

A Comparative Study of Two Polyelectrolyte Complexes

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ABSTRACT: This study reports on the synthesis and characterization of interpenetrating polymeric network (IPN) and polyelectrolyte complexes (PEC) produced by ion-complex formation between natural and synthetic polymer bearing opposed charge. PEC of sodium alginate (NaAlg) and poly(acryloxyethyl-trimethylammonium chloride-co-2-hydroxyethyl methacrylate) (poly(Q-co-H)) were formed by addition of 2.0 wt % sodium alginate solution to 1.5 wt % poly(Q-co-H) solution, and by adding the poly(Q-co-H) solution to the NaAlg solution under magnetic agitation. The IPN were prepared using the sequen-

tial method with three different compositions, in which Q and H monomers were mixed in the 95/5 proportions in presence of NaAlg. The mixture was polymerized at 60°C using potassium persulfate as initiator. The characterizations of scaffolds were investigated by Fourier-transform infrared spectroscopy and thermogravimetric analysis. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: polyelectrolyte complexes; interpenetrating polymer network; sodium alginate; acryloxyethyl-trimethylammonium chloride; 2-hydroxyethyl methacrylate

INTRODUCTION

During the last decade, the development of scaffolds based on the intimate mixture of natural or synthetic polymers has been significantly improved. These complexes are known to exhibit important applications in the form of hydrogels, films, membranes, etc.^{1–3} Polymer complexes are formed by association of two or more complementary polymers as a result of electrostatic forces [polyelectrolyte complex (PEC)], hydrophobic forces, hydrogen bonding, van der Waals forces, or combination of these interactions.⁴ pH sensitive hydrogels usually contain pendant acidic or basic groups, such as carboxylic acids and primary amines, or strong acid and bases, such as sulfonic acids and quaternary ammonium salts, which change ionization ability in response to variation in pH, thus changing the properties of the materials.⁵ pH sensitive hydrogels can be prepared by covalent crosslinking or by physical crosslinking of PECs, where one of the ionic species is in excess.⁶ These hydrogels have been proposed as suitable for

drug-delivery systems, protein and material separations, anticoagulant coatings, and even as skin substitutes, among other applications.

An interpenetrating polymer network (IPN) is defined as a combination of two polymers, which have the following two characteristics: first, one of the polymers must be synthesized or crosslinked in the immediate presence of the other, and second, the combination provides the possibility of effectively producing advanced multicomponent polymeric systems with new property profiles.^{7,8} Recently, IPNs have gained widespread acceptance in industrial applications and newer IPNs showing the possibility of a wider range of applications are emerging daily.⁹

Herein we report on the synthesis and characterization of IPNs and PECs produced by ion-complex formation between natural and synthetic polymers having opposed charge. Thus, we prepared a copolymer composed for 2-hydroxyethyl methacrylate (H) and acryloxyethyl-trimethylammonium chloride (Q). Polymeric quaternary ammonium compounds have historically been the most extensively used cationic polyelectrolyte. The hydrophilic permanently charged quaternary ammonium groups provide good water solubility, and the solution properties correspond to those of a strong polyelectrolyte.^{10,11}

On the other hand, alginic acid is a well-known natural polysaccharide obtained from cell walls of brown algae (Phaeophyta) such as the seaweeds *Laminaria* sp. and *Ascophyllum* sp.¹² It is a linear

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block copolymer consisting of uronic acid residues, namely, β -D-mannuronic and α -L-guluronic acid, linked by (1 \rightarrow 4)-linkages. Alginate-based products are popular for wound management because they offer many advantages, for example, biocompatibility, hemostatic capability, and gel-forming ability upon absorption of wound exudates.¹³ Because of the presence of the carboxylic acid groups in the saccharide residues, alginic acid has an anionic nature, forming alginate salts with cationic metals, such as Ca^{2+} and Na^+ . Sodium alginate (NaAlg) is water-soluble biopolymer that has been widely exploited as an anionic template for the formation of the scaffolds combined with cationic polymers.

Recently, poly(Q-co-H)/NaAlg complexes have been proposed as scaffolds for drug delivery and tissue regeneration.^{14,15} All these factors are taken into account in this study.

MATERIALS AND METHODS

Materials

2-Hydroxyethyl methacrylate (H, Merck), acryloxyethyl-trimethylammonium chloride (Q, AQUATECH), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, Fluka; 0.001%N), and acetonitrile (CH_3CN , Merck) were used as received.

Sodium alginate from *Macrocystis perforata* was purchased from Sigma Chemical Co. (Germany). Its viscosity average molecular weight was 3.83×10^4 , which was determined by viscometry in 0.2M NaCl at 25°C. The polysaccharide samples were carefully purified prior to use. Pure water was employed during the experiments and was prepared with A Milli-Q apparatus. All other reagents were of extra pure grade and used as purchased.

Methods

Preparation of synthetic copolymers

The poly(acryloxyethyl-trimethylammonium chloride-co-2-hydroxyethyl methacrylate) copolymers were prepared by free-radical polymerization of the corresponding monomers (i.e., Q and H) in aqueous

TABLE I
Characteristic Absorption Bands (cm^{-1}) of Poly(Q) and Poly(H) Homopolymers

Functional group	Poly(Q) (cm^{-1})	Poly(H) (cm^{-1})
ν (OH)	3368	3366
ν (C—H)	3013	2946
ν (C=O)	1725	1707
δ ($\text{N}^+(\text{CH}_3)_3$)	1482	—
ν (C—O—C)	1158	1151
ν (C—O) fragment —O—	950	—
δ (OH)	—	770–650

TABLE II
Feed Composition and Designation for the Preparation of Poly(Q-co-H)/NaAlg IPN

Sample ID	Matrix NaAlg	Monomers		Initiator $\text{K}_2\text{S}_2\text{O}_8$
		Q	H	
IPN 70/30	2.1×10^{-4}	9.7×10^{-3}	9.3×10^{-4}	6.1×10^{-5}
IPN 80/20	3.2×10^{-4}	3.9×10^{-3}	3.2×10^{-4}	2.4×10^{-5}
IPN 90/10	3.6×10^{-4}	2.0×10^{-3}	1.6×10^{-4}	1.3×10^{-5}

solution without the use of any crosslinking agent by a previously described procedure.¹⁵ The poly(acryloxyethyl-trimethylammonium chloride) and poly(2-hydroxyethyl methacrylate) homopolymers were synthesized following the same procedure. The structural changes were followed by ATR-FTIR technique. The spectra of homopolymers and copolymer were analyzed comparatively. The characteristic absorption bands of ATR-FTIR of poly(Q) and poly(H) are summarized in Table I.

Preparation of PECs

It is well known that poly(acryloxyethyl-trimethylammonium chloride-co-2-hydroxyethyl methacrylate) is a polycationic macromolecules,¹⁴ unlike alginate which is polyanionic. The procedure for preparation of the PEC consisted in mixing under magnetic stirring an aqueous 1.5 wt solution of the cationic polymer (poly(Q-co-H)) with an aqueous 2.0 wt solution of the anionic polymer (NaAlg).

Preparation of the IPN

The IPN was prepared using the sequential IPN method in water solution. NaAlg was dissolved in pure water for 4 h to make a 2 wt % aqueous solution. Next, Q and H monomers were mixed in the 95/5 proportions, respectively. The detail composition and designation of poly(Q-co-H)/NaAlg IPN are listed in Table II. Poly(Q-co-H) was polymerized in the presence of NaAlg at 60°C, using $\text{K}_2\text{S}_2\text{O}_8$ as initiator in Pyrex glass flask under nitrogen atmosphere. After the proper reaction time, the flask content was poured into a large excess of acetonitrile to the unreacted monomers and other subproducts were leached out. The precipitated IPN was rot evaporated to remove acetonitrile and dried under vacuum until the constant weight.

Spectroscopic analysis (ATR-FTIR)

Fourier-transform infrared (FTIR) spectrophotometer (Nicolet 6700) was employed to obtain spectra of IPNs and PEC. The spectrums were collected using Attenuated Total Reflectance (ATR) Smart Orbit accessory. All the spectra were average of 100 scans

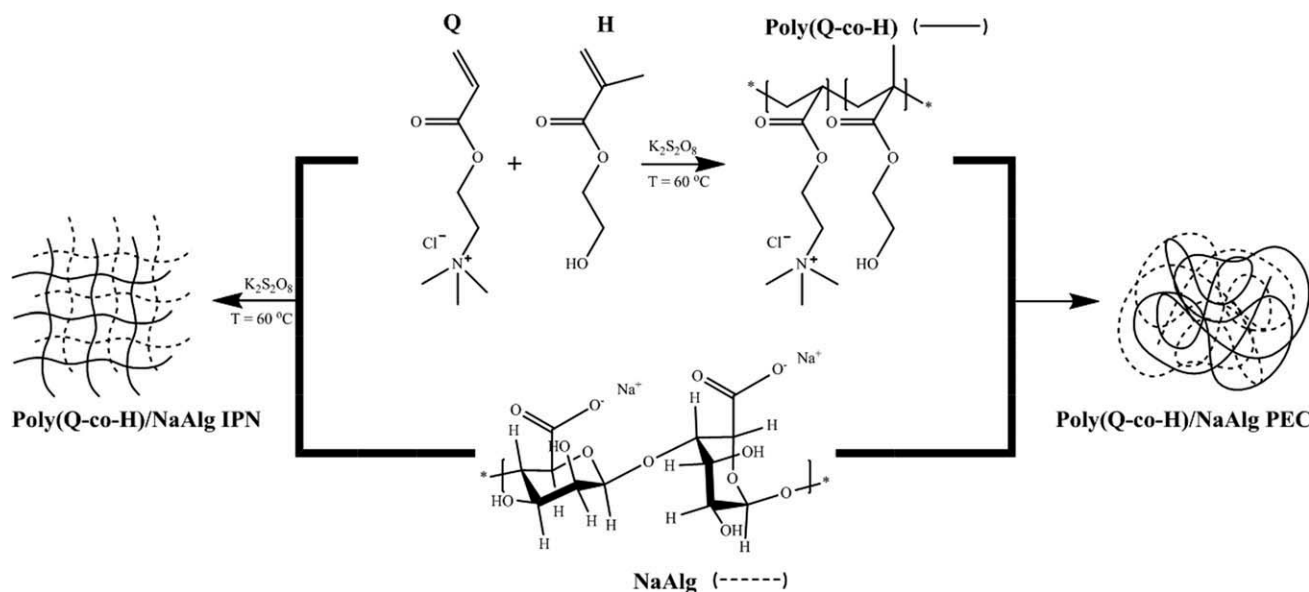


Figure 1 Schematic representation for the synthesis of PEC and IPN.

with a resolution of 4 cm^{-1} . The IPNs were characterized by a comparison of the ATR-FTIR spectra of the homopolymers with those of IPNs. The different compositions of IPNs were also analyzed.

Thermogravimetric analysis

The dynamic weight loss tests were conducted on a TA Instruments SDT Q600 for the determination of the thermal stabilities of the homopolymers, PEC and IPNs. All tests were conducted under nitrogen atmosphere using sample weights of 4–10 mg over a temperature range $0\text{--}600^\circ C$ at a scan of $10^\circ C/\text{min}$.

RESULTS AND DISCUSSION

Preparation of PEC and IPNs

The formation of ion complexes between natural and synthetic polymers with opposed charge has been investigated only by few groups.¹ The complexation mechanism involves the formation of electrostatic attraction between amino group of the poly(Q-co-H) and carboxyl group of acrylic acid. In our case, PECs are formed by an ion-exchange reaction. On the other hand, IPNs were prepared by free-radical polymerizations of H and Q monomers in aqueous solution of the natural polymer of NaAlg using redox initiators. Figure 1 exhibits the scheme of the syntheses of PEC and IPN.

ATR-FTIR analysis

ATR-FTIR is of importance to study the molecular structures. The width and intensity of spectral bands, as well as the peak positions are very sensi-

tive to environmental changes and the conformations of the macromolecule. It is well-known that in IPNs the intermolecular interactions are of widely occurrence. Therefore, the ATR-FTIR spectra of the IPN are different from those of the pure polymers and PEC, which is advantageous for studying the IPN formation.

Figure 2 shows the infrared spectra for NaAlg, poly(Q-co-H), IPN 80/20, and PEC in the wavelength range of $4000\text{--}400\text{ cm}^{-1}$. In the sodium alginate infrared spectra, the widest and most intense bands found in the region $3454\text{--}3202\text{ cm}^{-1}$ are assigned to the acids stretching. The most intensive band at 1592 cm^{-1} was assigned to the C=O stretching vibrations. Others intense signals arising at 1406 and 1025 cm^{-1} and were assigned to the vibration of the COO^- and C–O groups, respectively. The

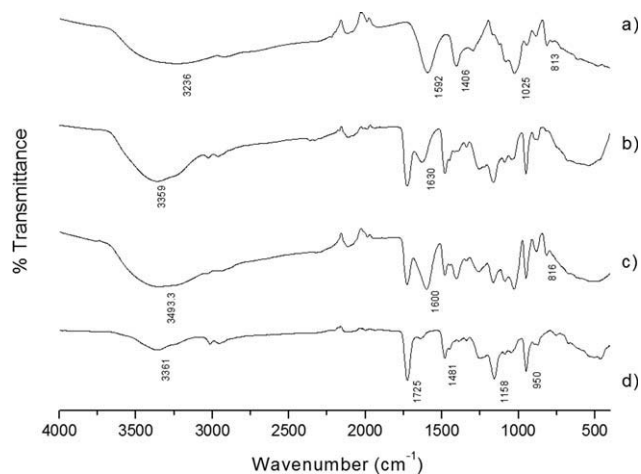


Figure 2 ATR-FTIR of NaAlg (a), IPN 80/20(b), PEC (c), and poly(Q-co-H) (d).

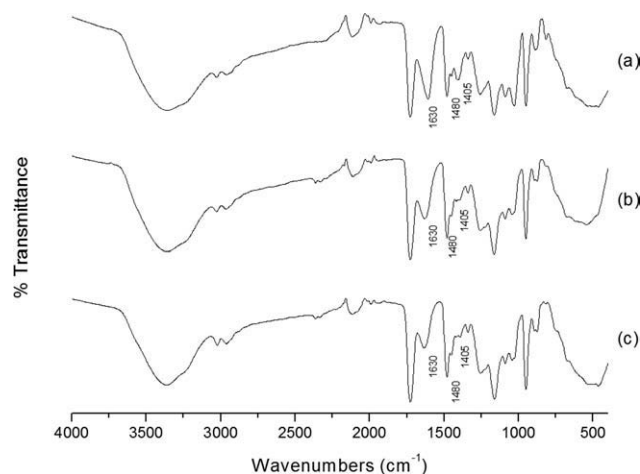


Figure 3 ATR-FTIR spectra of IPN 90/10 (a), IPN 80/20 (b), and IPN 70/30 (c).

characteristic peak of sodium alginate appeared at 813 cm^{-1} (Na—O). The band positions were within the range reported in the literature for these functional groups in polysaccharides.¹⁶

The IR spectrum of poly(Q-co-H) [Fig. 2(d)] demonstrates all characteristic absorption bands of the both homopolymers. Thus, the spectrum showed a broad structureless band at 3360 cm^{-1} because of OH groups, two peaks at 1725 and 1481 cm^{-1} , which were assigned to a C=O and $\text{N}^+(\text{CH}_3)_3$ groups, respectively, and one sharp peak at 1158 cm^{-1} , which is for the C—O group. In 950 cm^{-1} appears a singular band presented in the Q monomer spectrum and may be related to the C—O stretching vibration in a fragment —O—. The bands at 2932 cm^{-1} (CH stretching) and $1500\text{--}1300\text{ cm}^{-1}$ (various C—H bending) were also detected. The signals presented in $\sim 1600\text{ cm}^{-1}$ and $\sim 800\text{ cm}^{-1}$ regions, which were attributed to C=C stretching of the H

and Q monomers disappeared in the copolymer spectra, indicated that the carbon–carbon double bonds were converted into C—C single bonds during the polymerization reaction.

Spectra of the IPN 80/20 and PEC hydrogel are presented in Figure 2(b,c), respectively. These spectra are characterized by the presence of absorption bands typical of the pure components; however, the PEC spectrum in a contrast to that of IPN shows more absorption bands. The fact is attributed to better mobility of poly(Q-co-H) chains and the NaAlg amount present in the reaction mixture. The absorption peaks at 1630 cm^{-1} assigned to the asymmetrical stretching vibration of COO^- groups present in both spectra suggest that new hydrogen bonds are formed between the COO^- groups of NaAlg and the CH_2OH groups of poly(Q-co-H).

Following the same analysis, the bands of poly(Q-co-H) at about 3360 cm^{-1} , i.e., the stretching vibrations of OH groups involved in both intermolecular and intramolecular hydrogen bonds, are broadened and coupled with the OH bands of NaAlg at 3236 cm^{-1} . Finally, the characteristic peak of NaAlg at 813 cm^{-1} was not observed in the IPN spectra.

It is important to explain that the detailed spectroscopic investigation of the interactions between NaAlg and poly(Q-co-H) when brought together in a range of structural assemblies has illustrated the difficulty in quantifying the strength of this interaction.¹⁴ There is no doubt that the electrostatic attraction is sufficient to induce an interaction between the two charged macromolecules through IPN and PEC structures, forming a stable construction.

The IR spectra of the IPNs with different NaAlg contents are shown in Figure 3. The most important peaks appear at approximately 1630 and 1405 cm^{-1} . The peaks increased gradually with increasing

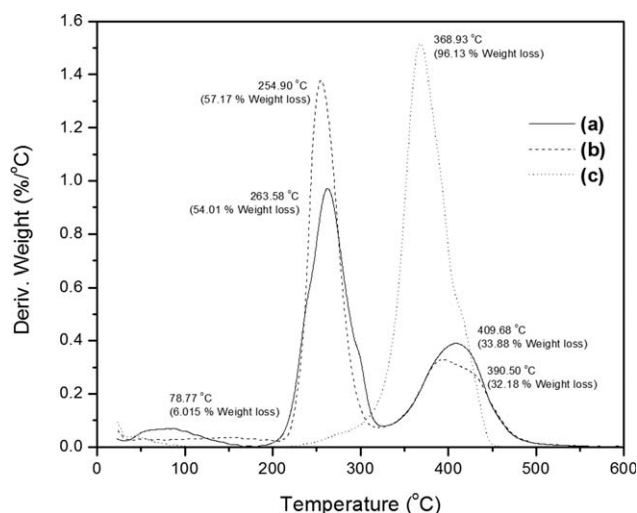


Figure 4 TG-DTG thermograms of poly(Q-co-H) (a), poly(Q) (b), and poly(H) (c).

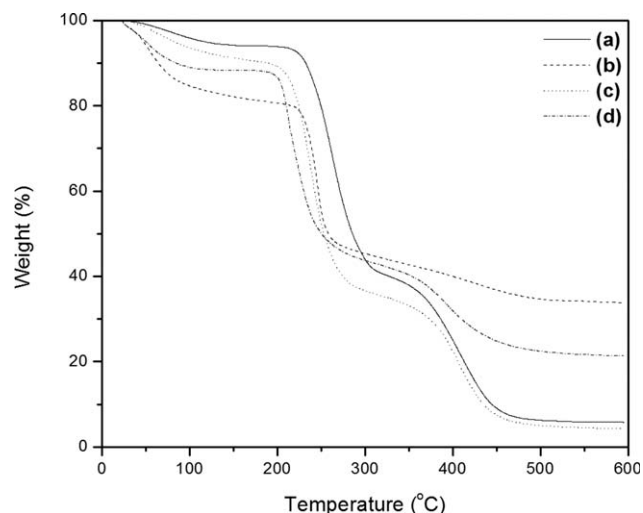


Figure 5 TG-DTG thermograms of poly(Q-co-H) (a), NaAlg (b), IPN 80/20 (c), and PEC (d).

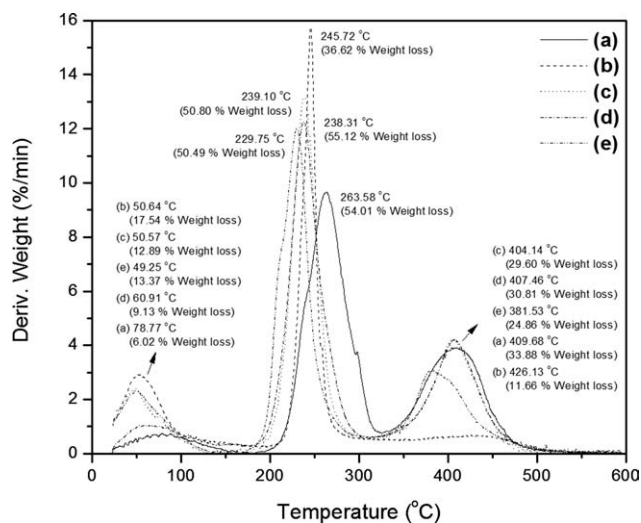


Figure 6 TG-DTG thermograms of poly(Q-co-H) (a), NaAlg (b), IPN 70/30 (c), IPN 80/20 (d), and IPN 90/10 (e).

NaAlg content in the IPNs. The same behavior occurs with the assigned peaks of the poly(Q-co-H) that appears at $\sim 1480 \text{ cm}^{-1}$.

Thermogravimetric analysis

To verify influence of the structure and composition on thermal degradation of the obtained materials, the thermal analyses of the samples were undertaken in the interval from 20 to 600°C. The weight loss (TG) and derivate (DTG) curves are presents in Figures 4 and 5. The thermograms of the homopolymers of H and Q are also given for comparison.

The TG curve of poly(H) indicates only one degradation stage [Fig. 4(c)], which is reflected as a single peak in the DTG curve. The overall decomposition process (96% weight loss) consisted in the depolymerization to the monomers, which started at 369°C. On the other hand, quite different decomposition mechanism was observed for the poly(Q): its decomposition occurred in two steps started at 295 and 390°C, respectively. The total weight loss was about 90%. The degradation mechanism consists of the degradation due to random chain scissions during the first step and the ammonium salt decomposition during the second higher temperature step. The obtained data agree with the results reported by Demirelly et al.¹⁷ and Rivas et al.¹⁸ In both studies,

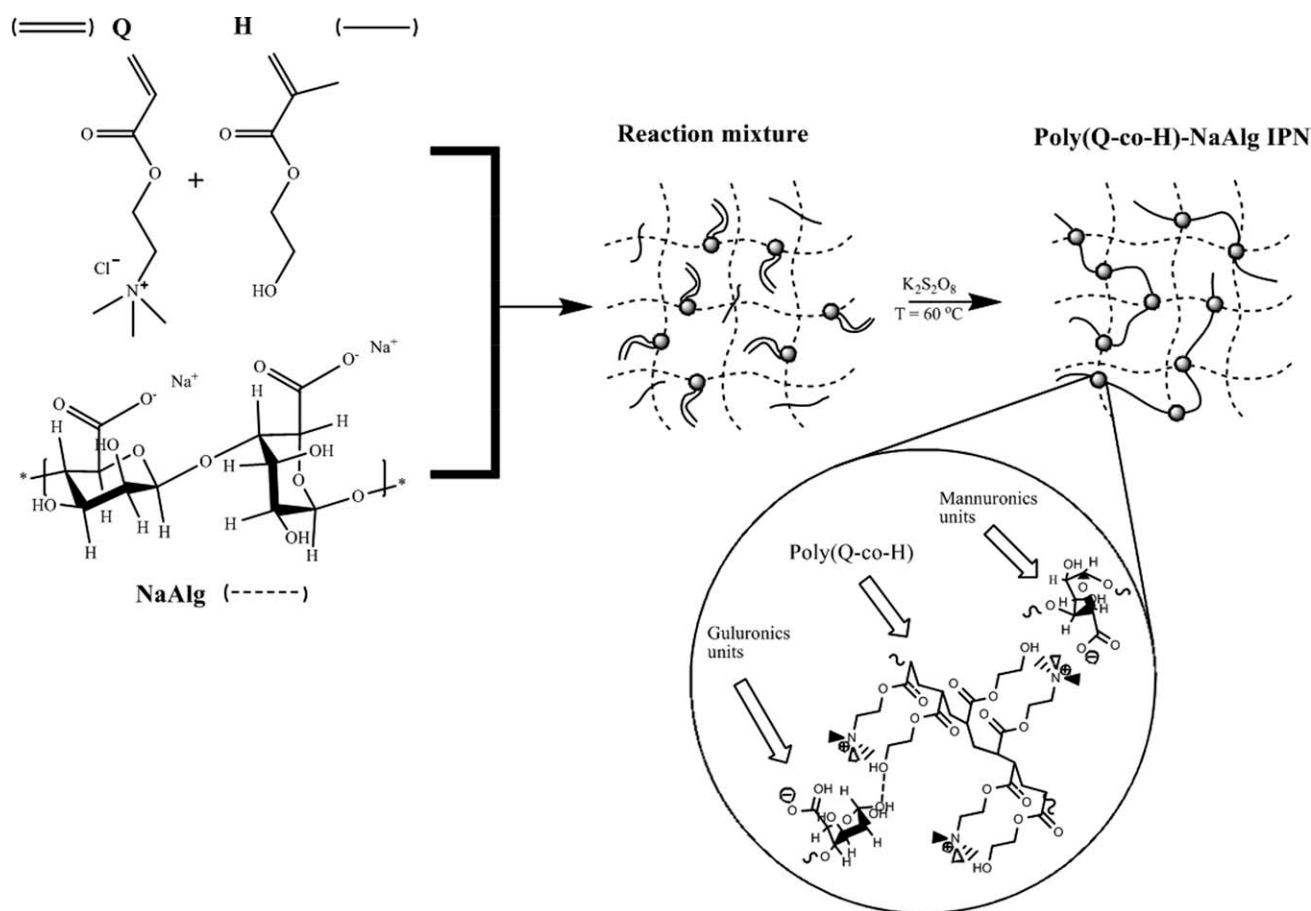


Figure 7 Schematic representation for possible interactions presents in PEC and IPN compounds between the poly(Q-co-H) and NaAlg.

they have mentioned the presence of many degradation products for poly(H) and poly(Q), respectively.

As seen from Figure 4(a), the weight loss curves for the thermal degradation of poly(Q-co-H) reminds closely the TG and DTG curves of the poly(Q) since the copolymer was enriched by Q monomer. Slight, about 6%, low-temperature weight loss of the copolymer observed at 79°C was likely caused by water present.

Following the same protocol, the thermal behavior of NaAlg, IPN 80/20, and PEC were investigated. Analyzing the thermograms shown in Figure 5(a), it can be noted that NaAlg decomposes in three steps, with a total mass loss of 66%, which is in agreement with the data reported by Zohuriaan et al.¹⁹ The first step (a minor dehydration) was followed by degradation into Na₂CO₃ and carbonized material that decomposed slowly in the two steps. Formation of sodium carbonate was also observed by Soares et al.²⁰ that reported a similar behavior for NaAlg decomposition and pointed out that the alginic acid decomposed in two steps without residue.

The IPN 80/20 and PEC thermogravimetric analysis (TGA) curves [Fig. 5(c,d)] also showed three-step weight loss processes, with peaks centered at 61, 238, and 407°C for the IPN and at 47, 212, and 392°C the PEC. These peaks were attributed to degradation process of NaAlg described above.

The peaks of the biggest weight loss (second step) for IPN and PEC were significantly shifted to the higher temperatures compared with that for NaAlg. This result may be explained by the addition poly(Q-co-H), which is more of more thermoresistant, to NaAlg. To confirm this thermogravimetric analysis of IPNs obtained with different feed compositions of poly(Q-co-H)/NaAlg was performed. The data are shown in Figure 6. As can be seen from the figure, shown in Figure 5, the thermal stability was under those of NaAlg and poly(Q-co-H). This behavior was observed in Figure 6 for the different feed composition of poly(Q-co-H)/NaAlg IPNs. We suggest that this behavior is due to the interactions that take place in PECs and IPNs between the poly(Q-co-H) and NaAlg (see Fig. 7). This fact would prevent the chain arrangement, thus results in a loss of stability in these compounds. This behavior was observed in Figure 6 for the different IPNs.

CONCLUSIONS

In conclusion, two forms of scaffolds (e.g., IPN and PEC) composed by natural and synthetic polymers

were obtained. The ATR-FTIR data indicated the presence of ammonium groups of poly(Q-co-H), which reacted with the carboxylate groups of NaAlg, which confirm the IPN and PEC formation. TGA measurements further confirmed the existence of interactions between poly(Q-co-H) and NaAlg. The TGA studies show that the PECs as IPNs show a degradation temperature lower than the starting polymers. This behavior is due to electrostatic interactions and hydrogen bonding between the polymer blue and red. These interactions constrain the ordering of the chains within the compounds consequently resulting in the loss of thermal stability.

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