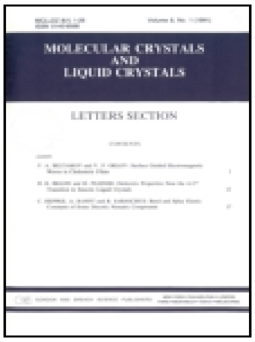
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Alginate-Jeffamine Covalently Crosslinked Hydrogel

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The alginate-Jeffamine hydrogels were synthesized throughout the reaction of alginate with O,O′-bis(2-aminopropyl)polypropylene glycol (Jeffamine) in HCl solution. The network formation was confirmed by presence of N-H bonds in FTIR and Raman spectra. The swelling properties of the hydrogels revealed water absorption of 330% after 18 h that reached maximum value of 430% in 18 days. The optical microscopy evidenced regular porosity of the hydrogels and the SEM micrographs of the hydrogels plasticized with glycerol showed homogenous and compact surfaces. The results showed that the alginate-based hydrogels are very good materials that can be applied successfully as moisture-soil-control agents in agriculture.

Keywords Alginate; network; hydrogels

Introduction

The increasing alerts concerning the contribution of synthetic polymers to the environmental degradation is turning toward the natural macromolecules [1, 2]. Natural polymers are particularly interesting when compared with synthetic ones, due to their natural abundance, low price and environmental friendly nature [3]. The bio-polymers can be easily obtained from fast growing plants, animals or by means of bacterial synthesis [4, 5] being, consequently, biodegradable. These polymers are also water soluble and/or have hydrophilic properties and can be processed in a membranes' form with excellent transparency and good adhesion to glass and metal surfaces [6].

Natural polymers are mainly polysaccharides, where starch, cellulose or pectin are found in terrestrial plants and carrageenan and alginate are found in seaweed [7]. Most of polysaccharides are water soluble so can't form hydrogels. To overcome this problem chemical crosslinking throughout chemical covalent and ionic bonds formation [8] or physical crosslinking throughout physical interactions, such as van der Waals forces are investigated [9, 10].

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Sodium alginate is a heteropolysaccharide extracted from brown marine *algae phaeophyceae* and is composed of two uronic acids, β-D-mannuronic (M) and α-L-guluronic (G), linked by glycosidic ($1 \rightarrow 4$) bonds. These acids form three types of polymeric segments, G-, M- and MG-blocks [11, 12]. M-blocks consist of D-mannuronic acid units, G-block is constituted by a L-guluronic unit and MG-blocks consist of a combination of M and G residues [12]. The interesting property of alginate is its capacity to form insoluble gels when complexed with Ca^{2+} ions [13–15], or when crosslinked in acidic solutions either (*i*) by hydrogen bonding of COOH and OH groups [11, 16] or (*ii*) due to the reaction with glutaraldehyde [17, 18].

This paper presents the results of sodium alginate and Jeffamine (O,O′-bis(2-aminopropyl)polypropylene glycol) hydrogels as candidates for controlled drug or fertilizer release and/or moisture-soil-control agents in agriculture. The samples were synthesized throughout chemical crosslinking and characterized by FTIR and Raman spectroscopies, water absorption, weight loss, optical and scanning electron (SEM) microscopies.

Experimental

1.4 g of sodium alginate (Aldrich) was dispersed in 60 mL of Millipore Milli-Q water with the controlled resistivity of 18.2 $m\Omega^{-1}cm^{-1}$ at 25°C under constant magnetic stirring and heating at 80°C until the complete dissolution. Then, 5 mL of HCl 18 wt% (Synth) was added and stirred for 2 h. After that, 0.3 g of O,O′-Bis(2-aminopropyl)polypropylene glycol (Jeffamine 230; Aldrich) was added and stirred for next 18 h. As a result a dense whitish gel was formed that was washed with portions of ethanol and water resulting in a white gel that was filtered and dried in a fridge.

The membranes were obtained by mixing small amount of this product with 12 drops of glycerol and 40 mL of Millipore Milli-Q water.

FTIR analyses were performed with the Bomem MB-102 equipment on samples pressed with KBr (spectroscopic grades) to form thin pellets.

Raman spectroscopy analyses were performed with the Spectrophotometer LabRam HR 800 operating at 630 nm equipment.

The moisture determination was performed with the Moisture Determinator Mars Series ID version 1.8.

Optical microscopy analyses were performed using a Carl Zeiss JENA-Gnaval and Scanning Electronic Microscopy (SEM) with LEO.

Results and Discussion

Figure 1 shows the crosslinking reaction between alginate and Jeffamine throughout urea bond formation.

The alginate powder and alginate-Jeffamine hydrogels were characterized by FTIR showed on Fig. 2 where one can observe a very large band at $\sim$3400 cm^{-1} for both pure alginate and alginate-Jeffamine. This band corresponds to deformation and at 1033 cm^{-1} to vibration of polysaccharide macromolecules OH groups. The bands located at $\sim$2900 cm^{-1} can be assigned to the CH_3 and CH_2 stretching vibration groups. In the wave numbers region from 700 to 2000 cm^{-1}, the pure alginate shows a strong band at 1615 cm^{-1} that is attributed to glycosidic bond [19] and also to asymmetric deformation of COO^- grups [12, 20]. The symmetric deformation of COO^- is observed at 1421 cm^{-1} [12, 20] and, that at 1409 cm^{-1}

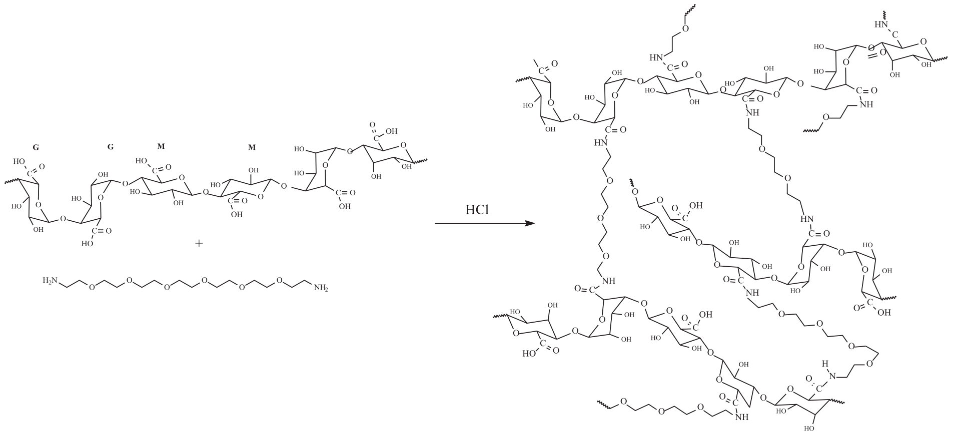

Figure 1. Alginate-Jeffamine hydrogel synthesis reaction.

is due to the C—H bending. At 1297 cm^{-1} a skeletal vibration is observed and the bands at 1093–1033 cm^{-1} are due to the C—O—C asymmetric stretch [20].

Some new bands at 1269, 1734, 2924 and 3363 cm^{-1} which does not exist in the spectrum of pure alginate is proof that alginate-Jeffamine network was formed (Fig. 2). Differently of alginate-chitosan ionically crosslinked hydrogels [21] in present case probably a network formation is throughout urea bonds [8]. Considering as amide I, primary C=O stretching with minor contribution of C—N stretching, amide II as C—N stretching with N—H bending coupled out-of-phase and amide III as C—N stretching with N—H bending coupled in-phase it can be observed, on Fig. 2 that amide I FTIR vibrations appear at 1636 cm^{-1} and are probably overlapped with no reacted asymmetric stretching of alginate COO$^-$ shifted band. Amide III appear at 1269 cm^{-1}. Moreover, N-H bending is observed at 1510 cm^{-1} [8] and also N—H stretching that normally occurs in the 3315–3215 cm^{-1}

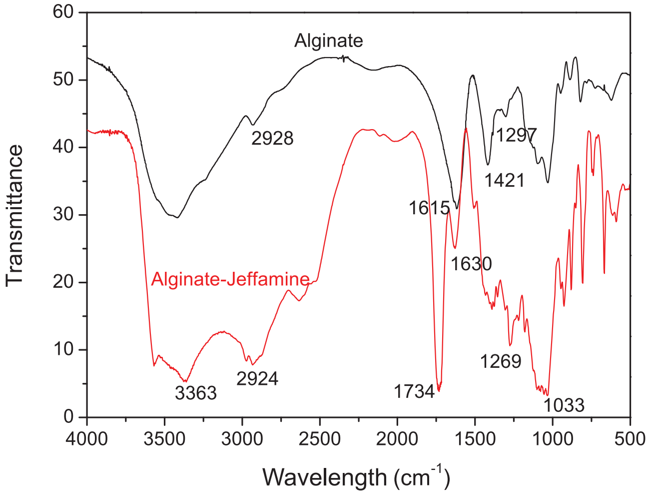

Figure 2. FTIR spectra of alginate (black line ____) and alginate-Jeffamine hydrogel (red line ____).

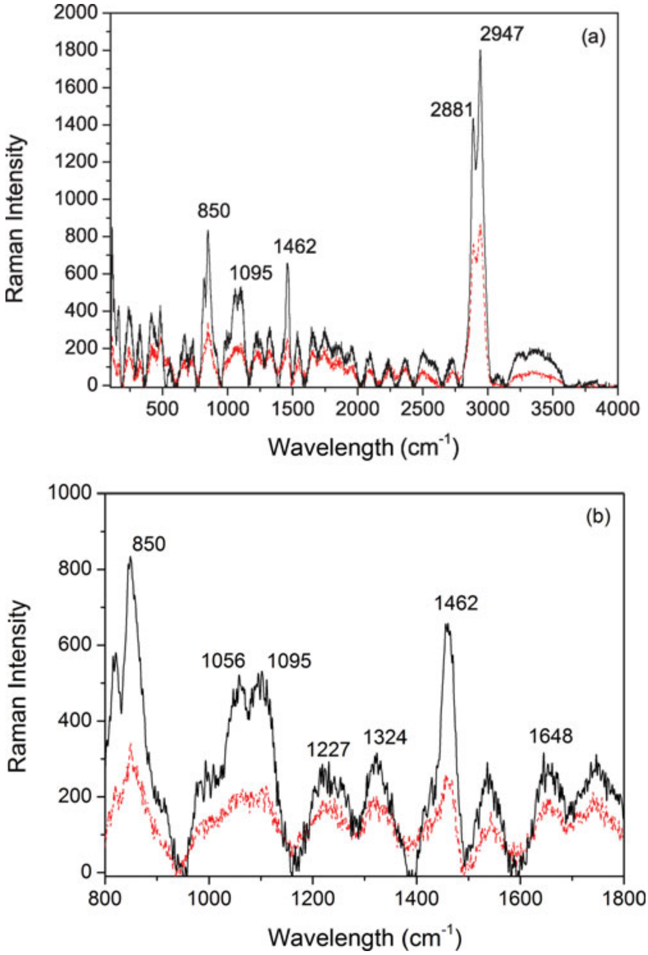

Figure 3. Raman spectra of alginate-Jeffamine granules (red line ––) and membrane (black line ––) hydrogels; 200–4000 cm^{-1} (a) and 800–1800 cm^{-1} (b) wavelength range.

region is in present case shifted to 3363 cm^{-1} and overlapped with the OH stretch from the carbohydrate ring [20, 22].

The two synthesis products, i.e., pure network in the form of granules and membrane form were characterized by Raman spectroscopy. As can be seen in Fig. 3(a) the both spectra are very similar exhibiting main bands at 850, 1095, 1462, 2881 and 2947 cm^{-1}. Analyzing these results it can be stated that the bands at 850 cm^{-1} are due to the stretching vibration of the polymer backbone and at 1095 cm^{-1} to the glycosidic ring breathing [23]. The symmetric and asymmetric vibrations of COO^{-} can be seen at 1462 cm^{-1} and 1648 cm^{-1}, respectively (Fig. 3(b)). However, the band at 1462 cm^{-1} can be overlapped with amide I as well as the bands around 1648 cm^{-1} [24]. The bands around 1227 cm^{-1} can be attributed to amide III [24] confirming the alginate-Jeffamine network formation.

The hydrogels were characterized by swelling property when in contact with water. The water absorption of hydrophilic gels is due to the hydration forces counterbalanced by the crosslinking network forces. The equilibrium is reached when these forces are equal [25]. Aiming to evaluate the water absorption degree (S) the alginate-Jeffamine hydrogels

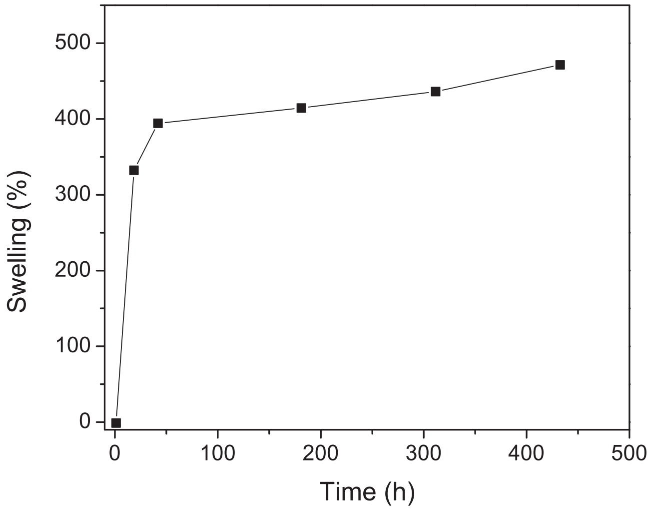

Figure 4. Water absorption of the alginate-Jeffamine hydrogel.

where immersed in water and the samples weight were obtained and inserted to the Eq. (1).

$$S(\%) = \frac{W_S - W_o}{W_o} \times 100\% \tag{1}$$

where S is a swelling absorption degree, W_S is a weight of wet sample and W_0 is a weight of dry sample.

The swelling kinetics of alginate-Jeffamine hydrogel is depicted in the Fig. 4 where one can observe water absorption of 330% after 18 h of sample immersion in water. The water sorption increases to 395% in next 24 h and after that only small increase up to 430% is observed. The maximum water absorption occurs in 18 days.

The moisture content of the alginate-Jeffamine hydrogels were then evaluated by sample weight loss as a function of time during drying at 80°C. The result of this analysis is shown on Fig. 5(a) where one can observe that the sample loss is 28% of its weight after 15 min of being at 80°C. Next 15 min promotes more 25% of weight loss reaching in total 53% of weight loss that is attributed to the water removal. After 90 min the remaining weight is of 20% of initial weight and no more change is observed up to 115 min. Thus, the remaining sample was subjected to the increase of temperature and, consequently to the degradations process. As can be seen on Fig. 5(b) the sample weight loss is practically linear as a function of temperature and at 180°C only 10% of its initial weight remains. This weight loss is attributed to the sample degradation processes.

The alginate-Jeffamine hydrogel were then subjected to optical microscopy analysis and the results are shown on Fig. 6. As can be observed on these pictures the samples show regular porosity that is important for water absorption. Also these samples seem to be different when compared with alginate-chitosan granules superabsorbent hydrogels reported by Yoshimura et al. [21].

Figure 7 reveals SEM micrographs of the alginate-Jeffamine membranes. The pictures show homogenous surface of the samples that probably became more uniform after plasticization with glycerol. Also addition of glycerol probably promoted amorphous membranes formations similarly to the granules' surface reported by Yoshimura et al. [21].

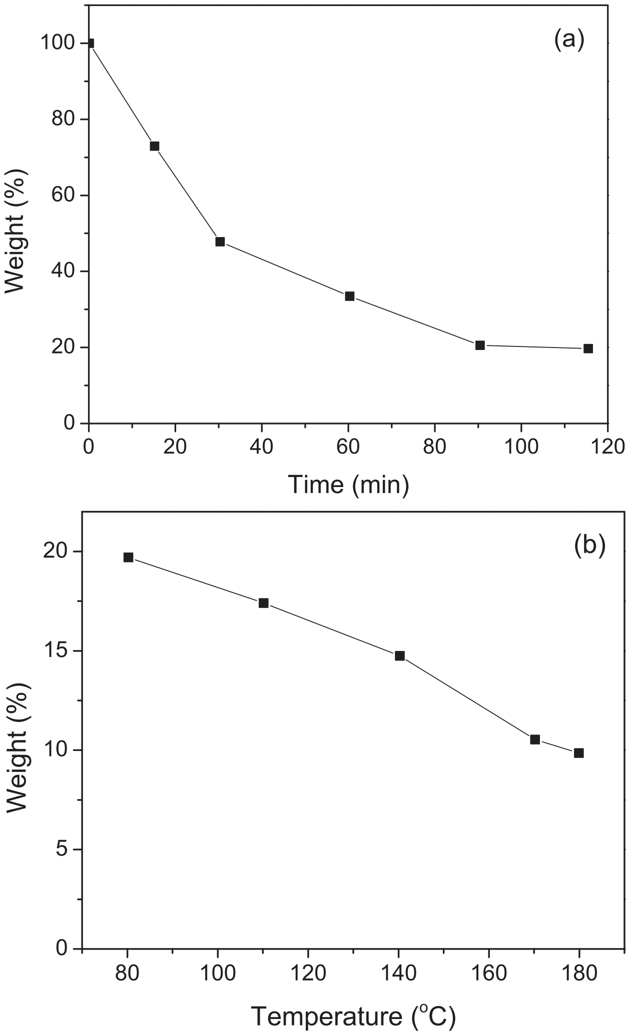

Figure 5. Weight loss a function of time at 80°C (a) and temperature, (b) for the alginate-Jeffamine hydrogel.

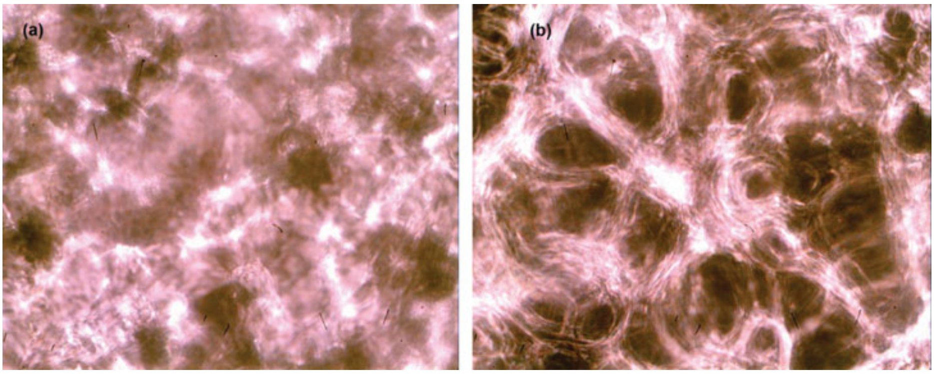

Figure 6. Micrografies of alginate-Jeffamine membrane surface at 25x (a) and 100x (b).

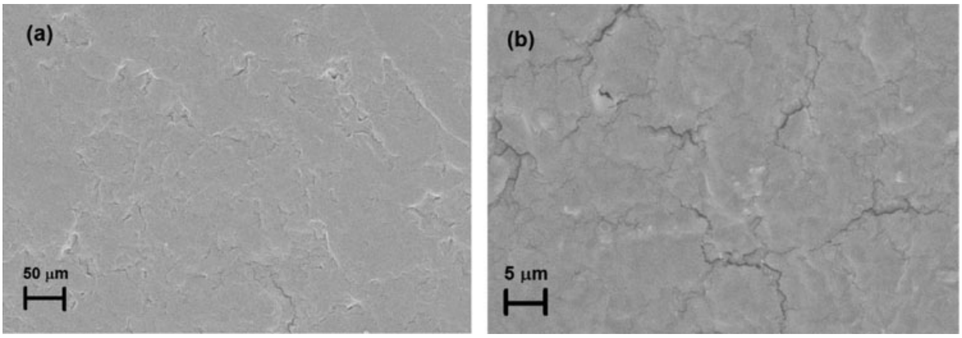

Figure 7. SEM micrografies of alginate-Jeffamine membrane surfaces at 500x (a) and 5000x (b).

Conclusions

The alginate-Jeffamine hydrogels were synthesized throughout the reaction of alginate with O,O′-bis(2-aminopropyl)polypropylene glycol in hydrochloric solution. The network formation was confirmed by FTIR spectra evidencing N—H bonds at 1269, 1510, 1636 and 3363 cm^{-1} and C—H vibrations at 2935 cm^{-1}. Moreover, amide I and III bands at 1227, 1462 ans 1648 cm^{-1} are observed in Raman spectra confirming the alginate-Jeffamine network formation. The swelling properties of the hydrogels revealed water absorption of 330% after 18 h that reached maximum value of 430% in 18 days. The 80% of moisture content of the sample was lost in 90 min at 80°C. The degradation of the sample was observed when heating up to 180°C after that, only 10% of initial weight remained. The optical microscopy evidenced regular porosity of the samples that is important for water absorption. The SEM micrographs of the samples plasticized with glycerol showed homogenous and compact surfaces. The presented results demonstrated that the natural polymers-based hydrogels are very good materials that can be applied successfully in environmentally friendly agriculture as controlled-fertilizers-release and moisture-soil-control agents.

Acknowledgments

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