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Thermal Degradation Studies of Polystyrene Sulfonic and Polyacrylic Carboxylic Cationites[1]

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Abstract—The thermal degradation of polyacrylic carboxylic and polystyrene sulfonic cationites was investigated using thermal analysis (TG) combined with Scanning Electron Microscopy (SEM). Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the resins degradation steps. The carboxylic cationite undergoes degradation through dehydration forming polyanhydrides, decomposition of polyanhydrides through decarboxylation with elimination of CO_2 and CO. The sulfonic cationite undergoes degradation through dehydration, followed by decomposition of sulfonic acid functional groups liberating SO_2. It was observed that strong acid ($–SO_3H^+$) cationite shows small mass loss of 55%, as against 88% mass loss shown by low-acidity carboxylic cationite. The possible reason for small mass loss of sulfonic cationite is discussed.

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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 industry for treatment of liquid waste, pharmaceutical, food industry, etc. [1–15]. Owing to their versatile properties, the cation-exchange resins are used both in the ion-exchange area and in the heterogeneous catalysis [16–18]. These resins exhibit a high exchange capacity and an excellent osmotic shock resistance. So, the cation-exchange resins, produced with a high degree of purity, became important as catalysts in various food technologies [19] and for purification in heavy-water moderated nuclear reactors in nuclear industries [20–22]. In many cases their use is limited by the relatively low thermal stability [23]. Hence, the knowledge of the thermal behavior of cation-exchange resins is necessary. Abundant data exist on the thermal degradation of polyacrylic acid and of its mixtures with other polymeric and non-polymeric species [24–29]. While in the case of carboxylic cationites with low acidity [30, 31], and polystyrene-divinylbenzene sulfonic cationites [32–37], the literature seems to offer relatively poor information. Therefore, in the present investigation the thermal degradation of polystyrene sulfonic and polyacrylic carboxylic cationites was performed to understand the degradation steps and to compare the relative thermal stability.

EXPERIMENTAL

Materials. The following commercial cationites were used:

– gel-type resins in weak acid form (–COOH) based on acrylic polymerization matrix : Indion-236 (Ion Exchange India Ltd., Mumbai).

– nuclear grade resin in strong acid form ($–SO_3H^+$) based on styrene polymerization matrix: Tulsion T-46 (Thermax Ltd., Pune,India).

[1] The text was submitted by the authors in English.

The main characteristics of the investigated cationites

Cationites	Exchange capacity, meq ml^{-1}	Particle size, mm	Moisture content, %	Maximum temperature stability, °C
Indion-236	4.0	0.3–1.2	50	100
Tulsion T-46	1.8	0.3–1.2	52	120

The details regarding physicochemical properties of cationites used are presented in the table.

The soluble impurities of the resins were removed by repeated Soxhlet extraction using water and occasionally with distilled methanol to remove non-polymerized impurities. The resins were then dried over P_2O_5 in desiccators at room temperature.

Thermal analysis. The thermogravimetric experiments were performed on a DTG-60H, (Shimadzu, Japan) thermal analysis system between 30–550°C using aluminum cell (6 mm in diameter and 2.5 mm in depth). The measurements of resin samples were carried out in nitrogen flow (50 ml min^{-1}) at heating rate (β = 10 K min^{-1}). The mass of resin sample used was ~5–20 mg. In order to characterize the decomposition steps of the investigated ion-exchange resins, FTIR and Scanning Electron Microscopy (SEM) were used in addition to thermal analysis.

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

Since in the thermal analysis the major weight loss was observed between 200–400°C, the resin samples were heated in a vacuum oven for 3h at 200, 400, and also at 10°C higher than temperatures of the maximum operating temperature. The thermal degradation of resin was studied by comparing the spectra of fresh and heated resin samples.

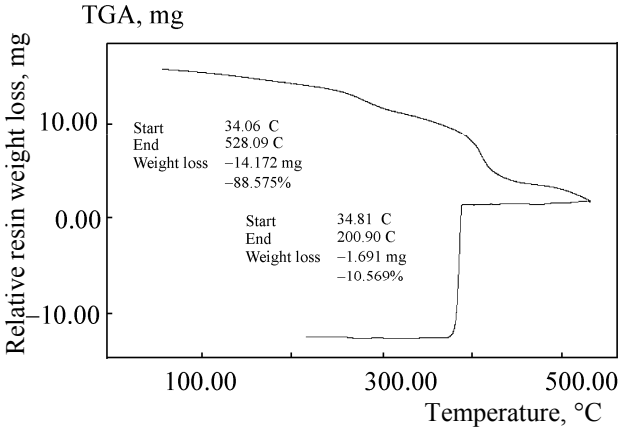

Fig. 1. TG curve of Indion-236.

Scanning Electron Microscopy (SEM). The thermal degradation samples of ion exchange resins was also studied by examining the surface morphology of fresh and of resin samples heated at 400°C using JSM-6380LA Scanning Electron Microscope (Jeol Ltd., Japan). The powders were precisely fixed on an aluminum sublayer using double-sided graphite tape and then were made electrically conductive by coating in a vacuum with a thin layer of carbon, for 30 seconds and at 30 W. The pictures were taken at an excitation voltage of 10 kV and a magnification of ×100 and ×130.

Characterization and Thermal Degradation Study of Indion 236

TGA analysis. Figure 1 represents a dynamic weight loss profile of an Indion 236 from room temperature to 550° C under nitrogen atmosphere. The TGA results shows that 88% of weight loss takes place up to 530°C. The initial 10% mass loss was observed up to 200°C, which is due to the elimination of the osmotic water existing in the pores of the resin matrix and also due to the decomposition of two neighboring (–COOH) groups resulting in the formation of cyclic polyanhydrides [31]. The second mass-loss step between ~210 and ~390°C can be assigned to polyanhydrides decomposition processes through decarboxylation with the elimination of CO_2 and CO. The last decomposition step between ~400 and ~530°C corresponds to the total degradation of the polymeric matrix and of the depolymerization fragments.

FTIR analysis. Figure 2 shows the IR spectrum of the fresh resin sample Indion 236. The assignments of various bands and peaks made in this study are in reasonable agreement with those reported in the literature for similar functional groups [38–42]**.** The bands at 2923 and 2876 cm^{-1} are, respectively, due to the C–H stretching vibrations of methyl group and of

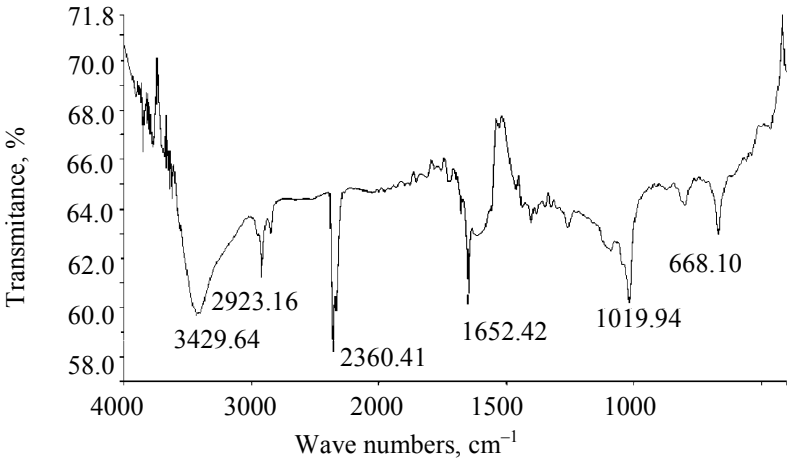

Fig. 2. IR spectrum of Indion-236 at room temperature.

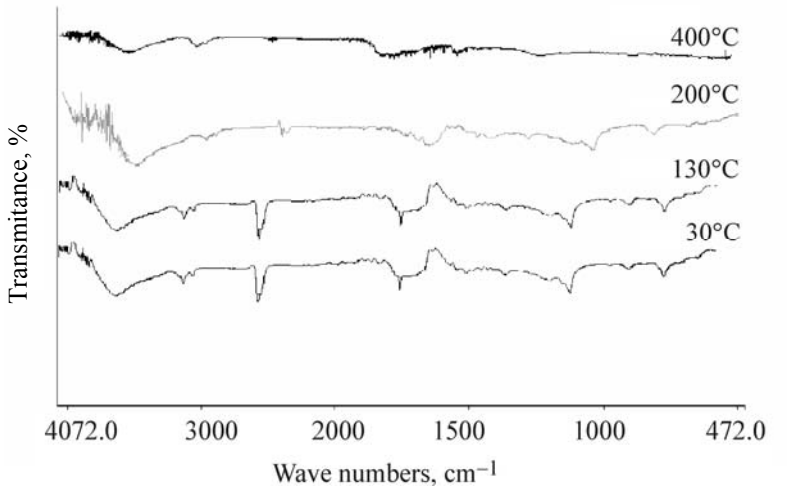

Fig. 3. IR spectra of Indion-236 at different temperatures.

methylene group. Strong band at 1652 cm^{-1} indicates carbonyl stretching vibration. The medium broad bands at 1243 cm^{-1} and 1176 cm^{-1} are due to CH_2 deformation. A band is displayed at 1019 cm^{-1} which may be attributed to –C–O– stretching vibrations. As the heating proceeds, the degradation of polyacrylate is initiated, as shown by the increase of the band at 1733 $cm^{-1}$of C=O stretching vibration. Bands appear at 2919 cm^{-1}, 2852 cm^{-1} which may be assigned to O–H stretching vibration originating from the polymer. As concerns the first mass loss decomposition step recorded at 35–200°C for the thermally degraded resin samples, Figs. 2 and 3 show alteration in the FTIR spectra intensity in the region 3400–3600 cm^{-1}; this region is specific for the water molecules bound through hydrogen bonds. Concerning the second mass-loss decomposition step located between ~210–390°C from the FTIR spectra (Fig. 2 and 3) a considerable decrease in intensity of the aliphatic carboxylic acids bands at 1180 and 1652 cm^{-1} (assigned to the stretching vibrations of –C–O– and C=O groups) was observed. At 400°C the above carbonyl peaks are hardly noticeable. On the basis of FTIR analysis we can say that 10% weight loss is due to nothing but moisture and 78% weight loss can be attributed to breaking of C–H bond with the liberation of CO [31].

SEM analysis. Indion-236 was heated in a silica crucible in electric heater. After cooling in a dessicator the resin was viewed in SEM and the surfaces were examined by a Jeol JSM-6380LA scanning electron microscope (Figs. 4, 5). The morphology of Indion-236 resin polymer exhibits dent on the surface at 400°C.

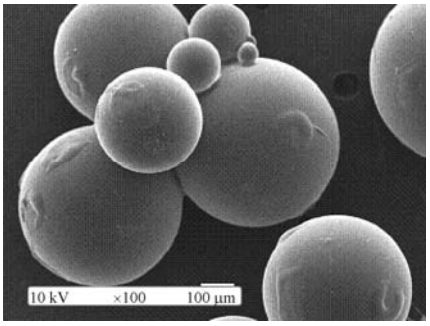

Fig. 4. Scanning electron micrograph of the surface of the Indion-236 at room temperature.

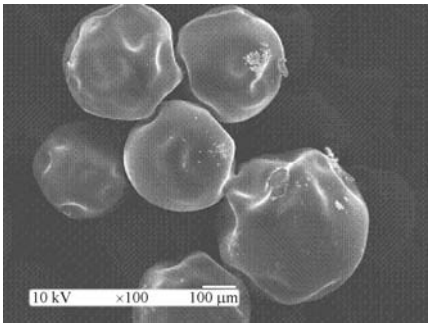

Fig. 5. Scanning electron micrograph of the surface of the Indion-236 at 400°C.

Characterization and Thermal Degradation Study of Tulsion T-46

TGA analysis. Tulsion T-46 shows minor weight loss due to moisture content up to 200° C. The major mass loss starts at 280°C and shows 55% loss up to 530°C (Fig. 6). In the temperature range of 280–400°C the weight loss and volatilization of degradation products take place rapidly. According to the studies of thermal behavior of the sulfonic cationites [30, 40], the decomposition steps are as follows: dehydration, destruction of the functional groups by SO_2 elimination, and oxidative degradation of the polymeric matrix. To elucidate the major steps in the production of the volatile compounds, FTIR spectra of the cationite have been recorded at higher temperatures up to 400°C.

FTIR analysis. FTIR spectral analysis of Tulsion T-46 in the 3700–400 cm^{-1} region shows sharp symmetric stretching vibrations band at 1007–1172 cm^{-1} corresponding to the functional sulfonic acid group ($–SO_3H$), O–H stretching vibrations at 2900–2400 cm^{-1}, S–O stretching vibrations at 671 cm^{-1}, C=C aromatic nucleus skeletal vibrations band at 1500–1600 cm^{-1}, and O–H hydrogen bonded broad stretching vibrations band at 3200–3500 cm^{-1}. The peak at 2920 cm^{-1} attributed to C–H stretching skeletal vibrations in polystyrene DVB matrix (Fig. 7). The strong bands between 1000 cm^{-1} and 1200 cm^{-1}, due to symmetric and asymmetric stretching vibrations of sulphonic groups were observed up to 200°C in the IR spectrum (Fig. 8). Concerning the minor weight loss due to moisture content up to 200°C for the thermally degraded resin samples, Figs. 7 and 8 show changes in the FTIR spectra intensity in the region 3400–3600 cm^{-1}; this region is specific for the water molecules bound through hydrogen bond. However, at higher temperatures above 200°C most of the functional sulfonic acid groups get decomposed liberating SO_2. This is evident from the fact that peaks corresponding to functional $–SO_3H$ group are vanished from the IR spectra at higher temperature (Fig. 8).

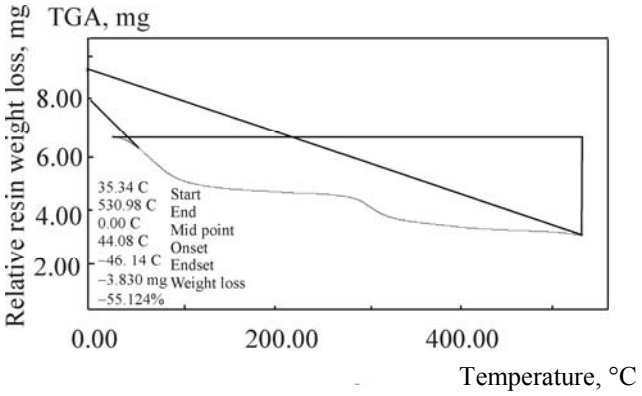

Fig. 6. TG curve of Tulsion T-46.

SEM analysis. From Fig. 9 it can be seen that Tulsion T-46 resin particles are of different sizes. SEM photographs of resin at 400°C show complete cracking of the spherical structure and because of difference in size, smaller resin species got inserted into the larger broken speres (Fig. 10).

CONCLUSIONS

In the present experiment, major weight loss of 78% for low-acidity carboxylic cationite was observed in the temperature range of 200 to 530°C due to polyanhydrides decomposition processes through decarboxylation, finally due to total degradation of the polymeric matrix and of the depolymerization fragments. The thermal degradation study of strong acid ($–SO_3H^+$) cationite shows small mass loss of 55%,

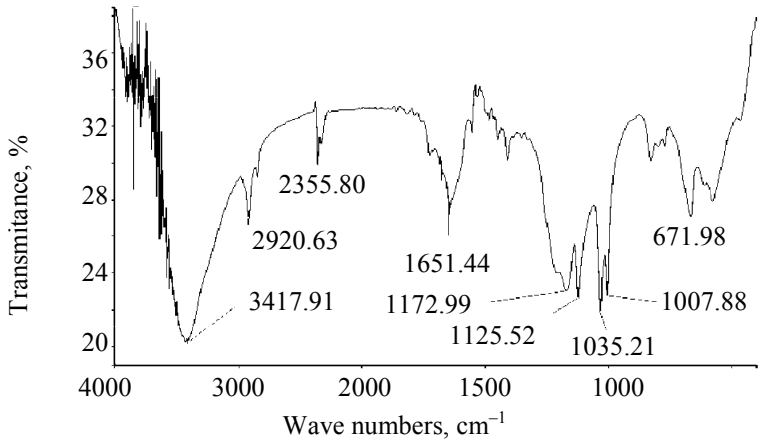

Fig. 7. IR spectrum of Tulsion T-46 at room temperature.

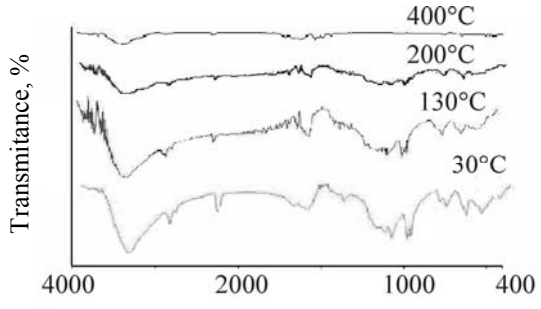

Fig. 8. IR spectra of Tulsion T-46 at different temperatures.

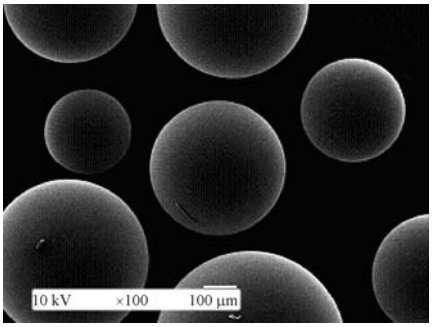

Fig. 9. Scanning electron micrograph of the surface of the Tulsion T-46 at room temperature.

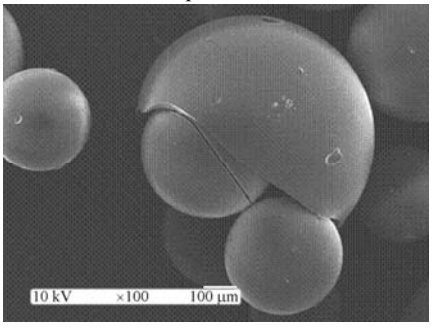

Fig. 10. Scanning electron micrograph of the surface of the Tulsion T-46 at 400°C.

as against 88% mass loss shown by low-acidity carboxylic cationite up to 530°C. The small weight loss of strong acid cationite was attributed to the formation of sulfonyl and sulfur bridges between base polymers after dehydration reaction. These bridges made the base polymer thermally stable [35]. On the other hand, low-acidity carboxylic cationite was easily decomposed because it contained no sulfonic acid group.

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