A Comparative Study of Two Polyelectrolyte Complexes

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ABSTRACT: Interpenetrating polymeric networks (IPNs) based on natural sodium alginate (NaAlg) biopolymer matrix and synthetic hydrophilic polymer were synthesized using sequential method. Poly(acryloxyethyl-trimethylammonium chloride-co-2-hydroxyethyl methacrylate) (poly(Q-co-H)) with high content of quaternary ammonium groups (Q units) was used as a synthetic polymer for the purpose. Since NaAlg has anionic nature and poly(Q-co-H) is a polycation polyelectrolyte complex (PEC) was also prepared via ion interaction between these natural and synthetic components by mixing their water solutions. The all prepared materials were characterized by thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (ATR-FTIR). The comparative analysis of IPNs of different compositions was carried out. Behavior of IPNs was also compared to PEC, material obtained via simple ionic interaction between oppositely charged polymers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2283–2290, 2012

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

INTRODUCTION

During the last decade, the development of materials for cell growing or scaffolds based on the intimate mixture of natural or synthetic polymers has been significantly improved. These materials may be produced in the form of hydrogels, films, membranes, etc. and have important existing and potential applications in the tissue ingenering.[1–3] Polymer complexes are formed by association of two or more complementary polymers as a result of electrostatic forces (PEC), hydrophobic forces, hydrogen bonding, van der Waals forces, or combination of these interacctions.[4] pH sensitive hydrogels usually contain pendent acidic or basic groups, such as carboxylic acids and primary amines, or sulfonic acids and quaternary ammoniums, which change ionization ability in response to variation in pH, and thus changing the properties of the materials.[5] pH sensitive hydrogels can be prepared by chemical (covalent bonding) or physical crosslinking of polyelectrolyte complexes where one of the ionic species is in excess.[6] These hydrogels have been proposed as suitable material for drug delivery systems, protein separations, anticoagulant coatings, and even as skin substitutes, among other applications.[7]

An interpenetrating polymer network (IPN) is defined as a combination of two or more polymers in network form that are synthesized in juxtaposition.[8,9] Such combination provides the possibility of effectively producing advanced multicomponent polymeric systems with new property profiles. Generally IPNs can be prepared by so called sequential method which consists of the polymerization or crosslinking of one of the polymers in the immediate presence of the other. IPNs have found widespread industrial applications and there are many other proposed applications for newer synthesized IPNs.[10] IPNs represent one of the fastest growing fields in polymer science.

Conversely, 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.[11] It is a linear block copolymer consisting of uronic acid residues, namely, β-D-mannuronic and α-L-guluronic acid, linked by (1→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.[12] Because of the presence of the carboxylic acid groups in the saccharide residues, alginic acid has an anionic nature and easily forms corresponding salts with metal cations, 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 in combination with cationic polymers.

Herein we report the synthesis and characterization of interpenetrating polymeric networks (IPN) and polyelectrolyte complexes (PEC) produced by formation of the ionic complex between the anionic natural (NaAlg) and synthetic hydrophilic polymers having opposed charges. For this purpose hydrophilic copolymer composed from 2-hydroxyethyl methacrylate (H) and acryloxyethyl-trimethylammonium chloride (Q) was prepared. Polymeric quaternary ammonium compounds historically have 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.[13,14] Recently, poly(Q-co-H)/NaAlg complexes have been proposed as scaffolds for drug delivery and tissue regeneration.[15,17]

MATERIALS AND METHODS

Materials

2-hydroxhyethyl methacrylate (H, Merck), acryloxyethyl-trimethylammonium chloride (Q, AQUATECH), potassium persulfate ($K_2S_2O_8$, Fluka; 0.001%N), acetonitrile (CH_3CN, Merck), were used as received. Sodium alginate from *Macrocystis periferia* was purchased from SIGMA Chemical Co. Its molecular weight ($\overline{M}_W$) was estimated to be 3.83×10^4 g/mol as determined by viscosimetry in $0.2M$ NaCl at 25°C, using the Mark-Houwink constants K and α, 7.97×10^{-5} and 1.0, respectively, ($[\eta] = 3.06$ L/g). The polysaccharide samples were purified prior to use by the following procedure. An aqueous solution of NaAlg of aprox. 5 g/L concentration was filtered using glass filters (pore diameters 2, 3, 4, and 5 μm) and membranes of 0.8 and 0.45 μm porosities. Then NaAlg was precipitated by addition of ethanol to the filtered aqua solution. The precipitator was filtered off and dried in vacuum at 45°C till the constant weight. Deionized water prepared with A Milli-Q apparatus was employed in all experiments. All other reagents were of extra pure grade and used as purchased.

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 ($N^+(CH_3)_3$)	1482	–
ν (C—O—C)	1158	1151
ν (C—O) fragment —O—	950	–
δ (OH)	–	770–650

Methods

Preparation of synthetic copolymers

The poly(acryloxyethyl-trimethylammonium chloride-co-2-hydroxyethyl methacrylate) copolymer (poly(Q-co-H)) was prepared by free radical polymerization of the mixture of corresponding monomers (i.e., Q and H) in aqueous solution without the use of any crosslinking agent by a previously described procedure.[15,16] The polymerization was carried out for 48 h at 60°C that permitted to achieve high (>90%) conversions. Since cationic polyelectrolyte was required for this study the copolymers with high content of Q units was synthesized. For this purpose the feed monomer composition of Q/H = 95/5 weight %, that corresponds to 92/8M %, was used. Copolymerization of these two monomers was detailed investigated previously and it was this ratio between Q and H was optimum for synthesis of the copolymer with the highest concentration of quaternary ammonium (cationic) units in the polymer chain[15,16] It was also shown that using 95/5 proportion in the monomer feed the copolymer synthesized at high conversions contained 80% of Q units. Thus the poly(Q-co-H) prepared under these conditions was significantly enriched by the cationic units. The homopolymers, poly(acryloxyethyl-trimethylammonium chloride) [poly(Q)) and poly(2-hydroxyethyl methacrylate) (poly(H)], were also synthesized separately following the same procedure. The structural changes were followed by ATR-FTIR technique. The spectra of homopolymers and copolymer were analyzed comparatively. The ATR-FTIR characteristic absorption bands of poly(Q) and poly(H) are summarized in Table I.

Preparation of polyelectrolyte complexes

It is well known that poly(Q-co-H), enriched by Q units, has a strong polycationic structure, unlike alginate which is polyanionic. At first 1.5 wt % aqueous solution of poly(Q-co-H) and 2.0 wt % solution of NaAlg biopolymer in water with $CaCl_2$ (4 g/L) added were prepared. The polyelectrolyte complex (PEC) was obtained by mixing 15 mL of the solution

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

| | Polymer matrix | | Monomers | | | |
| | NaAlg | | Q | | H | |
Sample ID	mol	g	mol	g	mol	g
IPN 70/30	2.1×10^{-4}	0.0417	9.7×10^{-3}	1.8959	9.3×10^{-4}	0.1217
IPN 80/20	3.2×10^{-4}	0.0641	3.9×10^{-3}	0.7658	3.2×10^{-4}	0.4160
IPN 90/10	3.6×10^{-4}	0.0727	2.0×10^{-3}	0.3938	1.6×10^{-4}	0.0211

of the cationic poly(Q-co-H) with 2 mL solution of the anionic NaAlg under constant stirring at room temperature. Thus a big excess of poly(Q-co-H) was taken for the synthesis of PEC. The precipitator was formed almost immediately. The mixture was let stirring 10–15 min more and then the precipitator was filtered off, washed carefully with acetonitrile and water and dried in vacuum at 40°C until a constant weight was attained.

Preparation of the IPN

The IPNs of different compositions were synthesized using the sequential IPN method in water solutions. First, NaAlg was dissolved in the purified water with $CaCl_2$ (4 g/L) for 4 h to make a 2 wt % solution. Then Q and H monomers were added to the solution in the 95/5 weight (92/8M) proportion respectively, to obtain the copolymer of the same composition as the poly(Q-co-H) used in the PEC synthesis described above. This molar ratio between Q and H was hold in all compositions. Thus, varying ratio between NaAlg and the Q-H monomer mixture, compositions containing 70, 80, and 90 wt % of NaAlg were prepared (IPN 70/30, 80/20, and 90/10 in Table II).The detail composition and designation of poly(Q-co-H)/NaAlg IPN are listed in Table II. The polymerization of Q-H monomer mixture was carried out in water in the presence of NaAlg at 60°C, using $K_2S_2O_8$ (1 wt % relatively to the monomers) as initiator in Pyrex glass flask under nitrogen atmosphere till high monomer conversions (90% or more). After the proper reaction time, the flask content was poured into a large excess of acetonitrile. The precipitated IPN was washed carefully with water and acetonitrile again to remove the unreacted monomers and other possible subproducts, then filtered off and dried under vacuum till the constant weight.

Spectroscopic analysis (ATR-FTIR)

Fourier transform infrared (ATR-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 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 (TGA)

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 to 600°C at a scan of 10°C/min.

RESULTS AND DISCUSSION

Preparation of PEC and IPNs

Polyelectrolyte complexes have attracted considerable attention because of their unique properties and easeness of preparation. Because of their ability to change their phase after insignificant alterations of the external factors (pH, ionic strength, temperature, etc.), PEC solutions can be regarded as smart polymer systems. The formation of ion complexes between natural and synthetic polymers with opposed charges has been investigated by several groups.[14–21] The complexation mechanism comprises the electrostatic attraction between the ammonium groups of the poly(Q-co-H) and the carboxylates of NaAlg. Such a formation of PECs between poly(Q-co-H) and NaAlg has been previously demonstrated by our group via conductimetric measurements.[15] Alternatively, the IPNs were prepared by free radical polymerizations of H and Q monomers in aqueous solution of the natural polymer (NaAlg) using redox initiators. Figure 1 illustrates the scheme of the synthesis of PECs and IPNs.

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 sensitive to environmental changes and the conformations of the
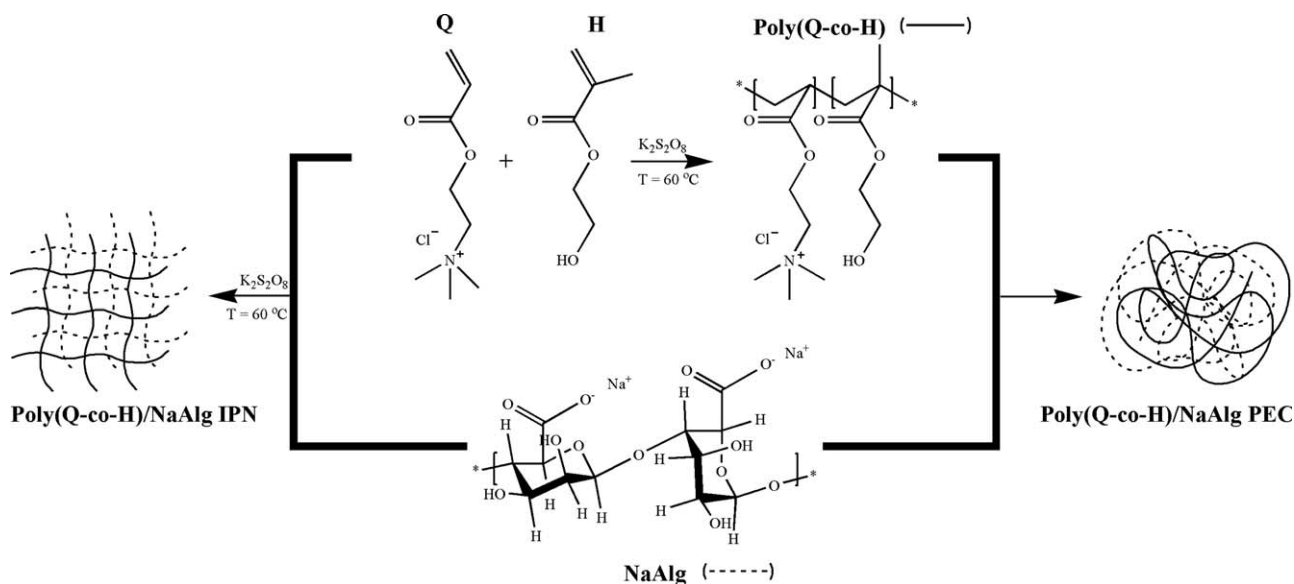
**Figure 1** Scheme of the synthesis of PEC and IPN.

macromolecule. It is well-known that the intermolecular interactions are of widely occurrence in IPNs. So, 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 4000–400 cm^{-1}. In the sodium alginate infrared spectrum [Fig. 2(a)], the broad band found in the region 3454–3202 cm^{-1} was assigned to the O-H stretching vibration; the absorptions at 1592 and 1406 cm^{-1} were assigned to COO$^-$ asymmetric and symmetric stretching vibrations of the carboxilate groups, respectively.[22] In addition, the absorptions observed as peaks or shoulders around 1306 (C—O stretching), 1124 (C—C stretching), 1083 (C—O stretching), 1022 (C—O—C stretching), 950 (C—O stretching), and 813 cm^{-1} (Na-O) are typical for the saccharide structures. The band positions were within the range reported in the literature for the functional groups in polysaccharides.[23]

The IR spectrum of poly(Q-co-H) [Fig. 2(d)] demonstrates the 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 stretching and N$^+$(CH$_3$)$_3$ bending vibrations groups, respectively.[22] A sharp peak at 1158 cm^{-1} arises because of C—O stretching vibration, and a band at 950 cm^{-1} rather related to C—O stretching vibration in a fragment —O— of the Q units.[12] Bands at 2932 cm^{-1} (C-H stretching) and 1500–1300 cm^{-1} (various C—H bending) were also detected. Signals presented in (1600 cm^{-1} and (800

cm^{-1} regions in the spectra of both (Q and H) monomers which were attributed to C=C stretching and bending vibrations disappeared in the copolymer spectrum,[22] that indicated that the carbon–carbon double bonds were converted into the single bonds during the polymerization reaction.

Spectra of the IPN 80/20 and PEC hydrogels are presented in Figure 2 as b and c, respectively. Both spectra are similar and characterized by the presence of absorption bands typical of the pure components. Slight difference between the spectra may be attributed to the different compositions and preparation methods employed in each case. Band of poly(Q-co-H) at 3360 cm^{-1}, i.e., the stretching vibrations of OH groups involved in both intermolecular and intramolecular hydrogen bonds, is broadened and coupled
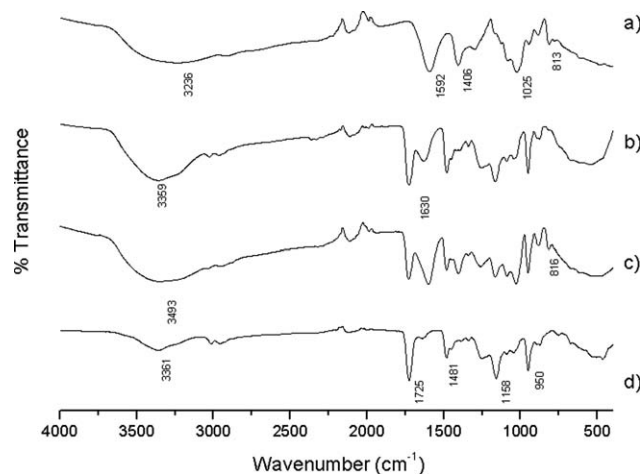
Figure 2 ATR-FTIR of NaAlg (a), IPN 80/20(b), PEC (c), and poly(Q-co-H) (d).
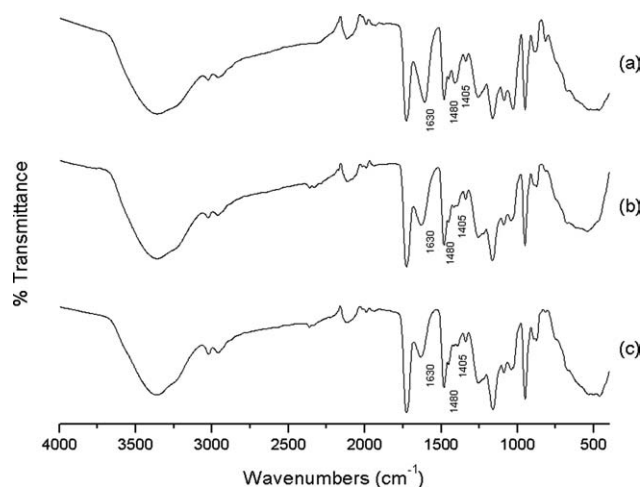
Figure 3 ATR-FTIR spectra of IPN 90/10 (a), IPN 80/20 (b), and IPN 70/30 (c).

with the OH band of NaAlg at 3236 cm^{-1}. Additionally, shift of the COO$^-$ band from 1590 to 1630 cm^{-1} observed in the spectra of both materials is due to ionic interaction between the carboxylates of NaAlg and the quaternary ammonium groups of poly(Q-co-H). Finally, the characteristic peak of NaAlg at 813 cm^{-1} was observed as very weak shoulder in the spectrum of IPN 80/20.

The IR spectra of the IPNs with different NaAlg contents are shown in Figure 3. As should be expected the peaks corresponding to COO$^-$ absorption at 1630 and 1405 cm^{-1} increased gradually with increasing NaAlg content in the IPNs. Also, the band of NaAlg at 813 cm^{-1} appeared as a peak in the spectrum of IPN with the highest NaAlg concentration (IPN 90/10). Obviously, the reverse tendency was observed with respect to the bands assigned to the poly(Q-co-H) at 1725 and 1480 cm^{-1}.

It may be concluded from the IR spectral analysis that content of NaAlg in the PEC should be very high, since relative intensities of the characteristic bands at 1630, 1405, and 813 cm^{-1} are close to the intensities of those in the IPN 90/10 spectrum. Thus, regardless of the fact that PEC was obtained in a big excess of the poly(Q-co-H), the proportion of NaAlg is very high in its composition. According to the spectral data the composition of PEC is close to the composition of IPN 90/10.

Although it is clear that the overall electrostatic attraction is sufficient to provoke an interaction between NaAlg and poly(Q-co-H) leading to stable IPN and PEC structures; the detailed spectroscopic investigation performed—when brought together in a range of structural assemblies—proved the difficulty of such interactions to be quantified.[23] Therefore, the difference between the PEC and the IPN materials cannot be certified exclusively by IR analysis.

## Thermogravimetric analysis

TGA 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 integral (TG) and derivative (DTG) curves are presents in Figures 4 and 5. The thermogramms of the homopolymers of H and Q are also given for comparison.

The TG curve of poly(H) indicates one stage of breakdown principally [Fig. 4(c)], which is reflected as asymmetric peak in the DTG curve. The overall decomposition process (96% weight loss) consisted in a great extent in the depolymeration to the monomer. It started at 300°C and completed at $\sim$ 450°C. According to the literature[23] decomposition of
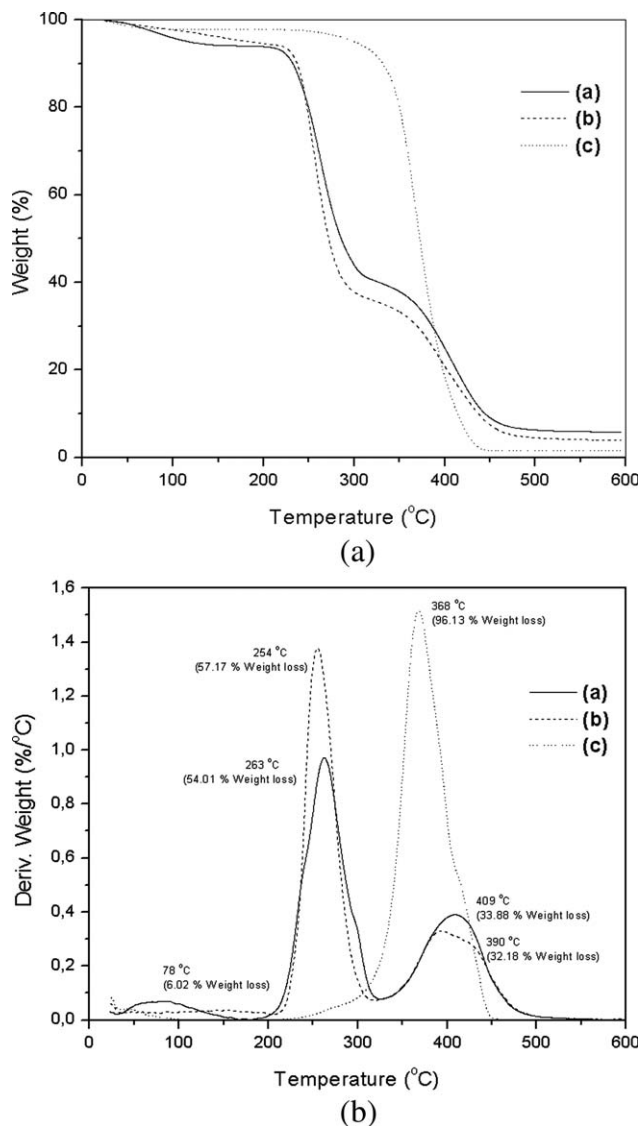
Figure 4 TGA thermograms and differential curves of poly(Q-co-H) (a), poly(Q) (b), and poly(H) (c).

(a)

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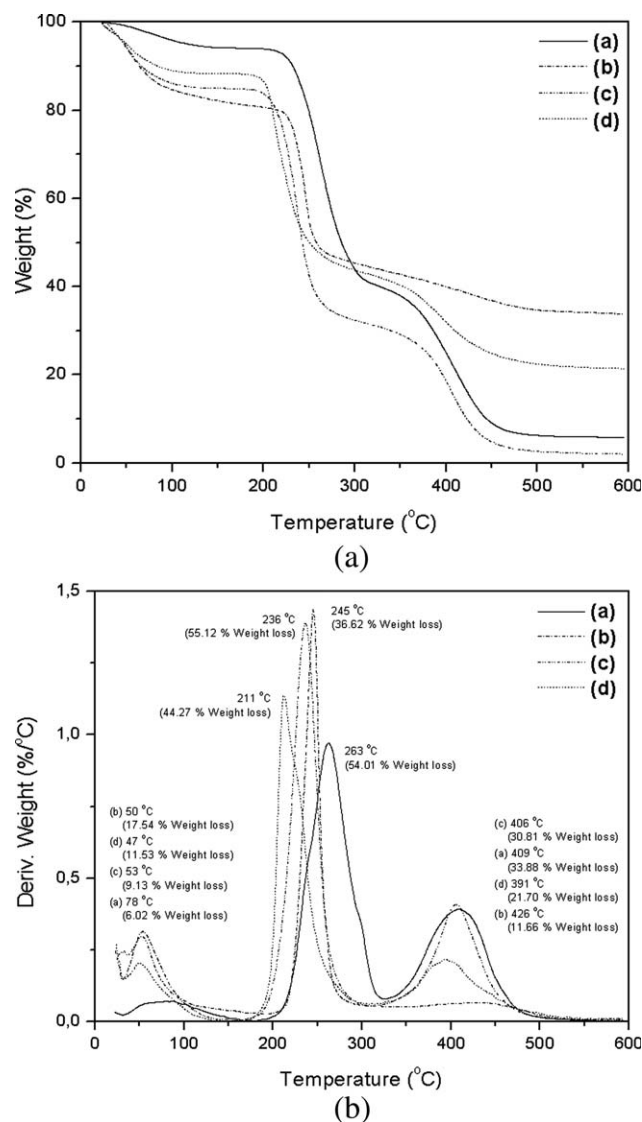
Figure 5 TGA thermograms and differential curves of poly(Q-*co*-H) (a), NaAlg (b), IPN 80/20 (c), and PEC (d).

poly(H) is a two stage process, although according to the TG curve it rather looks as one stage process, and it reflects in an asymmetry of the DTG peak. Except the monomer, 2-isopropenyloxyethyl methacrylate is another main product of the degradation. A quite different decomposition was observed for the poly(Q): it decomposed obviously in two steps started at 208 and 319°C respectively, with a total weight loss around 90%. The 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 Demirelli et al.[24] and Rivas et al.[25]

As seen from Figure 4(a), the weight loss curves for the thermal degradation of poly(Q-*co*-H) remind closely the TG and consequently the DTG curves of the poly(Q) since the copolymer was enriched by Q

monomer. Slight, about 6%, low temperature weight loss of the copolymer started at 80°C was likely caused by water present.

Following the same protocol, the thermal behavior of NaAlg, IPN 80/20 and PEC was investigated. An analysis of the thermograms shown in Figure 5(a) reveals 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.[26] The first step (a minor dehydration) was followed by deep degradation into Na_2CO_3 and carbonized material that decomposed very slowly further. Formation of sodium carbonate was also observed by Soares et al.[27] who 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 TGA curves [Fig. 5(c,d)] also showed three step weight loss processes, with

(a)

(b)
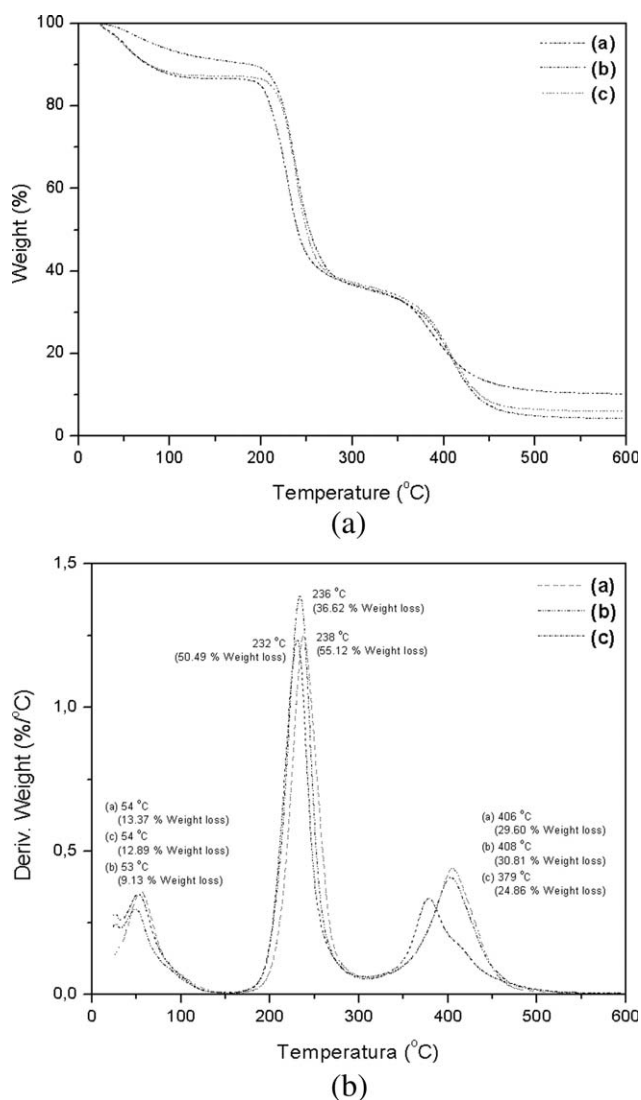
Figure 6 TGA thermograms and differential curves of IPN 70/30 (a), IPN 80/20 (b), and IPN90/10 (c).
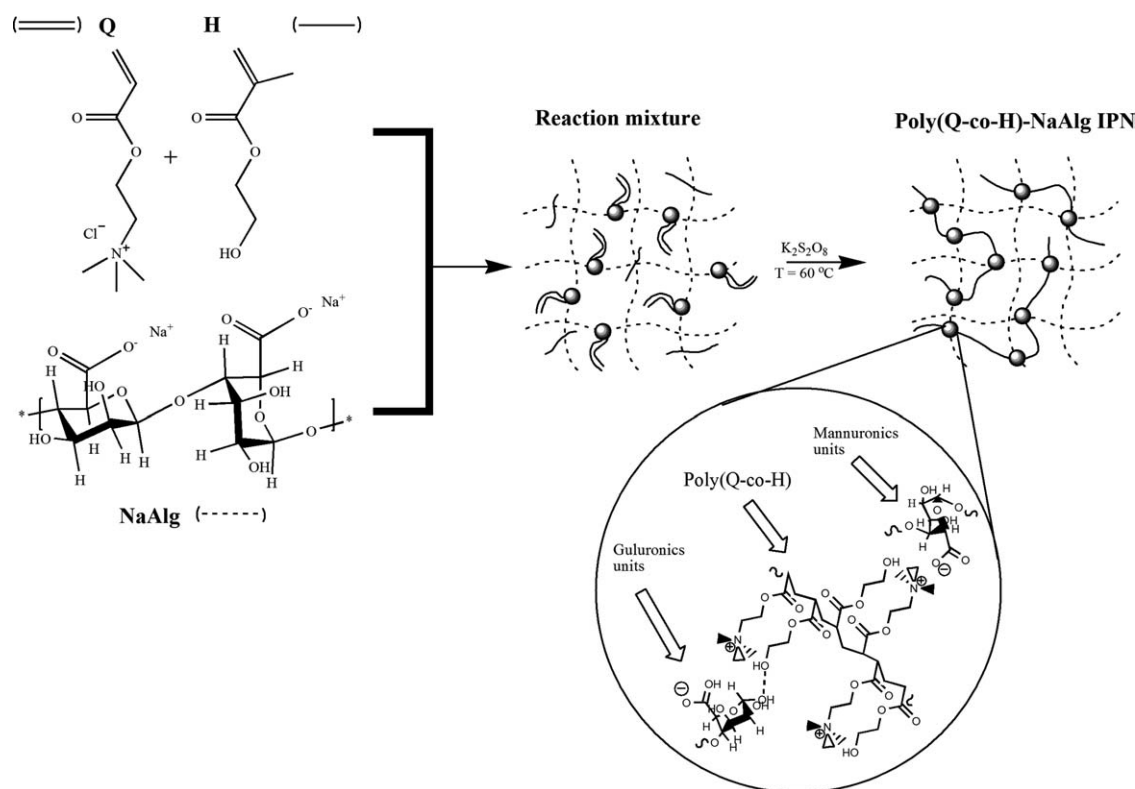
Figure 7 Scheme of possible interactions presented in PEC and IPN compounds between the poly(Q-*co*-H) and NaAlg.

peaks centered at 53, 236, 408°C for the IPN and at 47, 211, 391°C the PEC, respectively. The first, most low temperature peaks are rather because of dehydration of NaAlg presented in the samples.

Surprisingly, the peaks of the biggest weight loss (second step) for IPN and PEC were shifted to the lower temperatures compared with those for original compounds, poly(Q-*co*-H) and NaAlg. The most significant shift was observed for PEC. Thermogravimetric analysis of IPNs obtained with different feed compositions demonstrated the low temperature shift of the biggest weight loss peak for all IPN compositions. The data are presented in Figure 6. As can be seen from the figure, the IPN samples started decomposing at lower temperature than poly(Q-*co*-H) but this is probably because of presence of NaAlg, the first step of decomposition of which started at very low temperature. However the biggest weight loss of the IPNs started at lower temperature as well in comparison with the original NaAlg and poly(Q-*co*-H). The low temperature shift depends on the composition. The IPNs with higher content of NaAlg also decomposed at lower temperature. The difference is not significant; the peak of biggest weight loss shifted from 239°C for IPN 70/30 to 230°C for IPN 90/10. Thus, PEC is the less thermoresistant between all the materials synthesized.

It should be noted that in spite of high weight concentration of NaAlg in the IPN samples their decom-

position did not lead to a formation of the carbonized residual material characteristic for the NaAlg. Total weight losses for all IPNs synthesized were more than 90%. We suggests that such thermal behavior may be explained by interactions that took place in PECs and IPNs between the poly(Q-*co*-H) and NaAlg (see Fig. 7). The interactions may prevent the NaAlg chain arrangement indispensable for the formation of the carbonized residue as schematically shown in Figure 7. PEC gave more carbonized residue at the thermal decomposition and this is probably because of both higher content of NaAlg in comparison with IPNs and the ionic interaction between NaAlg and poly(H-*co*-Q) is weaker and less dense.

CONCLUSIONS

In conclusion, two types of polyelectrolyte complexes (IPN and PEC) composed of natural and synthetic polymers were obtained. IPNs were synthesized by sequential method while PEC was obtained via ionic interaction by simple mixing the oppositely charged polymer compounds, anionic NaAlg biopolymer and cationic synthetic poly(Q-*co*-H). The ATR-FTIR data indicated the occurrence of hydrogen bonding and electrostatic interactions within both materials. Relative intensities of bands in IR spectrum supposed high content of natural NaAlg in PEC although its synthesis was carried out in the

presence of big excess of poly(Q-*co*-H). The TGA studies showed that both materials, PEC and IPNs, have degradation temperatures lower than the starting polymers. IPNs with higher NaAlg content were slightly less thermostable. PEC was the least thermostable between all the materials obtained but at the same time produced carbonized residue at the thermal decomposition.

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