

THERMOGRAVIMETRIC STUDY OF CARBONIZATION PROCESSES FOR INDUSTRIAL POROUS CO-POLYMERS OF SPHERICAL GRANULES

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Abstract

The industrial porous co-polymers and resins in the form of spherical granules include three main matrices which serve as the basis of the large-scale production of ion-exchange materials: styrene/divinylbenzene, vinylpyridine/divinylbenzene and acrylonitrile/divinylbenzene. Complex thermal methods (TG, DTG and DTA) were used to study the carbonization processes of various industrial products utilized as starting materials for the preparation of synthetic active carbons. The DTG results, the thermal effects observed during the programmed heating of samples, and the mass-spectrometric and IR-spectroscopic data up to 800°C provided a picture of a multi-stage carbonization process. This includes the removal of moisture from the polymer matrices, the primary cross-linking of the chains, their aromatization and condensation due to the cross-linking of polynuclear structures, and the removal of 'excess carbon' as simple molecules and free radicals of hydrocarbon type. The results promoted the choice of the optimal regimes in which to carry out the isothermal pyrolysis of various polymer matrices and preliminary chemical modifications to increase the yields on carbon and to prepare synthetic active carbons such as those of SCN, SCAN and SCS types. General schemes were proposed for the chemical reactions accompanying the carbonization process for these polymer matrices.

Keywords: DTA, DTG, IR-spectroscopy, mass spectrometry, porous co-polymers and resins in the form of spherical granules, pyrolysis, TG

Introduction

The success attained in the field of the synthesis of new carbon adsorbents with improved properties is connected not only with the selection of optimum technological regimes of carbonization and activation processes, but also with the use of new kinds of initial carbon raw materials. The intensive growth in the volume of production of synthetic materials (rubber, polyolefins, macroreticular ion-exchange materials, etc.) allows their consideration as valuable starting materials for the preparation of improved active carbons. Thus, the use of polymers with spatially linked structures yields active carbons with

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(other things being equal) a more developed porous structure and a specific surface area highly suitable for the adsorption of large organic molecules.

Among the porous co-polymers and resins in the form of spherical granules produced commercially in many countries, the leading position is occupied by three main matrices on which the large-scale production of ion-exchange materials is based: styrene (ST), vinylpyridine (VP), and acrylonitrile (AN) cross-linked by divinylbenzene (DVB) [1]. The choice of such matrices with a low degree of linkage (up to 10% of DVB) to a certain extent results in improved characteristics of the materials of these types. It has to be taken into account that the yield of the final product (carbon adsorbent) from a mass of initial polymeric raw material is only 5–20%. It is also important to choose the optimum mode of performance of the pyrolysis process, in order to obtain an appropriate ratio of the alternative routes of carbonization and decomposition, resulting in the maximum yield of the final material on carbon.

The purpose of the present research was a thermogravimetric study of the carbonization process for some typical co-polymers and resins. The data obtained, together with mass spectrometric, and IR-spectroscopic data form the basis of the description of the effects of temperature and the chemical reactions accompanying this process on the polymer.

Experimental

The following macroporous co-polymers and resins in the form of spherical granules were investigated: AN/DVB; 2-methyl-vinylpyridine/DVB (VP/DVB), methylated on the nitrogen with dimethyl sulfate; ST/DVB in the initial and the chloromethylated form (CMC), and also their sulfomethylated and sulfated variants. The content of the cross-linking agent (DVB) for all matrices was 10%. The diameter of the granules was 0.314–1.6 mm, the total volume of the pores was 0.8–1.2 cm³ g⁻¹, and the specific surface area of the pores was 10–20 m² g⁻¹.

Thermal data in the temperature range 20–800°C were obtained with a Paulik–Paulik–Erdey system derivatograph. Samples of polymers were situated under a layer of thermally treated Al₂O₃. The heating rate was 10°C min⁻¹.

The mass-spectrometric data were obtained on an MX-1310 apparatus, working on the principle of field desorption. Heating was performed in vacuum at a rate of temperature rise of 40°C min⁻¹ in the interval 150–850°C.

IR-spectra of polymers after chemical modification and thermal treatment were recorded on Specord-IR-71 and UR-20 spectrophotometers. Before spectroscopy, the samples of polymers were pressed into tablets with KBr.

Results and discussion

Competing processes of destruction and cross-linking can accompany the pyrolysis of a polymeric material. The predominance of the destruction process leads to the full disintegration of the initial material to monomers and simple compounds, and to a

carbon frame representing the carbonized product (raw carbon). The main chemical processes involved are dehydration and dehydrogenation, the removal of low molecular compounds of hydrogen with carbon and heteroatoms, oxidation, and the linkage of fragments of polymeric chains with the formation of polynuclear structures. The molecular and radical products consisting of various combinations of C, H, N and O that are formed during carbonization should clearly be identified.

Figure 1 presents TG, DTG and DTA curves of the nitrogen-containing matrices AN and VP. For AN, the DTA curve reveals an exoeffect ($\sim 350^\circ\text{C}$) and two endoeffects (410 and 545°C). The former process relates to the elimination of moisture (105°C) and the regrouping of nitrile groups (~ 200 and 260°C) in the polymer (see DTG curve). The exoeffect is not accompanied by a sharp alteration in mass of the sample (see TG and DTG curves). The endoeffects reflected by the two pronounced peaks in the DTA curve (and especially that at 410°C) correspond to sharp losses in mass from the polymer. These are most likely connected with the polycondensation of aromatic chains. Thus, carbonization of the AN matrix obviously necessitates long isothermal pyrolysis at $\sim 350^\circ\text{C}$ for more complete cyclization, aromatization of the chains and their cross-linking, to attain the maximum yield on carbon.

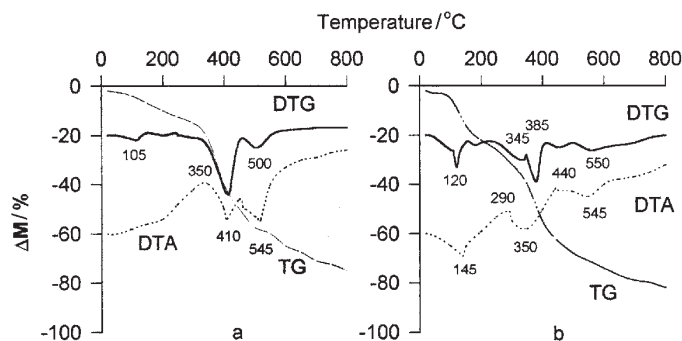


Fig. 1 TG, DTG and DTA curves of nitrogen-containing matrices; a – VP; and b – AN

The DTA curve for VP is characterized by peaks corresponding to endoeffects (145 , 350 and 545°C) and exoeffects (290 and 440°C). The endoeffect at 145°C relates to the loss of water from the pores in the polymer, and molecules of water connected with HSO_4^- . The processes of primary cross-linking, aromatization of the linear chains and consequent linking-condensation of the polynuclear structures give rise to a long exoeffect with a maximum at 290°C . These processes are not accompanied by a sharp loss in mass (see TG and DTG curves). The endoeffect at 350°C reflects processes connected with integration of the polynuclear structures. 'Redundant' carbon is removed (as hydrocarbons), and peripheral hydrocarbon radicals are also lost. The less marked exoeffect at 440°C and the endoeffect at 545°C , accompanied by an essentially smaller loss in mass, probably correspond to the burn-out of the carbon structures (due to 'internal' oxygen) and their further ordering. Isothermal pyrolysis at 290°C is most essential for VP matrix carbonization. Without it, primary

cross-linkage, aromatisation of the chains and linking-condensation takes place. The course of these processes predetermines the yield of carbonized product.

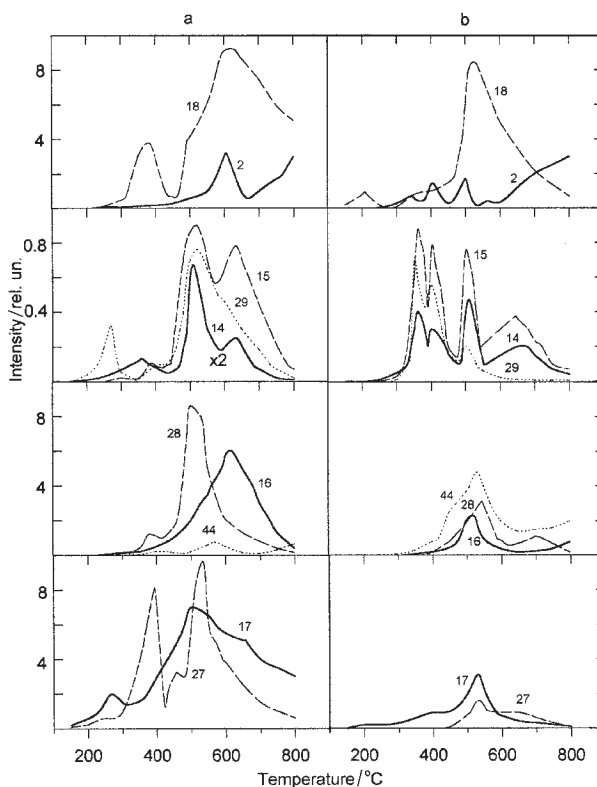


Fig. 2 Mass spectrometric data on temperature dependences of appearance of some products during co-polymer pyrolysis: a – AN matrix; b – VP matrix

Figure 2 depicts the temperature dependences of the intensity of elimination of some products, with mass numbers of from 2 to 44 a.u.m., in the pyrolyses of the polymeric matrices of AN and VP. Table 1 lists the most probable molecular and radical products corresponding to the indicated mass numbers.

The data allow the following conclusions. For a polymeric matrix based on AN, the main loss in mass takes place in the temperature interval 250–600°C, and one of the main products of pyrolysis is HCN. After 600°C, molecular hydrogen is among the main products. For a polymeric matrix based on VP, the main chemical processes take place in the temperature interval 300–550°C. Most of the mass loss involves hydrocarbon compounds (C_2H_5 , CH_4 , C_2H_4) or products of oxidation (CHO , CO , CO_2). The nitrogen loss mainly occurs as NH_3 ; HCN appears in minor amount. Hydrogen is eliminated mainly as hydrogen-containing compounds of C, N and O.

The carbonization technology of AN and VP matrices comprises the basis of the first stage of producing synthetic carbons such as SCAN and SCN [2].

The carbonization of co-polymers and resins is the most significant stage in the technology of synthetic carbon formation, as the ratio of the elements H, C and O in the initial matrices is far from optimum [3]. In the nitrogen-containing polymeric matrices, the role of oxygen is to a certain extent taken over by the availability of nitrogen atoms. In the ST/DVB co-polymer, the ratio H:C is approximately 1:1, and oxygen and other heteroatoms are absent. The ST matrix is therefore almost unsuitable as a raw material for the formation of carbon because of the very low yield of carbonized product. The weakest links in the co-polymer are the linear chains of C–C bonds. The energy of their rupture is only 346 kJ mol⁻¹, whereas for C=C bonds in an aromatic ring the energy of rupture is 617 kJ mol⁻¹, while the energies of C–H bonds in a chain or in a ring are almost equal, at 413 and 427 kJ mol⁻¹, respectively. In this connection, in the pyrolysis of ST it is necessary to expect an intensive elimination of the simplest hydrocarbons, formed by destruction of the polymeric chains. A major feature in the carbonization of a matrix is the degree of its cross-linkage. A carbonized product can be obtained from an ST matrix if it has a high initial degree of cross-linkage (20–60% of DVB) [4] or if there is the necessary degree of cross-linkage in this matrix during the process of pyrolysis [5].

Table 1 Elementary products of the pyrolysis of nitrogen-containing polymeric matrices

Mass/a.u.m.	Molecular and radical products	Mass/a.u.m.	Molecular and radical products
2	H ₂	18	H ₂ O
14	:CH ₂	27	HCN, ·C ₂ H ₃
15	·CH ₃ , :NH	28	C ₂ H ₄ , CO, N ₂
16	CH ₄ , ·NH ₂	29	·C ₂ H ₅ , ·CHO
17	NH ₃ , ·OH	44	C ₃ H ₈ , CO ₂ , CH ₃ COH, N ₂ O, C ₂ H ₅ ·NH

Figure 3a presents the TG, DTG and DTA curves of the ST matrix (10% of DVB). It is clear that, even under conditions of the limited access of oxygen at about 150°C, the process of polymeric chain destruction occurs, followed by the process of burning of low molecular products (exothermal peak with a maximum at 350°C). Otherwise, practically total loss of the mass of the initial product is observed.

To prevent destruction of the ST matrix, it is quite acceptable to carry out its modification before pyrolysis, by sulfation in the presence of the cross-linking agents. Formaldehyde, monochloromethyl ether, methylal and other methylating agents may be chosen. The sulfation process is carried at increased temperature (usually 130–200°C). Additional cross-linkage of the matrix is achieved due to sulfone and methylene bridges.

Figure 3b presents the TG, DTG and DTA curves of the ST matrix after modification with sulfuric acid at 130°C during 5 h in the presence of methylal. The DTA curve reveals a long endothermal peak with maximum at 225°C, and a transient exothermal peak with maximum at 515°C. The first peak probably refers to the process of desulfation, and the second to the condensation of the benzene rings in the matrix. In the corre-

sponding temperature intervals, the rate of mass loss for the modified matrix is maximum. During pyrolysis, the carbonization process is complete at 600–700°C.

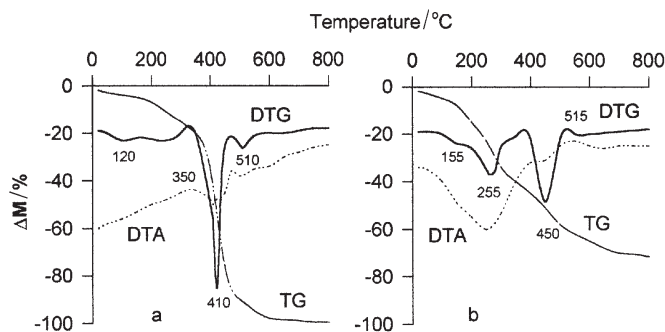


Fig 3 TG, DTG and DTA curves of a – initial ST matrix; and b – after treatment with sulfuric acid and methylal at 130°C for 5 h

In industrial practice, the technique of ST matrix modification to chloromethylated co-polymer (CMC) is well developed; this is a starting material for anionites. Chloromethylation is carried out as a rule with monochloromethyl ether in the presence of the Friedel–Crafts catalyst. It is possible to introduce up to 22% Cl as chloromethyl groups ($-\text{CH}_2\text{Cl}$) into the ST matrix, i.e. practically one chloromethyl group for each styrene ring of the co-polymer. It was therefore interesting to study the pyrolysis of the initial CMC matrix and also after its treatment with sulfuric acid.

The TG curve of CMC (Fig. 4a) shows that decomposition begins at 260°C and is accompanied by the splitting-off of chlorine, as the C–Cl bond is the weakest (339 kJ mol^{-1}). The outcome of pyrolysis is the carbonized product (a difference from the practically full destruction in the case of the ST matrix). This means that, simultaneously with the partial destruction of the polymeric chains, cross-linking occurs at the sites of elimination of hydrogen chloride. As the energies of the C–C and C–Cl bonds are close, the thermal splitting-off of chlorine and hydrogen without C–C

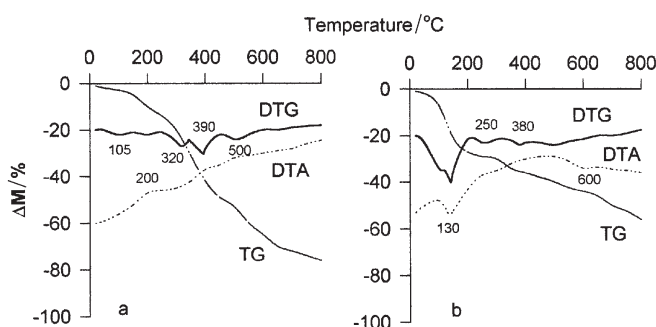


Fig. 4 TG, DTG and DTA curves of a – initial CMC matrix; and b – after treatment with sulfuric acid at 130°C for 6 h

bonds rupture is impossible. Thus, the loss in mass during the pyrolysis of CMC also involves the removal of various hydrocarbons.

Modification of the CMC matrix with sulfuric acid permits intensification of the process of dehydrochlorination at rather low temperature, and it results in additional cross-linking of the matrix. Figure 4b depicts thermal curves of modified CMC. The DTA curve indicates a minor endothermic process with maximum at 130°C (partial desulfation), and then a long (200–500°C) exoeffect, apparently relating to the concatenation of aromatic structures. The loss in mass (see TG curves) for the modified CMC is much less, than that for the initial material.

By means of IR spectroscopy, the results of the chemical modifications in the structures of the ST and CMC matrices (sulfomethylation and sulfation) can be followed (Fig. 5).

Analysis of the IR spectra with the aid of the absorption bands listed in Table 2 unequivocally demonstrates the stabilization of the initial matrices during modification. This holds for the additional cross-linkage (the increase in the share of C–H bonds in tri-substituted aromatic rings, and the emergence of sulfone bridges and C–S bonds), the increase in the share of C=C bonds, and also the emergence of various oxygen-containing structures. For CMC, the process of modification is linked with a decrease in the chloromethyl groups and accordingly the C–Cl bonds.

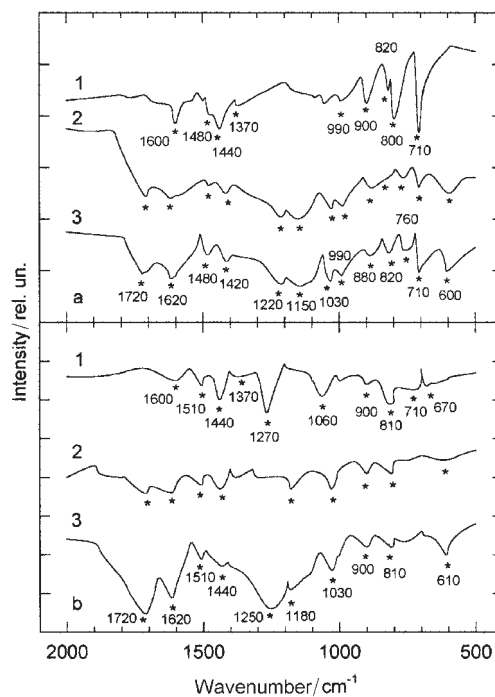


Fig. 5 IR spectra: a – (1) – initial ST matrix; and after treatment with H_2SO_4 and methylal for 3 h at (2) – 130°C or (3) – 180°C; b – (1) – initial CMC matrix; and after treatment with H_2SO_4 for 3 h at (2) – 130°C or (3) – 180°C

Table 2 Identification of absorption bands in IR spectra of initial and modified ST and CMC matrices

Band/cm ⁻¹	Group or bond	Band/cm ⁻¹	Group or bond
1720, 1620	C=O in carboxyl groups, aldehydes and ketones	990	C–O in various structures
1600, 1480–1370	C=C in aromatic structures	700–900	C–H in mono-, di- and trisubstituted aromatic rings (out-of-plane bending vibrations)
1270	–CH ₂ Cl (bending vibrations)	670	C–Cl in various structures
1250–1220	–COH (bending vibrations)	600–610	C–S in various structures
1180–1150, 1030	=SO ₂ (antisymmetric stretching vibrations)		

Accordingly, ST/DVB matrices can be used to produce carbon adsorbents. However, the yield of the carbonized product (raw carbon) is determined by the degree of cross-linkage of the initial material. Thus, for the ST matrix, an increased content of DVB or appropriate modification before pyrolysis (sulfomethylation), is necessary causing additional cross-linking and stabilization of the matrix. In the variant of the CMC, a suitable yield of carbonized material is possible on pyrolysis. However, besides the cross-linking and the stabilization of this matrix, the sulfation of CMC results in a much higher yield of product on carbon. The additional cross-linking of CMC occurs in consequence of dehydrochlorination, and also the creation of sulfone bridges. The partial oxidation of the matrix also results in its stabilization (non-melting). Oxygen is necessary to achieve dehydration during formation of the carbon frame structure in the final stages of carbonization.

The principles of the carbonization of matrices based on ST were utilized in the industrial technology of the first stage of producing synthetic carbons of SCS type [2].

Conclusions

Methods of producing synthetic carbons (first stage: preparation of raw carbon) from porous industrial co-polymers and resins with spherical granules based on matrices of AN, VP and ST cross-linked by DVB have been experimentally justified. The essential points for the effective carbonization of polymeric matrices with high yields on carbon are:

- the presence of nitrogen heteroatoms and the absence of oxygen in the structure of the polymers;
- initiation of primary cross-linking of the structure of the polymer at the expense of interactions of the hydrocarbon constituents;
- partial oxidation and sulfation of the matrices preventing their destruction and promoting cross-linking of the structure at elevated temperature.

For co-polymers based on ST, chemical modification (treatment of the polymers with sulfuric acid in the presence of cross-linking agents, or treatment of chloromethylated co-polymer with sulfuric acid) is justified. Such procedures increase the

yield of carbonized product (raw carbon) and also allow the use as raw materials of co-polymers with a low degree of cross-linkage (up to 10% of DVB).

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