THERMAL ANALYSIS OF AMMONIUM, MONO-, DI- AND TRIETHANOLAMMONIUM ALGINATES

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Thermal behaviour of ammonium (NH$_4$alg), mono- (MEAalg), di- (DEAalg) and triethanolammonium (TEAalg) salts of alginic acid (Halg) was investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC). Salts were prepared by the direct reaction of alginic acid with the ammonium hydroxide and with the respective ethanolamines. After preparation the compounds were lyophilized during 24 h and characterized by FTIR spectroscopy and elemental analysis (C, H and N). Under air the compounds exhibited three successive thermal decomposition steps: dehydration, decomposition of the polymeric matrix and finally, burning of carbonaceous residue. Under nitrogen two steps (dehydration and decomposition) were observed. The stability order of this series of compounds was: TEAalg<DEAalg<NH$_4$alg<Halg≈MEAalg. DSC curves between –50 and 150°C did not show any thermal events suggesting that after lyophilization probably non-freezing type water is present in the system.

Introduction

Alginic acid (Halg) is a linear polysaccharide extracted from brown seaweeds with several applications e.g. food and pharmaceutical industries [1–3]. The polymeric chain is composed of α-*L*-guluronic (G) and β-*D*-mannuronic (M) acid units, and can exist in different arrangements, joined with 1–4 glycosidic bonds [4]. A representative structure of the Halg is presented below, with *x* mannuronic (M) and *y* guluronic (G) acid units.
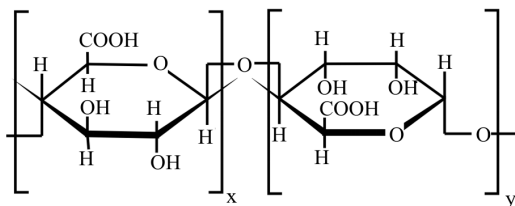
Due to the presence of the carboxylic groups in the polymeric chain, Halg can form alginate salts with some cations and amines [2, 5, 6]. The presence of different cations can change the properties of the alginates, depending on their charges, size and nature, defining the applicability of the salts [4–6].

Thermal analysis and the properties of alginate fibres have been recently published in [7].

Ethanolamines have great importance and a wide scale of application in pharmaceutical, chemical and cosmetic industries [8]. However, with regard to the interaction of these compounds with Halg [9], only few of them are known and to understand the nature of such interaction may possibly serve as a model for more complex problems, such as controlled drug release and the removal of organic pollutants from contaminated water.

In this work the thermal behaviour of ammonium (NH$_4$alg), mono- (MEAalg), di- (DEAalg) and triethanolammonium (TEAalg) salts of alginic acid were investigated using thermogravimetry (TG) and differential scanning calorimetry (DSC) in order to compare the thermal stability and the changes in their decomposition pathways.

Experimental

All the reagents were of analytical grade and used without further purification unless described. Water was distilled twice in a quartz distiller before use.

Preparation of the ammonium, MEA, DEA and TEA alginates

Initially a desired amount of alginic acid (Aldrich) was dissolved with a suitable volume 0.5 mol L^{-1} NaOH and stirred for 3 h at room temperature. After then 0.5 mol L^{-1} HCl was added until reaching pH=2.5 in the supernatant. The resulting solid was filtered in quantitative paper and washed with water until neutral pH and negative test to chlo-

ride ions. Then the Halg was lyophilized for 24 h and kept in a desiccator over silica gel under reduced pressure.

Alginates were prepared by direct reaction between alginic acid (purified see above) and stoichiometric amounts of ammonium hydroxide, mono-, di- or triethanolamine. For that, a desired amount of previously purified Halg was suspended under stirring in water for three hours at room temperature in a reaction vessel. Then, an appropriate amount of amine was added to this suspension and the mixture was stirred for 24 h at room temperature. After that the salts were precipitated in 0% (v/v) ethanol:water 50% and filtered then washed with cold ethanol until neutral pH. Finally the alginates were lyophilized for 24 h and kept in desiccator under silica gel.

Methods

The resulting salts were characterized by elemental analysis (C, N, H) performed in an EA-1110 CHNS-O CE Instruments apparatus and Fourier transform infrared absorption spectra (FTIR) obtained in the 4000–400 cm^{-1} region using a Nicolet 5SXC Infrared Spectrophotometer with 4 cm^{-1} resolution. Samples were analysed in KBr pellets. In order to minimize the water absorption during sample-handling, a 100 W incandescent lamp was used over the bench at ca. 50 cm far from the sample.

TG/DTG, DTA and DSC measurements

TG/DTG and DTA curves were recorded using an SDT-Q600 simultaneous TG-DTA thermal analyzer,

TA Instruments. ca. 7 mg of initial sample masses in an Al$_2$O$_3$ sample holder at 10°C min^{-1} heating rate from 25 to 1000°C under dynamic air and N$_2$ atmospheres (100 mL min^{-1}). DSC curves were recorded on a Q-10 Differential Scanning Calorimeter, TA Instruments, in hermetically closed aluminium sample holder. ca. 3 mg of initial sample mass and 10°C min^{-1} heating rate, from –50 to 150°C min^{-1} and 50 mL min^{-1} dynamic N$_2$ atmosphere.

All the thermoanalytical experiments were carried out under atmospheric pressure.

Results and discussion

Elemental analysis and the FTIR data for the prepared salts are described in Table 1. The amounts of C, H and N are consistent with the proposed formulas, but it should be considered that the water content might vary markedly during the sample handling. FTIR spectra showed changes in the carboxyl group bands that appeared at 1737 and 1637 cm^{-1} in the Halg and at ca. 1610 cm^{-1} in the ethanolammonium and 1600 cm^{-1} in the ammonium salts due to the asymmetrical stretching, and another at ca. 1400 cm^{-1} due to the symmetric stretching of the C–O bonds in the carboxylate anion for all salts. These results confirm that the salts were obtained.

Thermoanalytical results

The TG/DTG curves are presented in Fig. 1a under air and Fig. 1b under nitrogen. DTA curves are presented in Figs 2a and b also in air and nitrogen, respectively.
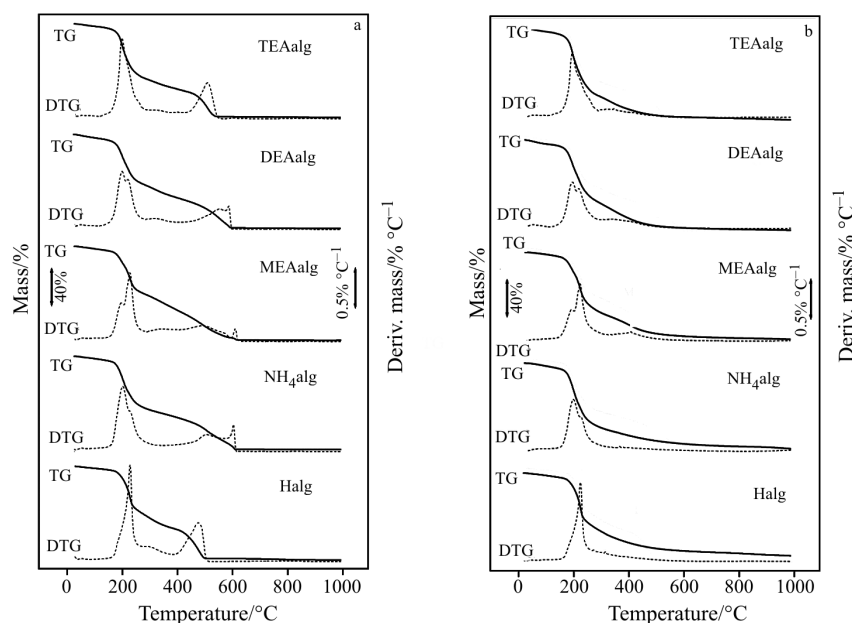

Fig. 1 —— – TG and --- – DTG curves under a – air and b – nitrogen for the compounds

Table 1 Amount of carbon, hydrogen and nitrogen found (calculated) and main infrared absorption bands for the prepared compounds

Compound	Found (calc.)/%			IR bands/cm^{-1}			
	C	H	N	C=O		COO_{as}^-	COO_s^-
Halg·1.5H$_2$O	35.46 (35.45)	5.77 (5.47)	– (–)	1737.7	1637.4	–	–
NH$_4$alg·1.5H$_2$O	32.16 (32.71)	6.01 (6.42)	5.09 (6.36)	–	–	1602.7	1404.0
MEAalg·0.25H$_2$O	38.73 (39.73)	5.57 (6.48)	5.59 (5.79)	–	–	1612.2	1409.7
DEAalg·1.5H$_2$O	39.1 (38.93)	7.57 (7.21)	4.41 (4.54)	–	–	1612.2	1413.6
TEAalg·2.5H$_2$O	38.7 (38.89)	7.62 (7.64)	3.48 (3.78)	–	–	1614.1	1405.9

The observed events in these curves are summarized in Table 2, which contains the temperature intervals and mass losses in air and nitrogen.

Halg

The acid presented a dehydration process in both atmospheres causing approximately 3.3% of water loss. Under air decomposition occurred after dehydration in two overlapping steps leading to a carbonaceous residue which burns in the sequence. Under nitrogen a single decomposition step represented by a continuous mass loss that extends up to the end of the experiment.

NH$_4$alg

After dehydration a first decomposition step appeared, which, according to the DTG curves splits in

Table 2 Temperature ranges and mass losses for the thermal events observed in the TG/DTG curves for the compounds

| Compound	Process	T_{range}/°C	Mass loss or residue/%
		Under air	
Halg	dehydration	27.92–128.91	3.18
	decomposition	128.91–384.20	62.79
	carbonaceous residue burn	384.2–995.30	33.64
	residue	995.30	0.28
NH$_4$alg	dehydration	23.17–126.14	3.84
	decomposition	126.14–366.16	58.66
	carbonaceous residue burn	366.16–995.03	36.69
	residue	995.03	0.81
MEAalg	dehydration	24.72–128.91	4.06
	decomposition	128.91–416.11	66.41
	carbonaceous residue burn	416.11–995.10	29.66
	residue	995.10	0
DEAalg	dehydration	21.45–117.81	4.77
	decomposition	117.81–428.60	65.61
	carbonaceous residue burn	428.60–994.62	29.94
	residue	994.62	0
TEAalg	dehydration	24.10–116.42	3.70
	decomposition	116.42–427.21	68.25
	carbonaceous residue burn	427.21–994.40	28.11
	residue	994.40	0
		Under nitrogen	
Halg	dehydration	20.51–136.11	3.53
	decomposition	136.11–991.90	73.22
	residue	991.90	23.23
NH$_4$alg	dehydration	23.89–119.20	3.30
	decomposition	119.20–993.82	72.40
	residue	993.82	24.28
MEAalg	dehydration	26.16–134.46	3.32
	decomposition	134.46–991.90	77.49
	residue	991.90	19.19
DEAalg	dehydration	25.21–117.81	4.43
	decomposition	117.81–993.27	79.89
	residue	993.27	16.03
TEAalg	dehydration	22.50–113.65	3.05
	decomposition	113.65–993.88	81.46
	residue	993.88	15.48
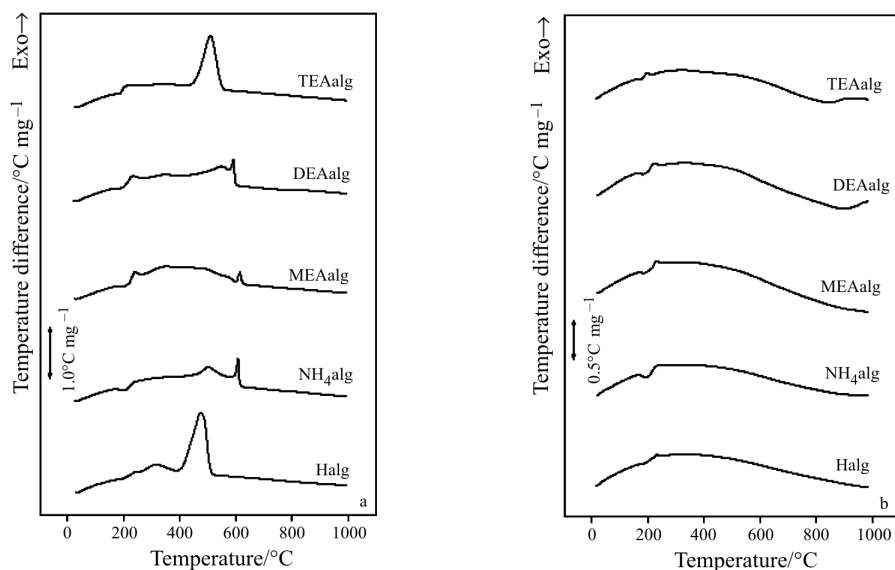
Fig. 2 DTA curves under a – air and b – nitrogen for the compounds

two consecutive ones. Then a carbonaceous residue is formed and burns slowly up to 600°C. Furthermore, a sudden oxidation process is evidenced. Under nitrogen only one step is observed that is not complete up to the end of the experiment, however, the split in the DTG peak is observed. Heating the sample in an open tube permitted to identify the characteristic smell of ammonia above 100°C.

MEAalg and DEAalg

Both compounds present very similar decomposition pathways. Under air the first splitted decomposition event is observed after dehydration. Then, a second mass loss is observed followed by the burning of the carbonaceous residue with the final sudden oxidation. Under nitrogen the splitted decomposition is followed by the second decomposition steps are also observed. Finally a continuous mass loss is observed up to end of the experiment.

TEAalg

Under air the first decomposition step appears after dehydration. The split in this peak is very discrete compared to the NH$_4$alg, MEAalg and DEAalg DTG curves. The second process represents the burning of the carbonaceous residue. Under nitrogen a single decomposition step was observed with a continuous mass loss up to end of the experiment.

The mass loss value in the first decomposition step observed after the dehydration for all the samples increases in the following order: MEA<DEA<TEA salts.

DTA data recorded in air (Fig. 2a) presented a series of exothermic peaks in agreement with the TG findings. A sudden decomposition of residual organic

matter can be observed at ca. 600°C. Under nitrogen (Fig. 2b) only a broad exothermic event is observed, without physical meaning related to the individual processes in all cases. In both atmospheres small endothermic peaks were observed at about 200°C for the salts. This could be related to the smell of ammonia described above for the NH$_4$alg, suggesting decomposition of the NH$_4^+$, MEAH$^+$, DEAH$^+$ and TEAH$^+$ cation.

The DSC curves obtained from –50 to 150°C, not presented, revealed any thermal event near to 0°C suggesting that after lyophilization the remaining water is probably non-freezing type (bonded water). The curves were recorded up to 150°C, since after then the decomposition starts (Table 2).

Conclusions

It is possible to synthesize the ammonium and the mono-, di- and triethanolammonium alginic acid salts. However, the compounds presented almost the same thermal behavior and the differences in the structure of the ammine group did not affected significantly the thermal stability of the resulting salt, except changes in the temperature in which the mass loss started.

The stability order of this series of compounds, after dehydration, was:

TEAalg<DEAalg<NH$_4$alg<Halg≈MEAalg

Labile water molecules can be removed by lyophilization, however a certain content of non-freezing water still remaining after drying according to the DSC data, since any melting was observed in the curves.

Acknowledgements

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