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Abstract

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On the Formation of a Microporous Structure in the Process of Thermal Decomposition of Saran

The mutual arrangement of polymer macromolecules and the density of their packing determine to a considerable extent the physicomechanical properties of polymeric materials. The packing density of macromolecules can be estimated for crystalline polymers from X-ray structural data. It is more difficult to estimate the packing density of solid amorphous polymers. The study of a number of properties has made it possible to establish that, in some amorphous polymers, the macromolecules are packed rather loosely. As a result, the idea arose that there are free spaces in the polymer structure with dimensions on the order of molecular dimensions, i.e., a microporous structure typical of solid adsorbents.

Many investigators have attempted to apply to polymers the methods, developed for adsorbents with rigid frameworks, for characterizing microporous structure on the basis of measurements of adsorption isotherms of vapors of various substances (nitrogen, argon, water, organic compounds). However, such methods, usually reducible to determining sorption volumes or estimating specific surfaces, have a sound physical basis for polymers that do not change their porous structure during adsorption, i.e., that are not capable of any appreciable swelling as a result of vapor uptake.

The study of the adsorption of vapors inert with respect to polymers, with practically no swelling, made it possible to establish that the volume of small pores of polymers, belonging to a variety of micropores, is one or two orders of magnitude smaller than the volume of micropores of activated carbons ([1]). Since activated carbons can be obtained by the thermal decomposition of certain polymers, it is of considerable interest to study the laws governing the development of porous structure during the thermal treatment of polymers as they are converted into carbon. In recent years, activated carbons have been obtained and studied from many synthetic polymers ([2–5]). Among them, carbons from polyvinylidene chloride, or saran (a copolymer of vinylidene chloride and vinyl chloride), have occupied a special position with respect to adsorption properties; these properties are caused by the large volume of micropores and their small dimensions ([4]). Since polyvinylidene chloride is a very densely packed polymer, we considered it important to investigate the development of porous structure at different stages of its thermal decomposition.

Fig. 1. Adsorption isotherms of nitrogen at −195° and benzene at 24°. Nitrogen: 1 –C, 2 –C-180, 3 –C-350, 4 –C-500, 5 –C-700. Benzene: 6 –C, 7 –C-180, 8 –C-350, 9 –C-500, and 10 –C-700.

Figure 1: Fig. 1. Adsorption isotherms of nitrogen at −195° and benzene at 24°. Nitrogen: 1 –C, 2 –C-180, 3 –C-350, 4 –C-500, 5 –C-700. Benzene: 6 –C, 7 –C-180, 8 –C-350, 9 –C-500, and 10 –C-700.

The object of investigation was saran, which is a copolymer of 85% vinylidene chloride and 15% vinyl chloride. With this ratio of monomers, 1 g of the initial copolymer contained 0.72 g, or 0.0198 mole, of hydrogen chloride according to a formal stoichiometric calculation. It is known that, when chlorine-containing vinyl polymers are heated, beginning at temperatures of 140–170°, elimination of hydrogen chloride is observed, accompanied by a change in the color of the polymer from white through yellow and brown to black, and by loss of solubility (6). This reaction proceeds without rupture of the macromolecular chains (7). According to (8), when polyinylidene chloride, hydrogen chloride is formed by a free-radical mechanism, and as a result a system of conjugated bonds arises, which is the cause of the appearance of coloration. The macromolecules of polyvinylidene chloride contain equal numbers of hydrogen and chlorine atoms. According to experimental data, at a sufficiently high temperature they are completely removed in the form of hydrogen chloride, and the final product of thermal decomposition consists only of carbon.

Thermal decomposition of charges of saran of 5–10 g was carried out in a quartz tube placed in a tubular electric furnace, with a prescribed temperature-increase regime and evacuation of the gaseous products of thermal decomposition (residual pressure in the tube 2–3 mm Hg). During the first hour the temperature was raised to 170°, and a one-hour isothermal hold was carried out at 170°. Then the temperature was raised from 170 to 180° and from 180 to 200° over two hours for each interval. Heating from 200 to 300°, as well as from 300 to 400°, was carried out over 1 hour. The temperature from 600 to 700° was raised over half an hour, and the complete thermal-treatment process, with a total duration of 9½ h, was completed by a half-hour isothermal hold at 700°. In this way sample C-700 was obtained. Samples C-180, C-350, and C-500, corresponding to intermediate stages of thermal decomposition, were heated according to the described regime until the corresponding temperatures were reached, and after this the quartz tube was removed from the furnace and cooled under evacuation. The yield of the thermal-decomposition product was expressed as fractions of the weight of the initial saran. From the difference between the weights of the saran and the product, the amount of hydrogen chloride evolved was calculated. The residual content of H and Cl in the form of

* V. V. Mamkina took part in the experimental work.

Fig. 2

Figure 2: Fig. 2

Fig. 1. Adsorption isotherms of nitrogen at −195° and benzene at 24°. Nitrogen: 1 –C, 2 –C-180, 3 –C-350, 4 –C-500, 5 –C-700. Benzene: 6 –C, 7 –C-180, 8 –C-350, 9 –C-500, and 10 –C-700.

Table 1

Final temperature, °C	Yield of thermal-decomposition product α	Amount of HCl evolved, q mol per 1 g of saran	Residual HCl content in the thermally treated product, mol/g	Sample designation
–	Initial saran	0	0.0206	C
180	0.580	0.0115	0.0157	C-180
350	0.404	0.0163	0.0106	C-350
500	0.296	0.0192	0.0048	C-500
700	0.248	0.0206	~0	C-700

HCl in each product of thermal treatment was calculated as the quotient of the difference between the formal HCl content in the initial saran and the amount of HCl evolved by the yield of the thermal-treatment product in fractions. The results of the experiments on the thermal decomposition of saran are given in Table 1.

According to the data of Table 1, the amount of HCl evolved upon complete decomposition of saran exceeds by 4% the amount calculated (0.0198 mol/g) from the composition of the copolymer. We considered it possible to neglect this difference and, with an error of about 4%, to regard the decrease in the weight of saran upon heating as equal to the amount of hydrogen chloride evolved.

For the original saran and for the products of its thermal treatment, nitrogen adsorption isotherms at −195° were measured by the volumetric method, and benzene isotherms at 24° by the gravimetric method. Preliminary evacuation of the adsorbents was carried out at temperatures substantially lower than the final temperatures of thermal decomposition; for example, at 350° for sample C-500. The isotherm curves shown in Fig. 1 for the products of thermal treatment of saran are typical of finely porous adsorbents possessing a molecular-sieve action. Thus, for sample C-700 the limiting values of nitrogen adsorption are 3.6 times greater than those for benzene, i.e., only a part of the micropores is accessible to the larger benzene molecules.

Fig. 2. Nitrogen adsorption isotherms in linear form. 2 –C-180, 3 –C-350, 4 –C-500, and 5 –C-700. Notation as in Fig. 1.

Fig. 3

Figure 3: Fig. 3

Fig. 3. Dependence of the limiting volume of the adsorption space for nitrogen on the amount of hydrogen chloride evolved in the formation of a unit mass of the product of thermal decomposition of saran.

The experimental values of the adsorption of nitrogen and benzene vapors are in agreement with the adsorption-isotherm equation for adsorbents of the first structural type of the potential theory of adsorption (9). As an example, Fig. 2 shows the nitrogen adsorption isotherms in linear form. For the final product of thermal decomposition, C-700, i.e., activated carbon, the isotherm equation is applicable over a wider range of equilibrium relative pressures than for the products of incomplete decomposition. Table 2 gives the structural constants of the adsorption equation—the limiting volumes of the adsorption space W_0, expressing the volumes of the micropores, and the constants B, which depend on the sizes of the micropores and have a decisive significance for the effect of increasing adsorption potentials. Nitrogen ($\beta = 1$) was taken as the standard substance in calculating the constants B.

Table 2

Sample	Nitrogen W_0^A, cm^3/g	Nitrogen $B \cdot 10^6$	Benzene W_0^B, cm^3/g	W_0^B/W_0^A
C	0.00	–	0.00	–
C-180	0.23	6.8	0.12	0.52
C-350	0.34	4.6	0.14	0.41
C-500	0.41	3.0	0.15	0.37
C-700	0.46	3.4	0.27	0.59

According to the data of Table 2, the micropore volumes of the samples accessible to benzene molecules are considerably smaller than those for nitrogen. According to the theory, the decrease in the constant B in going from C-180 to C-500 indicates a decrease in the siz-

of micropore sizes, which is in accord with the change in the ratio of the limiting adsorption volumes of benzene and nitrogen. Both the increase in the constant B and the ratio of the limiting adsorption volumes in going from C-500 to C-700 qualitatively indicate a marked decrease in micropore sizes at the final stage of the thermal decomposition of Saran. For Saran carbon in work [4] we had $B = 3.54 \cdot 10^{-6}$ for the standard nitrogen substance. This value is close to the constant B of carbon C-700.

The formation of a microporous structure in the products of the thermal decomposition of Saran is associated with the elimination of hydrogen chloride during decomposition. Therefore, the development of the limiting volume of the adsorption space, or the volume of micropores per unit mass of product, at the decomposition stage under consideration may be correlated with the amount of hydrogen chloride liberated during the formation of a unit mass of product, i.e., with the quantity q_i/a mol/g of product. This dependence is shown in the plot in Fig. 3. From the general character of the curve one may draw the qualitative conclusion that the liberation of hydrogen chloride at the initial stages of the thermal decomposition of Saran leads to the formation of a relatively large volume of micropores.

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Note: Figure translations are in progress. See original paper for figures.