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THE STUDY OF NON-ISOTHERMAL DEGRADATION OF ACRYLIC ION-EXCHANGE RESINS

Dorina Chambree[1,*], *Cornelia Idiţoiu*[1], *E. Segal*[2] *and A. Cesàro*[3]

[1]Research Centre of Chemistry and Technology, Faculty of Food and Environment Engineering, University 'Aurel Vlaicu' of Arad, Bd. Revoluïiei 81, 2900 Arad, Romania
[2]University of Bucharest, Faculty of Chemistry, Bd. Elisabeta 4-12, Bucharest, Romania
[3]Laboratory of Physical and Macromolecular Chemistry, BBCM Department, University of Trieste, I-34127 Trieste, Italy

The thermal behavior under non-isothermal conditions of some low-acidity carboxylic cationites with acrylic-divinylbenzene (DVB) matrix was investigated in air and nitrogen atmosphere up to 600°C. Thermal analysis (TG/DTG) combined with Mass Spectrometry (MS) and Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the resins decomposition steps and the degradation products. Five decomposition steps were observed. The first step is due to elimination of osmotic and bound water. The second decomposition step is due to dehydration of neighboring (–COOH) groups. The third and fourth mass-loss steps correspond to decarboxylation of the polyanhydrides and to some depolymerization of the polymeric matrix. The last decomposition step is associated with total degradation of the polymeric matrix. The shape and the temperature for each decomposition steps depend on the experimental conditions (heating rate and degradation atmosphere) and on the sample properties (i.e. granulation, cross-linking degree, porosity and physical form).

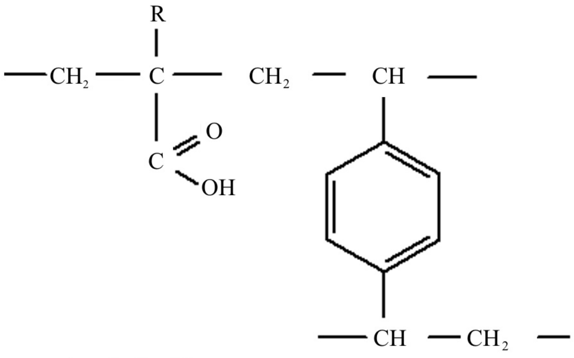
Keywords: *carboxylic cationites, cationite thermal behavior, FTIR, MS, polyacrylic resins, TG/DTG, thermal analysis*

Introduction

Ion-exchange resins are produced and commercialized in a wide range of formulations with different characteristics, and have now a large practical applicability in various industrial processes, such as chemical, nuclear, pharmaceutical, food industry, etc. [1]. For their versatile properties, the cationic resins are used both in the ion exchange area and in the heterogeneous catalysis field [2, 3]. So, the cationic resins, especially the carboxylic cationites, produced with a higher purity degree, became the potential catalysts in various food technologies [4]. In many cases their use as catalysts is limited by the relatively low thermal stability. Hence, knowledge of the thermal behavior of carboxylic cationites under non-isothermal conditions is necessary.

While for the polystyrene-divinylbenzene sulfonic cationites, the literature gives enough information about their decomposition and non-isothermal behavior [5–9], in the case of carboxylic cationites with low acidity, literature seems to offer relatively poor information [10, 11]. On the other hand, abundant data exist on the thermal degradation of polyacrylic acid and of its mixtures with other polymeric and non-polymeric species [12–17]. From these data it is clear that shape and size of degradation steps may largely depend upon composition and physical state of the sample. It has been shown that impurities (e.g. metals [18]) and cross-linkers [19] affect the degradation in an opposite way. However, no specific data are available on the cation exchange resins, here investigate, and literature studies do not show significant details as far as it concerns the thermal degradation curves.

Continuing some previously reported investigation [20, 21], this work presents data on the thermal behavior under non-isothermal conditions of some low-acidity carboxylic cationites with acrylic-divinylbenzene (DVB) matrix (Scheme 1), aiming at identifying and characterizing the resins decomposi-



where R: H, –CH$_3$

Scheme 1

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[*] Author for correspondence: dorinachambree@yahoo.com

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

tion steps. These resins exhibit a high exchange capacity and an excellent osmotic shock resistance. Industrially, these carboxylic resins are obtained through direct copolymerization of the acrylic acids with DVB or through hydrolysis of the resins obtained from copolymerization of some acrylic esters or even of acrylonitrile with the same cross-linking agent [2, 11].

The paper is organized as follows. The Results and discussion section firstly provide the analysis of the thermogravimetric results in order to identify the best experimental conditions and then the identification of degradation steps is given. In the Conclusions the few relevant implications are summarized.

Experimental

Materials

The following commercial carboxylic cationites (Purolite International Ltd, England), based on acrylic polymerization matrix, with different cross-linking degrees (%DVB) were used:

- macroporous resins in acid form (H^+): Purolite C 104, C106 and C107E
- gel type resins in acid form (H^+): Purolite C 105 and C106EP

The treatment of the samples and the procedure of the exchange capacity determination were described previously [20, 21].

Thermal analysis

The thermogravimetric experiments were performed on a Perkin-Elmer TGA 7 Thermal Analysis System between 35–250°C and 35–600°C using platinum crucibles. The measurements of granulated or ground samples (dried at the ambient temperature), were carried out both in air and nitrogen flow (50 mL min^{-1}) at three different heating rates (β=2.5, 5 or 10 K min^{-1}). The sample mass was ~2 mg. In order to characterize the non-isothermal decomposition steps of the investigated ion-exchange resins, FTIR and MS spectroscopy were used in addition to thermal analysis.

FTIR spectra

FTIR spectra (in 4000–450 cm^{-1} range) of thermal decomposed samples, up to the characteristics mass-loss steps temperatures, were recorded in KBr pellets (2 mg cationite/200 mg KBr) using a FTIR PerkinElmer 1750 spectrophotometer.

MS spectra

MS spectra of the oxidation volatile products of the investigated cationites were recorded. For this purpose, the Temperature Programmed Oxidation (TPO) in an O_2(5%)/He (25 mL min^{-1}) mixture was performed using a conventional flow reactor coupled with a quadrupole mass spectrometer (VG Sensorlab with PostSoft analysis software) as detector. The sample mass was 0.2 mg and the heating rate was 10 K min^{-1}.

Results and discussion

Identification of thermal decomposition steps

The main physical and chemical characteristics of the investigated carboxylic cationites are reported in Table 1, together with some producer data. From these data it can be noticed that the cross-linking degree values are in the range of 7 and 12% DVB [22] and the exchange capacity values are between 9.12 and 9.7 mEq g^{-1}.

As an example of the preliminary thermogravimetric results, Fig. 1 shows the TG/DTG curves recorded in air atmosphere between 35–600°C, for macroporous cationite Purolite C106 (H^+) with 35–50 mesh granulation (curves a and a’) and for gel type cationite Purolite C105 (H^+) with 50–60 mesh granulation (curves b and b’).

Table 1 The main characteristics of the investigated carboxylic cationites

No	Cationite	Cross – linking degree/ %DVB	Exchange capacity/ mEq g^{-1*}	Granulation/ mesh	Porosity [22]
1	Purolite C 104	10	9.42	35–50 50–60	Macroporous
2	Purolite C 105	7.2	9.38	35–50 50–60	Gel
3	Purolite C 106	12	9.31	35–50	Macroporous
4	Purolite C106 EP	12	9.12	20–30 35–50	Gel
5	Purolite C 107 E	9	9.69	35–50 60–70	Macroporous

*Experimentally measured values

The curves showed in Fig. 1 are characteristic for the granulated cationites, for which the existence of many decomposition steps associated with mass losses can be observed (see also the enlargement).

The first, small and broad, thermogravimetric step (Δm_1) was recorded between ~35°C and ~220°C. The DTG peak temperatures were T_{infl1}=150 °C for Purolite C106(H^+) macroporous cationite (curve a') and T_{infl1}=155°C for Purolite C105(H^+) gel type cationite (curve b'). The second decomposition step (Δm_2) was recorded between ~220 and ~330°C with maximum DTG peak temperatures at T_{infl2} = 295°C for Purolite C106(H^+) (curve a') and at T_{infl2}=295°C for Purolite C105(H^+) (curve b').

At higher temperatures, a third mass loss step for both types of cationite is characterized by a very sharp change of the TG curve slopes. Intense peaks on the DTG curves were recorded at about 420°C for Purolite C106(H^+) (curve a') and at about 437°C for Purolite C105(H^+) (curve b'), respectively. The TG/DTG profiles recorded for several samples, above this temperature, did not quantitatively describe the subsequent decomposition processes. Similar plots were reported by Chun *et al.* [23] for the oxidative decomposition of the polystyrene-divinylbenzene sulfonic cationites, but no interpretation has been given. We wish specifically to report, that by visual inspection, the loss of some cationite granules out from the crucible was always observed above the temperature range characteristic for this intense peak. This phenomenon (referred here as 'popcorn' effect) induced an abruptly mass diminution, which hides the underlying decomposition phenomenon and jeopardizes the following behavior. Similar behavior was shown by all other investigated cationites independently from the heating rates and the granulation.

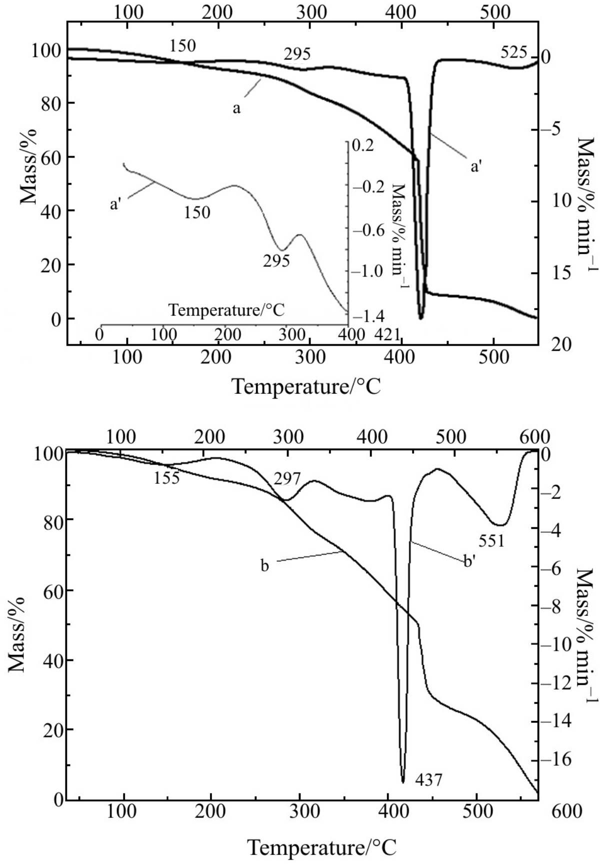


Fig. 1 The TG/DTG curves recorded in air atmosphere for Purolite C106(H^+) cationites with 35-50 mesh granulation; β=5 K min^{-1}; m=2.215 mg (curves a and a') and for Purolite C105(H^+) cationite with 50-60 mesh granulation; β =10 K min^{-1}; m=2.301 mg (curves b and b')

The sudden elimination of large volumes of gas at temperatures above 350°C may be the simplest explanation for the loss of the granules out from the crucible. The large amount of gas produced during decomposition was accumulated in the internal pores without having the possibility to diffuse outward rapidly, generating an over-pressure, which determined the 'popcorn' effect at a critical stage.

In order to decrease the intensity of this explosive phenomenon, cationites were ground to get fine-powdered samples. The TG/DTG curves recorded for the ground cationite Purolite C106 (H^+) dried at the ambient temperature are shown in the Fig. 2.

Some major modifications can be seen in the TG/DTG curves profiles of the sample (Fig. 2), the most important being a clear decomposition profile and well-resolved steps without abrupt discontinuities. From the analysis of the TG/DTG curves it can be noticed that the first decomposition step (Δm_1) is displaced to low temperatures giving an initial smooth decrease which, according to Brown *et al.* [24], is characteristic of a fast drying process. The second decomposition step (Δm_2) was recorded at lower temperatures (176–305°C, T_{infl2}=275°C) than in the granulated

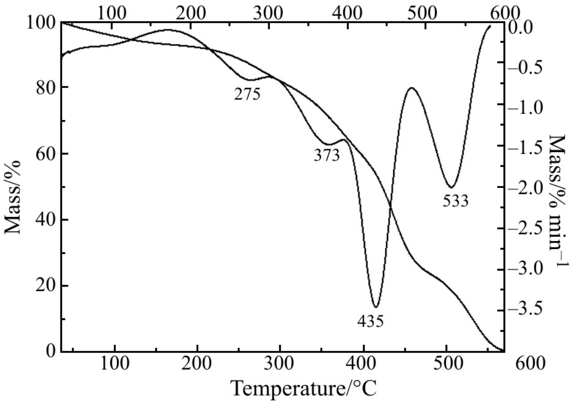


Fig. 2 The TG/DTG curves recorded in air atmosphere for the grinded cationite Purolite C106 (H^+), β=5 K min^{-1}; m=2.413 mg

cationite case. This phenomenon is probably due to the fact that the contact surface of the ground sample increases both with the crucible and with the decomposition atmosphere. In this way both heat exchange and gaseous compounds elimination are favored. In the temperature range where, for the granulated cationite the sharp change of the TG curve slope was recorded, the ground cationite exhibits two well defined mass loss steps, one (Δm_3) between 305–396°C, $T_{\text{infl}3}$=373°C and the other (Δm_4) between 396–484°C, $T_{\text{infl}4}$=435°C. The last mass loss step (Δm_5) was recorded between 484–589°C, $T_{\text{infl}5}$=533°C, the cationite being totally decomposed without residue, above this temperature.

In conclusion, the non-isothermal heating, in the air atmosphere, of Purolite C106 (H^+) cationite, dried at the ambient temperature and finely ground, shows five well-defined mass-loss steps. All the carboxylic (H^+) resins showed a similar behavior, provided that samples were finely ground. A summary of the temperature values characteristic for the decomposition steps of the different samples (granulated or ground) is reported in Table 2.

The data of Table 2 can be analyzed by comparing the characteristic temperature values of the cationite samples, for the different decomposition steps, and their dependence on the experimental conditions as well as on the samples properties.

As far as the scan rate is concerned, for all resins both in granulated and ground form, the increase of heating rate corresponds to an increase in temperatures for all five mass-loss steps. This effect is quantitatively reported by the data of Table 2 (lines 1 and 2; lines 5 and 6; lines 12, 13 and data of Fig. 3; lines 16 and 17) and by comparing the results of Fig. 2 with line 9 (Table 2).

The increase in the granulation, on the other hand, both for the macroporous cationites and for the gel type cationites, is shown by an increase in the temperature values of the first step ($T_{\text{infl}1}$) (see Table 2 lines 2 and 3; lines 6 and Fig. 1 curves b, b'; lines 10 and 11; lines 14 and 15).

For the macroporous cationites, an increase of the cross-linking degree from 9%DVB to 12%DVB, leads to higher temperature values, for all recorded decomposition steps (see Table 2 lines 1, 14 and Fig. 1 curves a, a'; lines 4 and 17; lines 16 and Fig. 2). A similar behavior was found for the gel type resins as a function of the cross-linking degree (see Table 2 lines 5 and 11; lines 7 and 12).

For the same cross-linking degree and the same granulation, the temperature for the first mass-loss step of the gel type cationite Purolite C106EP is higher than that for the macroporous cationite Purolite C106 (Fig. 1, curves a and a', and Table 2, line 11). In the case of the ground resins the porosity (macroporous or gel) did not influence significantly the temperatures of the decomposition steps (see Table 2 lines 9 and 12).

The effect of the decomposition atmosphere (air or nitrogen) on thermal degradation processes and implicitly on TG/DTG curves shape is shown in Fig. 3 for the ground Purolite C106EP (H^+) cationite, at β=10 K min^{-1}.

From Fig. 3 one can notice a decrease of the decomposition steps number in the 160–600°C range when nitrogen flow was used (b and b' curves): ($\Delta m_{2\ \text{nitrogen}}$) between 166–321°C, $T_{\text{infl}2\ \text{nitrogen}}$=282° and ($\Delta m_{3\ \text{nitrogen}}$) between 321–522°C, $T_{\text{infl}3\ \text{nitrogen}}$=447°C. In the case of the air atmosphere (a and a' curves) the mass losses steps were recorded: ($\Delta m_{2\text{air}}$) between 170–307°C, $T_{\text{infl}2\ \text{air}}$=280°C; ($\Delta m_{3\text{air}}$) between 307–424°C $T_{\text{infl}3\ \text{air}}$=350°C; ($\Delta m_{4\text{air}}$) between 424–488°C, $\mathrm{T}_{\text{infl}4\ \text{air}}$=450°C and ($\Delta m_{5\text{air}}$) between 488–597°C, $T_{\text{infl}5\ \text{air}}$=554°C. As a further difference, in air atmosphere the complete decomposition of the carboxylic cationite was reached at about 600°C, while in nitrogen atmosphere a residue mass of about 20% was observed at this temperature. The effect of nitrogen atmosphere, in reducing the number of decomposition steps and leaving a carbonaceous residue, is already known and has been specifically reported by Dubois *et al.* [25] in the study of the pyrolysis and thermal degradation of the polystyrene-divinylbenzene sulfonic resins in various media.

The change in the shape of TG/DTG curves from Fig. 3 suggests a change of the cationite decomposition mechanism at temperature higher than 300°C in nitrogen atmosphere in comparison with air atmosphere, when the oxygen (~21% volume) interacts with the macromolecular matrix and perhaps with the degradation products.

The decomposition steps characterization

The curves and the data reported in Table 2 clearly show a pattern of similarities and a common effect on the shape and position of degradation steps due to the physical form of the resins (granulated or finely ground). Characterization of the decomposition steps is necessary in order to validate the common assertion that the stability of polyacrylic and polymethacrylic acids toward thermal degradation is up to 170–200°C [19, 26, 27].

While water release, from interstitial (osmotic) state and from hydration sites of carboxylic groups, can be considered reversible to a first instance, it is not clear at all when and how the polymer degradation becomes effective in the ground resins. It has been reported that after dehydration, subsequent heating de-

Table 2 The temperature values characteristic for the decomposition steps of the Purolite (H^+) cationites dried in air atmosphere

Nr.	Cationite	Mass/ mg	β/ K min^{-1}	Granulation/mesh	Step I		Step II		Step III		Step IV		Step V	
					ΔT	$T_{\text{infl 1}}$	ΔT	$T_{\text{infl 2}}$	ΔT	$T_{\text{infl 3}}$	ΔT	$T_{\text{infl 4}}$	ΔT	$T_{\text{infl 5}}$
0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Purolite C104	2.113	5	35–50	35–200	145	–	–	–	–	–	–	–	–
2		2.072	10	35–50	35–220	160	–	–	–	–	–	–	–	–
3		2.122	10	50–60	35–210	145	–	–	–	–	–	–	–	–
4		2.273	10	grinded	–	–	140–280	238	280–353	335	353–459	377	459–590	543
5	Purolite C105	2.403	5	35–50	35–216	142	–	–	–	–	–	–	–	–
6		2.401	10	35–50	35–239	165	–	–	–	–	–	–	–	–
7		2.450	2.5	grinded	–	–	125–240	210	240–290	287	290–409	347	409–530	485
8	Purolite C106	2.114	2.5	35–50	35–201	120	–	–	–	–	–	–	–	–
9		2.336	2.5	grinded	–	–	144–278	224	278–320	292	320–444	350	444–566	500
10	Purolite C106 EP	2.003	5	20–30	35–206	166	–	–	–	–	–	–	–	–
11		2.321	5	35–50	35–222	160	–	–	–	–	–	–	–	–
12		2.432	2.5	grinded	–	–	142–279	225	279–328	298	328–444	354	444–566	503
13		2.323	5	grinded	–	–	172–320	270	320–392	370	392–482	430	482–588	530
14	Purolite C107E	2.361	5	35–50	35–167	132	–	–	–	–	–	–	–	–
15		2.401	5	60–70	35–133	120	–	–	–	–	–	–	–	–
16		2.535	5	grinded	–	–	133–263	217	263–315	280	315–366	337	366–570	480
17		2.508	10	grinded	–	–	142–270	232	270–342	293	342–422	360	422–590	510

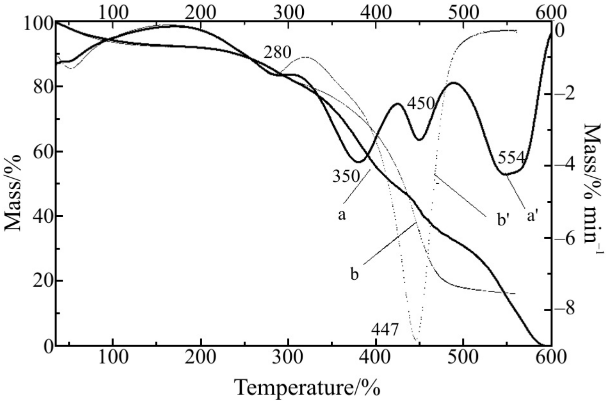


Fig. 3 The TG/DTG curves for the grinded Purolite C106 EP(H^+) cationite a and a' – curves recorded in air atmosphere; m=2.553 mg; β=10 K min^{-1}, b and b' – curves recorded in nitrogen atmosphere; m=2.612 mg; β=10 K min^{-1}

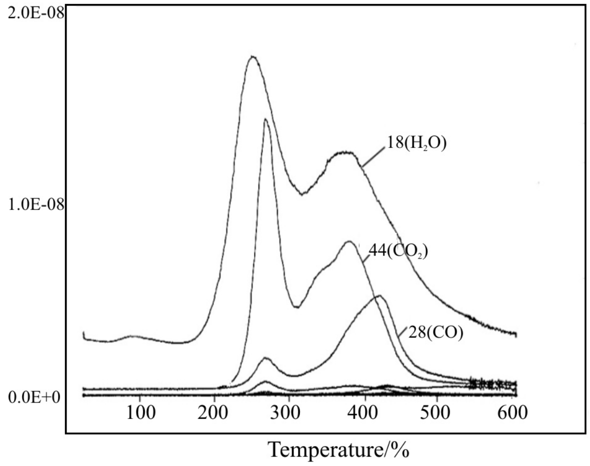


Fig. 4 The MS spectra for the (TPO) products of the Purolite C106EP (H^+) cationite in the O_2/He atmosphere, β= 10 K min^{-1}

termines a condensation reaction between carboxylic ionogenic groups forming a polyanhydride, through intra- and intermolecular water elimination. Thereafter, at still higher temperatures (~300°C) the resulted polyanhydrides can undergo decarboxylation and depolymerization. According to the studies for thermal behaviour of the sulfonic or carboxylic cationites [10, 28], the decomposition steps are: dehydration, destruction of the functional groups by SO_2 or CO_2 elimination and oxidative degradation of the polymeric matrix.

To elucidate the major steps in the production of the volatile compounds, MS spectra of the (TPO) products of cationites have been recorded by using a conventional flow reactor coupled with a quadrupole spectrometer. Figure 4 shows the MS spectra of the (TPO) products of the Purolite C106EP (H^+) cationite in the O_2/He atmosphere.

Concerning water compound, Fig. 4 shows the presence of a peak around 100°C temperature followed by another peak in the 200–350°C range. In this temperature range the spectra show a sequence of overlapping evolution processes of H_2O, CO_2 and CO species. In particular, the evolution of the two peaks of CO_2 and CO (centered at ~280°C) is slightly delayed respect to the peak of water evolution (centered at ~250°C). These results suggest a decarboxylation process of a previously dehydrated structure.

In the 350–550°C range the water peak overlap the peak of CO_2 (around ~400°C), therefore suggesting a possible oxidative degradation process. In this temperature region the peak of CO is recorded on the tail of water and CO_2 peaks.

Although the experimental set-up of the TG and MS experiments is somewhat different, the comparison of the curves for Purolite C106EP (H^+) shows a substantial agreement. However, a few comments seem necessary to underline similarities and differences between the results obtained by TG and by (TPO) procedure. In particular, a temperature shift is expected because oxidation is faster in the (TPO) experiment due to the flow-through setup. The (TPO) results confirm that in 200–350°C range, the decarboxylation (CO_2) occurs as a consequence of dehydration (see in Fig. 4 the peaks at 280°C and at 250°C, respectively). In this region the CO peak is directly associated to the formation of CO_2. In the 350–550°C range the formation of CO is clearly distinct from the presence of CO_2 and is therefore formed in a different mechanism.

Additional information on the structural changes during degradation has been gained by FTIR. Figures 5 and 6 show the FTIR spectra of the degraded Purolite C106EP (H^+) up to 150°C and up to 280°C, respectively, in air atmosphere at β=10 K min^{-1}.

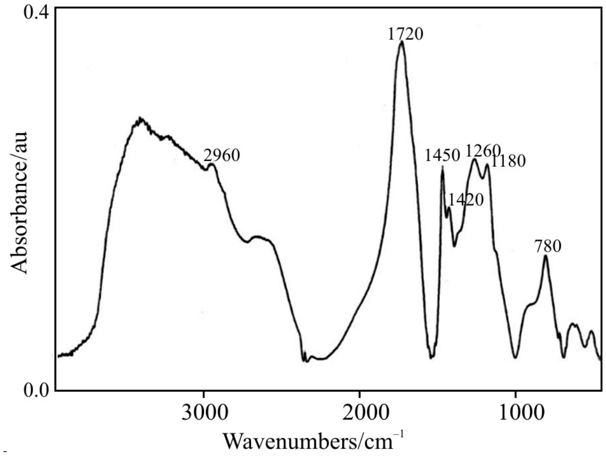


Fig. 5 The FTIR spectra of the degraded cationite Purolite C106 EP (H^+) up to 150°C in air atmosphere at β=10 K min^{-1}

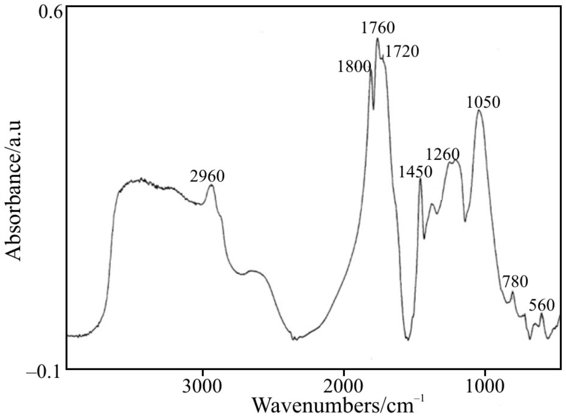


Fig. 6 The FTIR spectra of the degraded cationite Purolite C106 EP (H^+) up to 280°C in air atmosphere at β=10 K min^{-1}

On the basis of the above results, the analysis of decomposition curves has produced the following interpretation.

Concerning the first mass loss decomposition step (Δm_1) recorded at 35–230°C for the granulated samples (Table 2 columns 5, 6), Figs 5 and 6 show modification in the FTIR spectra intensity in the region 3400–3600 cm^{-1}; this region is specific for the bounded water molecules through hydrogen bond. On the other hand in the temperature range characteristic for the (Δm_1) decomposition step, the MS spectra (Fig. 4) show a peak around 100°C for the compound with molecular mass 18. Based on these results, in agreement with the literature data, the first decomposition step corresponds to a thermal dehydration process through elimination of the adsorbed or hydrogen bonded water.

Figure 7 shows the TG/DTG curves recorded in air atmosphere between 35°C and 250°C at β= 2.5 K min^{-1} for the Purolite C104, C105 and C106EP (H^+) cationites with granulation 35–50 mesh.

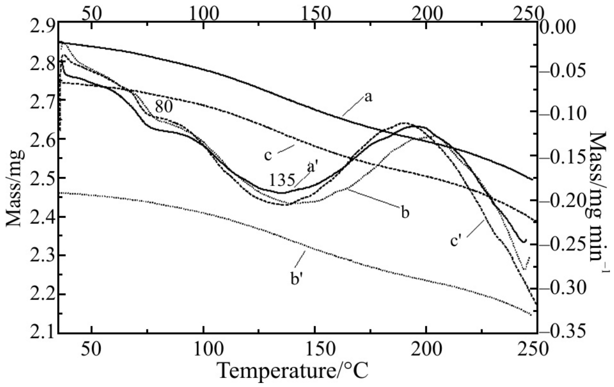


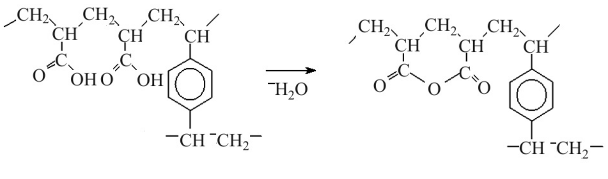
Fig. 7 The TG/DTG curves recorded in air atmosphere for the cationites: Purolite C104(H^+) (curves a and a’), Purolite C106EP(H^+) (curves b and b’) and Purolite C105(H^+) (curves c and c’) with the granulation 35–50 mesh; β=2.5 K min^{-1}

Two DTG peaks were recorded in the temperature range characteristic to the first thermal dehydration process (Fig. 7). The first peak located around 80°C is probably due to the elimination of the osmotic water existing in the pores of the granules. The second one, located between 135–145°C, is due to the elimination of the hydrogen-bounded water with the cationite carboxylic groups (–COOH). A similar behaviour was recorded for all investigated cationites even at higher heating rates.

Concerning the second mass-loss decomposition step (Δm_2), located between ~120–350°C (Table 2 columns 7, 8), from the FTIR spectra (Figs 5 and 6) it can be observed a considerable intensity decrease of the aliphatic carboxylic acids bands located at 1180 and 1760 cm^{-1} (assigned to the stretching vibrations of –C–O– and C=O groups) and the appearance of a new specific anhydride bands. These bands are in the 1800–1760 cm^{-1} range and are caused by the carbonyl band halving (due to vibrational conjugation of the two carbonyl groups) and the 1060 cm^{-1} band, assigned as the anti-symmetric stretching of C–O–C group. Pretsch *et al.* [29] have reported that the carbonyl stretching vibration of the cyclic anhydrides with 6-atoms ring are near 1800 and 1760 cm^{-1} and for those with 5-atoms ring are near 1850 and 1775 cm^{-1}. Matsuzaki *et al.* [30] investigating the effect of tacticity on the intramolecular water elimination of the polyacrylic acids, have reported that the isotactic samples dehydration is faster than the syndiotactic samples.

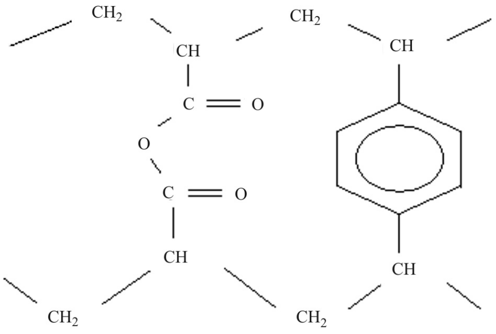
The results of the FT-IR spectra, completed with the identification of the intense peak of water in the MS spectra of the (TPO) products (Fig. 4, the peak centered at ~250°C) suggests that the second decomposition step might be assigned to the water elimination between two neighboring carboxylic (–COOH) groups. This intermolecular dehydration is likely to form some polyacrylic cyclic anhydrides with a 6-atom ring, such as glutaric anhydride type (Scheme 2).

The intermolecular dehydration probability with the isobutyric anhydride formation (Scheme 3) seems to be unlikely because of the steric limitation caused especially by cross-linker [27, 31].



Scheme 2

Elimination of superficially bound water is a phenomenon well studied in polysaccharides and



Scheme 3

other natural hydrophilic polymers [32–35]. Many of these systems can be easily degraded in the amorphous phase once hydrogen bonded water is removed. However, the different behavior of natural polymers *vs.* synthetic polymers can be in the separation between the first and the second steps.

The third mass-loss step (Δm_3) located between ~210°C and ~390°C (Table 2 columns 9, 10) can be assigned, on the basis of the MS spectra results, to polyanhydrides decomposition processes through decarboxylation with the elimination of CO_2 and CO (Fig. 4, the two peaks of the CO_2 and CO centered at ~280°C). In the next decomposition step (Δm_4) located between ~320°C and ~480°C (Table 2 columns 11, 12) the structures formed by decarboxylation, like cyclic polyketones [1, 11], can give the CO elimination and depolymerization processes without the formation of volatile depolymerization fragments. The CO elimination is confirmed by the presence of its peak in the MS spectra in the 350–550°C temperature range.

The last decomposition step (Δm_5) located between ~400°C and ~590°C (Table 2 columns 13, 14) corresponds to the oxidative degradation of the polymeric matrix and of the depolymerization fragments by the oxygen action with CO_2 and H_2O formation. The MS spectra of these gaseous products have shown the intense picks in the temperature range characteristic for this mass-loss step (Fig. 4, the peaks of the H_2O and CO_2 located around ~400°C).

Conclusions

The investigation of the non-isothermal behavior up to 600°C of the carboxylic cationites with polyacrylic-divinylbenzene (DVB) matrix shows that oxidative degradation of this resin takes place in several mass-loss steps. Although shape and temperature values characteristic for the decomposition steps depend on the experimental conditions as well as on the samples properties, all these steps have been reasonably attributed on the basis of the combined results here presented. The first decomposition step (Δm_1) is due to the elimination of osmotic water, existing in the pores of the granules and of the hydrogen-bounded water with the carboxylic groups (–COOH). The second decomposition step (Δm_2) is due to an anhydrification process by the dehydration of two neighboring (–COOH) groups which induces a cyclic polyanhydrides formation. The third and fourth mass-loss steps (Δm_3) and (Δm_4) correspond to a decarboxylation process of the polyanhydrides and to some depolymerization reactions of the polymeric matrix. The last decomposition step (Δm_5) may be associated with total degradation of the polymeric matrix and of the depolymerization fragments.

From the combination of TGA/MS/IR techniques it emerges that, after the elimination of osmotic water, the further dehydration is the preliminary reaction for a more severe degradation. The position and the extent of this degradation do not largely depend on the type and form of matrix but mainly, and obviously, on the scan rate. As ancillary practical result, the warning is made once more about the factors that influence the decomposition temperatures. As a consequence, the first decomposition step temperature should always be checked in the use of the carboxylic cationites as catalysts, especially when prolonged exposure time is needed. Whether some salt form of these cationites could be more stable seems possible and is worth of further investigation.

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