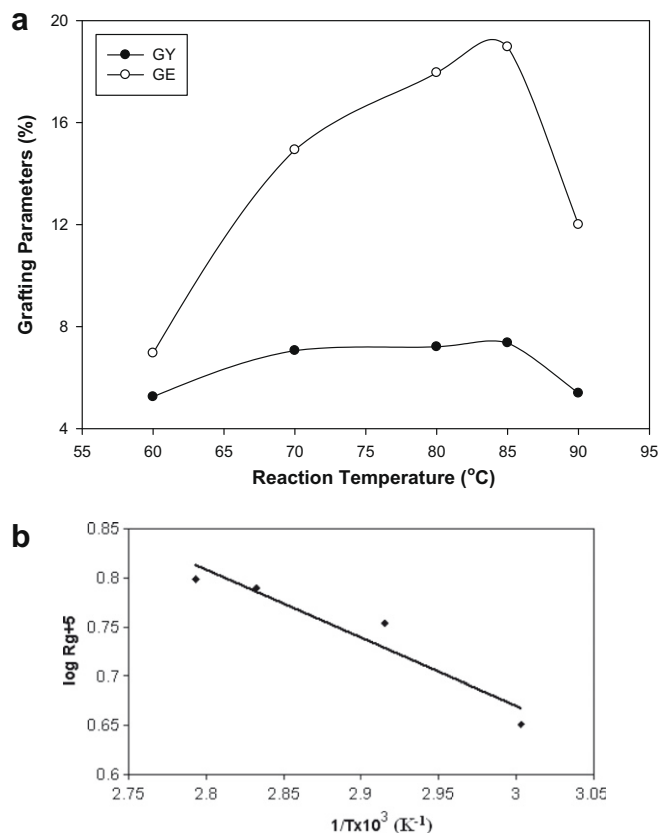

Fig. 5. Variation of the graft yield (●) and grafting efficiency (○) with temperature (a), and Arrhenius plot of $\log R_g$ vs. $1/T$ (b). Reaction conditions: Percentage of NaAlg (%) = 1.0; [IA] = 0.46 M; [BPO] = 9.12 × 10^{-3} M; t = 1 h.

The grafting rate of copolymerization at different temperatures has been used to determinate activation energy of the graft copolymerization. The overall activation energy for grafting was found to be 13.25 kJ/mol from the Arrhenius plot of $\log R_g$ versus reciprocal of the temperature $(1/T)$ as shown in Fig. 5b. In our previous work, the overall activation energy was calculated similarly to be 43.9 kJ/mol for the grafting of N-VP onto sodium carboxymethylcellulose (Yiğitoğlu et al., 2007). The small value of the obtained activation energy shows that the grafting reaction between IA and NaAlg is thermodynamically favored and needs little energy.

3.4. Effect of the monomer concentration

The monomer concentration has a remarkable effect on the graft yield and grafting efficiency. For this purpose, monomer concentration was changed from 0.153 to 1.61 M with all the other conditions kept constant. Results obtained are presented in Fig. 6a. The graft yield increased very rapidly with the monomer concentration up to 1.38 M and then decreased with a further increase in the IA concentration. However, grafting efficiency increased slowly up to 1.38 M and then decreased with a further increase in the monomer concentration. As the monomer concentration increase, the diffusion of the monomer molecules into the NaAlg backbone increase, and this lead to a higher graft yield. The decrease in the grafting after optimum value could be associated with the depletion of the available IA due to the simultaneous increase in the homopolymerization rate (as shown by the GE values) with the rising IA concentration in the polymerization medium. With a higher monomer concentration, the concentration of PIA macroradicals increases, and the rates of their combination and disproportionation is faster than the rate of their combination
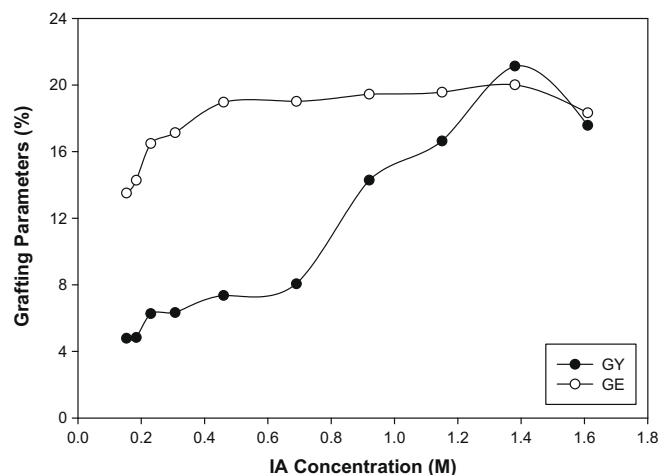
Fig. 6a. Variation of the graft yield (●) and grafting efficiency (○) with monomer concentration. Reaction conditions: percentage of NaAlg (%) = 1.0; [BPO] = 9.12 × 10^{-3} M; t = 1 h, T = 85 °C.

Fig. 6b. Variation of the graft yield (●) and grafting efficiency (○) with initiator concentration. Reaction conditions: Percentage of NaAlg (%) = 1.0; [IA] = 1.38 M; t = 1 h, T = 85 °C.

with NaAlg molecules. Therefore, the homopolymer and a lower percentage of grafting are produced. In addition, the medium viscosity also increases with the increasing amount of homopolymer that accumulated in the reaction medium, and the monomer diffusion into the NaAlg backbone become more difficult. Such behaviors have been also obtained in other studies in the literature (Makhlouf et al., 2007; Mostafa et al., 2005; Pulat & Babayiğit, 2001; Pulat & Isakoca, 2006; Sharma, Kumar, & Soni, 2003; Singh et al., 2008). In the study of Pulat and Isakoca (2006), they investigated the grafting of acrylic acid, acrylamide, crotonic acid, and itaconic acid onto cotton fibers, and observed that the graft yield increased as the IA concentration increased from 0.5 to 1 M and after that decreased with a further increase in the monomer concentration up to 3 M.

3.5. Effect of the initiator concentration

Another parameter that affects the grafting parameters is the initiator concentration. Fig. 6b. shows the effect of BPO concentration on the grafting parameters as the BPO concentration increased from 2.28×10^{-3} to 3.65×10^{-2} M. As seen from the figure the graft yield and grafting efficiency increased up to 1.824×10^{-2} M BPO concentration, and then decreased with a further increase in BPO concentration. This is a very common observation and has been reported by various authors (Coşkun, 2007; Coşkun, Saçak, & Karakışla, 2005; Gupta & Khandekar, 2003; Makhlouf et al., 2007; Pulat & Babayiğit, 2001; Qudsieh et al., 2004; Yiğitoğlu et al., 2007). The best graft yield and grafting efficiency were obtained to be 26.05% and 20.13%, respectively, in the 1.824×10^{-2} M BPO concentration. The free radical concentration of the BPO molecules in the polymerization medium, increases with increasing of BPO concentration. These radicals abstract a hydrogen atom from the NaAlg macromolecule and form active sites on the NaAlg backbone. In addition, the increase in BPO concentration increases the number of radical species, such as active polyitaconic acid chains. These active polymeric chains undergo chain transfer reaction with NaAlg macromolecules which causes the formation of a higher number of active sites on the NaAlg backbone. Therefore, the graft yield increases with the chain transfer and the hydrogen abstractions. However, the increase of BPO concentration above a critical value of 1.824×10^{-2} M makes the radical concentration excessive in the polymerization medium. Thus, the rate of termination reactions increases while grafting parameters decrease (Coşkun, 2007; Coşkun et al., 2005).
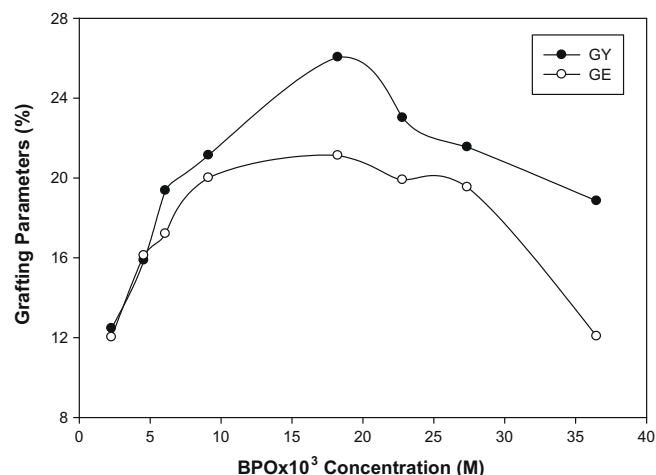
3.6. Effect of the NaAlg percentage

The effect of the NaAlg percentage on the grafting parameters was studied by the variation of the percentage of NaAlg from 0.5 to 2.5 g/dL and obtained results are presented in Fig. 6c. As can be seen from the figure, the grafting parameters increased initially with an increasing percentage of NaAlg up to 1.5 g/dL and thereafter decreased with further increase in percentage of NaAlg. The best graft yield and grafting efficiency were obtained to be 31.92% and 20.83%, respectively, in the 1.5 g/dL NaAlg percentage. The observed increases in both the graft yield and grafting efficiency with NaAlg may be due to the fact that number of NaAlg macroradicals available for grafting increase with increase in percentage of NaAlg. The reduction in the grafting parameters beyond optimum value could be attributed to the increase in the viscosity of the reaction medium, which hinders the movement of BPO, thereby reducing the grafting parameters. Moreover, a high sodium alginate percentage could produce more NaAlg macroradicals, which could interact with one another to terminate the reaction, thus lowering both the graft yield and the grafting efficiency values. Similar results have also been reported in the grafting of acry-
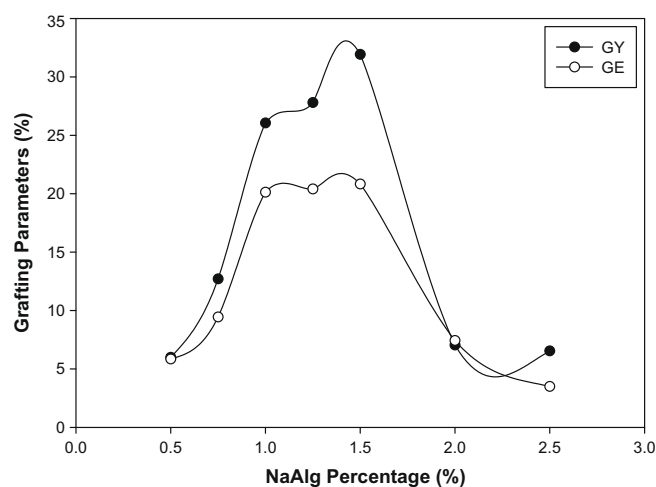

Fig. 6c. Variation of the graft yield (●) and grafting efficiency (○) with NaAlg concentration. Reaction conditions: [BPO] = 1.824×10^{-2} M; [IA] = 1.38 M; t = 1 h, T = 85 °C.

Table 1
Comparison amongst graft yield of reaction between polymers and itaconic acid.

Polymer	Reaction Condition				GY%	Reference
	IA(M)	Initiator	T(°C)	Time(h)		
Sodium alginate	1.38	BPO	85	1	31.9	This study
Chitin	0.1	Potassium persulfate	60	1	140	Mostafa et al. (2005)
Chitin	0.1	γ-radiation	60	1	377.5	Mostafa et al. (2005)
Poly(vinyl alcohol)	0.46	Cerium(IV) ammonium nitrate	45	4	10	Işıklan and Şanlı (2004)
Polyurethane	1.5	BPO	80	1	20	Pulat and Babayiğit (2001)
Cotton fiber	1	BPO	70	1	15.9	Pulat and Isakoca (2006)

lonitrile onto NaAlg (Shah, Patel, & Trivedi, 1994) and grafting of methyl methacrylate onto carboxtmethylated guar gum (Trivedi, Kalta, Patel, & Trivedi, 2005).

Results of the studies reported in the literature on the graft copolymerization of itaconic acid onto different polymers are listed in Table 1 for comparison purposes. As can be seen from the table, grafting of IA onto NaAlg has high graft yield compared to the other IA grafted polymers which were initiated with BPO. Furthermore, the best graft yield of IA was obtained to be 377.5 in the grafting of IA onto chitin with γ-radiation as shown in Table 1.

4. Conclusions

IA that contains polar functional groups was successfully grafted onto sodium alginate under N_2 atmosphere with BPO for new applications of this natural product. SEM picture displayed that the surface of the NaAlg-g-PIA copolymer was a more spongy structure than that of NaAlg. The obtained results also showed that control of the grafting parameters was possible by varying the reaction conditions such as reaction time, temperature, concentration of monomer and initiator. The maximum GY and GE were obtained to be of 31.92% and of 20.13%, respectively. The overall activation energy for grafting was calculated to be 13.25 kJ/mol. According to the TGA results we also found that thermal stability of NaAlg decreased due to incorporation of PIA.

Acknowledgement

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