Thermal behavior of alginic acid and its sodium salt

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Abstract: An evaluation of hydration and thermal decomposition of HAlg and its sodium salt is described using thermogravimetry (TG) and differential scanning calorimetry (DSC). TG curves in N_2 and air, were obtained for alginic acid showed two decomposition steps attributed to loss of water and polymer decomposition respectively. The sodium alginate decomposed in three steps. The first attributed to water loss, followed by the formation of a carbonaceous residue and finally the Na_2CO_3. DSC curves presented peaks in agreement with the TG data. In the IR alginic acid presented bands at 1730 and 1631 cm^{-1}, while sodium alginate presented a doublet at 1614 e 1431 cm^{-1}, evidencing the presence of salified carboxyl groups.

Keywords: alginic acid; thermogravimetry; differential scanning calorimetry.

Introduction

The HAlg (Figure 1) is a copolymer derived from the 1,4-linked-*b-D*-mannuronic (M) and *a-L*-guluronic (G) acids [1], containing carboxylic groups in their structures that define the adsorption capacity for metals [2,3].
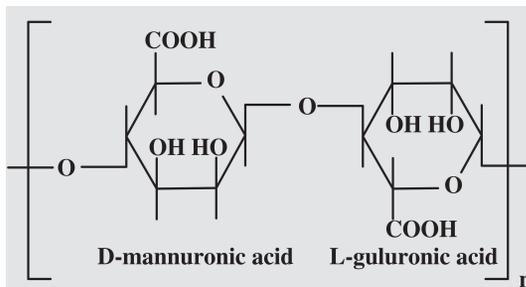
Figure 1. Chemical structures of components of the alginic acid.

According to Haug *et al* [4] *and* Aspinall [5] in alginates both residues can be combined to form homopolymer blocks (M-block, G-block) or copolymer blocks (MG-block) with several possible polymers. Each seaweed can present a specific proportion of M and G units, with a specific alginic acid from each species.

The biological properties of polysaccharides, especially of the algínates, have been explored since many decades in countless medical and surgical applications. Those properties, and the solubility in water, are due to the presence of inorganic ions in the alginate structure6.

Alginic acid form water-soluble salts with monovalent cations but is precipitated upon acidification. Alginates of many bivalent cations, particularly of Ca^{2+}, Sr^{2+} and Ba^{2+}, are insoluble in water and can be prepared when sodium ions of NaAlg are replaced by di- and trivalent cations. This property is used in the isolation of alginic acid from algae [7,8].

Due to their physical and chemical properties HAlg and sodium alginate (NaAlg), have widely been used in food processing, medical and pharmaceutical industries [9] such as drug carrier [5], moreover, sodium alginate has been

employed in the preparation of gels for the delivery of biomolecules such as drugs, peptides and proteins [10].

Toxicological data showed that alginates are safe when used in food. HAlg and its derivatives acts as stabilizers and thickeners facilitating the dissolution and improving viscosity of the ingredients preventing the formation of crystals that will prejudice the appearance and homogeneity, mainly in frozen products [11].

Nakamura *et al.* [12] investigated the thermal properties of water insoluble alginate films containing di and trivalent cations. The results indicated that the alginates form compact structures when the ionic radii of the cation is lower. Changes in the film structure during ionic exchange were studied on the basis of its glass transition temperature (T_g) and heat capacity using differential scanning calorimetry (DSC).

Hatakeyama *et al.* [13] determined the non-freezing water contents of mono and divalent cation salts of some polyelectrolites. The number of water molecules strongly bounded to the cations influences remarkably the polyelectrolyte structure.

Said *et al.* [14] investigated the thermal and electrical properties of silver, selenium and uranyl alginates using thermogravimetry and differential scanning calorimetry, concluding that metal oxalates were formed as decomposition intermediate.

Considering the importance of this polysaccharide and its derivatives and the lacking in information about its thermal behavior, the present work describes the purification, characterization and the thermal decomposition of the alginic acid and sodium alginate.

The thermal analysis is also important considering the fact that in industrial processes heat is commonly employed and the thermal decomposition data yields information regarding the stability and residues of decomposition. Water content is another important parameter that can be extracted from thermal measurements.

Experimental

Reagents and solutions

All the reagents were of analytical grade and used without further purification, except when indicated.

Purification of the HAlg

Alginic acid (Aldrich) was purified by dissolving 5 g in 0.5 mol L^{-1} NaOH and stirring for two h with a magnetic stirrer. After that 0.5 mol L^{-1} HCl was added slowly until pH 2-3 and stirred for 24 h. The resulting gel suspension was filtered in a quantitative filter paper and washed with ethanol. The resulting solid was then dried in a vacuum oven at 40 °C for 24 h. This purification procedure was performed since the commercial reagent presented sodium residue when submitted to thermogravimetric analysis and the conductimetric titration suggested that some carboxyl groups were not free.

Complete dehydration of both acid form and sodium salt was achieved only whether the compounds were used just after drying in a vacuum oven.

Conductimetric titration

Conductimetric titrations were performed by suspending 300 mg of alginic acid in 30.0 mL of water. 10.0 mL of 0.0969 mol L^{-1} HCl solution were added to this solution. The excess of HCl was titrated with 0.505 mol L^{-1} NaOH in a thermostated conductimetric cell at 25.0 ± 0.1 °C kept with a MA 184/6 thermostatic bath (Marconi).

Thermal analysis

Thermogravimetry (TG) measurements were performed in a TGA-2050 thermogravimetric modulus coupled to a TGA-2100 thermal analyser (both from TA Instruments) using sample mass of *ca.* 7 mg and an alumina sample holder at heating rates of 5, 10 and 20 °C min^{-1} under a dynamic air and nitrogen atmospheres flowing at 90 mL min^{-1}. Humidity and ash contents were determined by means of two determinations, with the help of the first derivative thermogravimetry (DTG) data under atmospheric pressure.

Differential scanning calorimetry (DSC) measurements were performed in a DSC-910 modulus coupled to a TGA-2100 thermal analyser (both from TA Instruments) using sample mass of 4,0 mg in a covered aluminum sample holder with a central pin hole at heating rates of 5, 10 and 20 °C min^{-1} under dynamic air and nitrogen atmosphere, flowing at 90 mL min^{-1} under atmospheric pressure.

Elemental analysis, IR and ^{1}H NMR spectroscopy

The C and H contents in the samples were determined in a EA1108-CHN-S elemental analyser (Fisons). IR spectra were recorded in KBr pellets from 4000 - 400 cm^{-1} in a MB102 FT-IR (Bomen-Michelson). The ^{1}H NMR spectra were recorded in a BZH 200/52 spectrometer (Brüker).

Results and discussion

Characterization of the HAlg and NaAlg

The elemental analysis of the samples are in agreement with the general formula $(C_6H_8O_6)_n$ for HAlg and $(C_6H_7O_6Na)_n$, only after complete dehydration. Dry material was obtained after 24 h under vacuum at 40 °C and the elemental analysis being performed just after removing from the oven and keeping in a dessicator under vacuum. If the compounds are manipulated at atmospheric air, they rapidly re-hydrate by absorbing water from the environment.

IR spectra obtained for the HAlg and NaAlg in the 2000 – 800 cm^{-1} range, presented the stretching of the C=O group of the protonated carboxylic group at 1730 and 1631 cm^{-1}. When the proton is displaced by a sodium ion, the peaks are observed at 1614 and 1431 cm^{-1} and they are assigned to the symmetric and antisymmetric COO^{-} stretching vibrations of the free carboxyl group as observed by Huang *et al.* [15].

Yeom [16] reported similar results when measuring the alginate content in films using IR. According to Chandia [17], the alginates FT-IR spectra present bands around 800 e 700 cm^{-1}, relative to mannuronic and guluronic acids respectively.

The main difference of the ^{1}H NMR spectra of acidic form is the singlet signal at 5.04 ppm assigned to carboxylic proton, which disappeared in the sodium salt spectra, according to the literature [17]. The spectra are also independent on the amount of G and M monomers since they are structural isomers.

Conductimetric titrations of excess HCl added to the alginic acid allowed to the determination of the number of acidic sites in the polymeric matrix. This number was determined in the range of 0.87 ± 0.07 (n = 3) and 0.99 ± 0.02 mol (n = 3), for carboxylic groups per mol of commercial and purified alginic acid, respectively.

Thermal analysis of HAlg and NaAlg

Initially, a study of the influence of heating rate in the thermal behavior of HAlg and NaAlg was performed under both air and N$_2$ atmospheres. Since every synthetic or natural polymer containing hydrophilic groups usually presents strong interaction with water, the humidity content may influences their properties and is an important characteristic to be determined [13].

Thermogravimetry is a technique that can yield information about humidity and ash contents in a simple and fast way, but factors such as heating rate present a severe influence on the resolution of the TG curve [18,19] and the definition of this parameter is fundamental for a thermogravimetric investigation.

Table 1 presents the percentage for humidity and decomposition mass losses, temperature ranges and residues for the alginic acid and sodium alginate at 5.0; 10.0 and 20.0 °C min^{-1} heating rates in both air and N$_2$ atmospheres as well as the related DSC peaks.

The TG curves presented in Figure 2 suggest that, under heating, the alginic acid presents initially a dehydration process followed by decomposition in two overlapping steps under nitrogen (Figure 2a), without residue at the end of the experiment. Similar behavior was observed in air (Figure 2b). The decomposition product around 400 °C was characterized as a carbonaceous material in both cases.
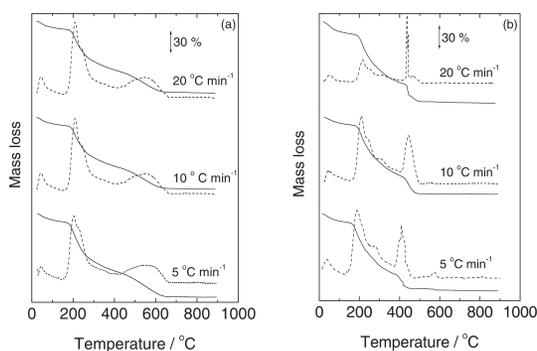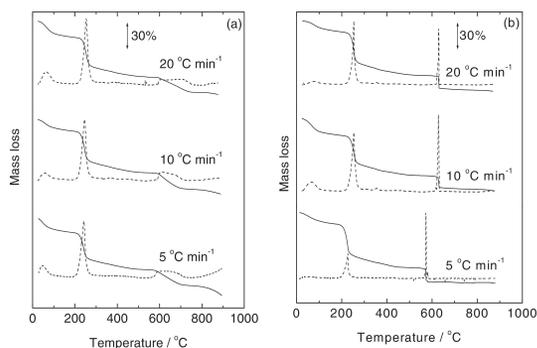

Figure 2. TG (solid)/DTG(dashed) curves of alginic acid in N$_2$ (a) and (b) under air flow of 90 mL min^{-1} in different heating rates.

Compound	Heating rate °C min^{-1}	Attribution	TG		DSC* peaks / °C	
			ΔT / °C	Mass loss %		
N$_2$ atmosphere						
HAlg	5	dehydration	28.6-148.4	10.0	77.2	(endo)
		decomposition	148.4-629.3	87.5	189.7	(endo)
	10	dehydration	25.0-159.3	11.0	86.0	(endo)
		decomposition	159.3-649.8	84.2	197.6	(endo)
	20	dehydration	25.3-169.3	14.9	100.2	(endo)
		decomposition	169.3-869.4	84.9	208.5	(endo)
NaAlg	5	dehydration	28.0-177.4	15.6	80.7	(endo)
		decomposition	177.0-523.5	41.6	220.0	(exo)
		Na$_2$CO$_3$ formation	523.5-749.5	17.9	-	-
		Na$_2$CO$_3$ residue	749.5	24.1	-	-
	10	dehydration	25.2-198.3	12.8	92.6	(endo)
		decomposition	198.3-587.0	46.4	250.6	(exo)
		Na$_2$CO$_3$ formation	587.0-710.3	16.6	-	-
		Na$_2$CO$_3$ residue	726.1	23.8	-	-
	20	dehydration	26.5-202.8	18.4	102.9	(endo)
		decomposition	202.8-585	44.5	260.3	(exo)
		Na$_2$CO$_3$ formation	588-751.0	16.3	-	-
		Na$_2$CO$_3$ residue	751.0	20.5	-	-
Air atmosphere						
HAlg	5	dehydration	25.6-150.9	11.1	76.5	(endo)
		decomposition	150.9-449.1	88.7	308.3	(exo)
	10	dehydration	25.4-152.1	7.85	88.4	(endo)
		decomposition	152.1-411.7	89.2	324.1	(exo)
	20	dehydration	25.6-164.5	9.72	96.1	(endo)
		decomposition	164.5-404.5	89.2	345.2	(exo)
NaAlg	5	dehydration	28.0-177.4	15.6	87.4	(endo)
		decomposition	177.4-559.2	47.3	248.1	(exo)
		Na$_2$CO$_3$ formation	559.2-704.2	14.4	-	-
		Na$_2$CO$_3$ residue	800.0	22.1	-	-
	10	dehydration	26.3-187.1	12.1	92.7	(endo)
		decomposition	187.1-521.2	49.2	254.7	(exo)
		Na$_2$CO$_3$ formation	521.2-744.8	16.7	-	-
		Na$_2$CO$_3$ residue	860.5	22.01	-	-
	20	dehydration	24.8-200.9	19.5	113.6	(endo)
		decomposition	200.9-610.1	46.2	360.1	(exo)
		Na$_2$CO$_3$ formation	610.1-800.0	14.6	-	-
		Na$_2$CO$_3$ residue	800.0	20.7	-	-

Table 1. Thermal decomposition data of the HAlg and NaAlg under N$_2$ and air atmosphere

Figure 3 shows the TG curves for the sodium alginate. According to such a results, the salt decomposed by dehydration followed by degradation to Na_2CO_3 and a carbonized material that decomposes slowly from 600-750 °C in N_2 (Figure 3a). According to Newkirk [20] the Na_2CO_3 decomposition is dependent of the sample holder and atmosphere used. In this work such decomposition appeared above 800 °C in agreement with the findings of those author using Pt crucible and N_2 atmosphere. Under air (Figure 3b) the dehydration occurs in a similar way, but the decomposition of the carbonized material is faster, around 600 °C, resulting in Na_2CO_3 that decomposes as described in N_2. The presence of Na_2CO_3 and carbonized residue was confirmed by heating the compound up to 550 °C, in an oven under the respective atmosphere and addition of HCl to the degradation product. A vigorous liberation of CO_2 was observed while a dark insoluble residue remained in the test tube, in both cases. If the residue percentage is correct for the water content values close to the expected 26.75% for ½ Na_2CO_3 for each $C_6H_7O_6Na$ unit can be found.

Figure 3. TG (solid)/DTG(dashed) curves of sodium alginate under N_2 (a) and air (b) under flow of 90 mL min^{-1} in different heating rates.

The presence of the metallic oxalates instead of carbonates as decomposition intermediates is a difference from the results observed by Said *et al.* [15] for alginates of Ag$^+$, Se^{4+} and UO_2^{2+}, in relation to the sodium salt.

As presented in Figures 2 and 3, the TG general profiles for each compound did not change markedly with these heating rates. It is possible to

observe from the data in Table 1 that the humidity values changed depending on the heating rate which can be related with the influence of the heating rates on the resolution of the dehydration step [18,19], as observed in the DTG curves. The ash contents are not severely affected by the heating rate. Similar results were obtained in all the scan rates, but at 20°C min^{-1} some overlap of the thermal events can occur. So it was concluded that at 10°C min^{-1} a better compromise between resolution and time of analysis can be reached and this was the heating rate chosen for the further analysis.

Figures 4 and 5 show the DSC curves, showing the heating rate influence on the thermal behavior of HAlg and NaAlg under both air and N_2 atmospheres, respectively.

Under N_2 (Figure 4a), HAlg decomposed showing three overlapping peaks. The first endothermic peak suggests the dehydration process at around 80 °C. Then, an endothermic peak close to 200 followed by an exothermic peak at *ca.* 240 °C, respectively, has appeared. Such processes were attributed to the decomposition of the polymer resulting in the carbonized residue, in agreement with TG results.

Figure 4b shows the thermal behavior of the HAlg in air atmosphere. The endothermic peak, centered between 75 and 96 °C depending on the heating rate, may be attributed to the dehydration process. The small endothermic process at 190 °C followed by a strong exothermic peak at *c.a.* 300 °C, correspond to the decomposition of the biopolymer. The TG/DTG data are in agreement with this assumption.
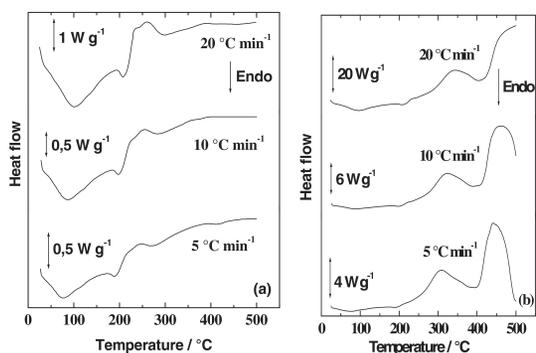
Figure 4 - DSC curves of alginic acid under N_2 (a) and under air (b) flow of 90 mL min^{-1} in different heating rates.

The DSC curves of NaAlg under N_2 are presented in Figure 5.a. The dehydration was evidenced by an endothermic peak close to 100 °C, then the decomposition of the biopolymer takes place represented by an exothermic peak at *c.a.* 240-260, depending on the heating rate. Finally the decomposition of the carbonaceous material occurred above 300 °C.
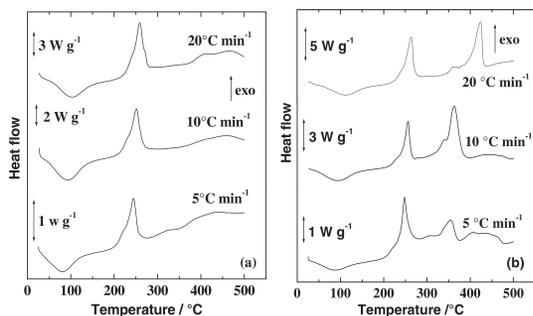
Figure 5. DSC curves the sodium alginate under N_2 (a) and under air (b) flow of 90 mL min^{-1} in different heating rates.

Under air (Figure 5b), the NaAlg presented a first endothermic peak at 100 °C attributed to the water release. The second and third exothermic peaks with a maximum at 250

and 340-410 °C (depending on the heating rate) may be attributed to the decomposition of the biopolymer and formation of the respective carbonate, which is in agreement with TG curves.

Conclusion

According to the present results it can be concluded that the heating rate do not presented significant influence on the TG and DSC profiles from $5 - 20$ °C min^{-1}. This suggests that higher heating rates can be used with gain in experimental time.

The alginic acid decomposed in two successive steps after dehydration under both air and nitrogen atmospheres, without residue in the sample holder at 700 °C. The sodium alginate decomposes also in two steps after the dehydration process. The decomposition leads to a Na_2CO_3 residue, the decomposes above 750 °C under nitrogen, due probably to the presence of carbonaceous residue and is stable under air atmosphere where the carbonaceous residue is totally decomposed above 600 °C. these differences in the Na_2CO_3 behavior have been already described by Newkirk [20].

J. P. Soares, J. E. Santos, G. O. Chierice, E. T. G. Cavalheiro. Comportamento térmico do ácido algínico e do seu sal de sódio.

Resumo: Uma avaliação da hidratação e de decomposição térmica do HAlg e seu sal de sódio foi realizada usando termogravimetria (TG) e a calorimetria exploratória diferencial (DSC). As curvas TG em N_2 e ar, para o ácido algínico apresentaram duas etapas de perda de massa correspondendo à saída de água e posterior decomposição do polímero. Já para o alginato de sódio, a decomposição térmica ocorreu em três etapas. A primeira corresponde à liberação de água, seguida da formação de resíduo carbonizado e formação do carbonato de sódio. As curvas DSC concordam com os eventos observados em TG. Na região do infravermelho, o ácido algínico apresentou bandas em 1730 e 1631 cm^{-1}, enquanto o alginato de sódio apresentou duas bandas em 1614 e 1431 cm^{-1}, evidenciando a presença de grupos carboxílicos salificados.

Palavras-chave: Ácido algínico; termogravimetria; calorimetria exploratória diferencial.

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