A. Ya. GELFMAN, D. S. BIDNAYA, L. V. SIGALOVA, M. G. BURAVLEVA,

V. S. KOBA

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Abstract

Full Text

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ELECTRICAL CONDUCTIVITY AND CONJUGATED DOUBLE BONDS OF THE PYROLYSIS PRODUCTS OF POLYVINYL ALCOHOL

(Presented by Academician A. N. Frumkin, September 25, 1963)

In a number of works the supposition has been expressed that the increase in electrical conductivity and the lowering of the activation energy, as compared with the initial material, in the products of pyrolysis (heat treatment) of polymers is connected with the formation of a system of conjugated double bonds (1–4), etc.

We have attempted to verify this proposition on the pyrolysis products of polyvinyl alcohol (PVA). According to literature data, during heat treatment of PVA, along with cross-links, a system of conjugated double bonds is formed (5–7). Powdered PVA was subjected to pyrolysis. The pyrolysis was carried out in a slow stream of air or of an inert gas (nitrogen, argon) for three hours, since further heating did not change the properties of the pyrolysate. The color of the pyrolysis products, depending on the temperature, changed from yellow through dark brown to black. We did not observe fading of the pyrolysis products in an inert gas after keeping them in air; nor was any increase in weight detected. The materials obtained were ground and triturated in a mortar; the powders were clamped by means of a glass tube between copper electrodes. Special experiments showed that in this way such a degree of compression of the samples was attained that the electrical resistance depended little on pressure. The glass tube with the sample was placed in an evacuated cell, and the measurements were made by the method described earlier (8). Since for all samples a dependence of the electrical conductivity on temperature is observed that corresponds to the equation $\sigma = \sigma_0 e^{\Delta E/2kT}$, we calculated the corresponding activation energies of electrical conductivity. In addition, the pyrolysates were studied by means of IR spectra and by X-ray analysis. The results are given in Table 1 and Figs. 1-4.

Fig. 1. IR spectra of the pyrolysis products of polyvinyl alcohol

In the IR absorption spectrum of the pyrolysis products of PVA (in air) at $t = 250°$, in the region of vibrations of double –C=C–bonds, two distinct bands are observed–1605 cm^{-1} (strong) and 1690 cm^{-1} (weak), which are barely noticeable at 200° and increase somewhat at 300° (see Fig. 1). The indicated absorption bands, in accordance with the chemistry of the pyrolysis process of PVA, may be assigned to conjugated and isolated –C=C–bonds. The lines characteristic of the original PVA gradually disappear, and in the spectrum of the pyrolysis products at 300° they are almost absent. Evidently, pyrolysis of PVA at 300° leads, as a result of the elimination of water molecules, to the formation of a product containing segments with conjugated and isolated C=C bonds (—CH = CH—CH = CH— and —CH$_2$—CH = CH—CH$_2$—CH$_2$—). This proposition is confirmed by the presence in the IR spectrum at 300° of bands corresponding to CH and CH groups. When the pyrolysis temperature is raised to 350°, bands appear in the IR spectrum which, according to literature data,

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Fig. 2. X-ray diffraction patterns of polyvinyl alcohol pyrolysis products:
a –initial sample, *b* –after pyrolysis at 200°, *v* –after pyrolysis at 250°, *g* –after pyrolysis at 300°, *d* –after pyrolysis at 350°, *e* –after pyrolysis at 450°, *zh* –after pyrolysis at 600°

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Fig. 2. Characteristic changes in the surface of specimens of technically pure iron after testing for resistance to seizure at a constant sliding speed of 0.0025 m/sec: *a* –without lubricant; *b* –in vaseline oil; *v* –in vaseline oil with the addition of 0.2% oleic acid.

Table 1

Change in the properties of PVA powders during pyrolysis for three hours

Specimen No.	Temp., °C	lgρ (ohm · cm) at 25°	$S_{\overline{\lg\rho}}$	ΔE (eV)	$S_{\overline{\Delta E}}$	n
1	Initial powder Pyrolysis in a nitrogen atmosphere	12.858	0.33	2.51	0.14	4
2	100	13.028	0.55	2.48	0.05	2

Specimen No.	Temp., °C	lgρ (ohm · cm) at 25°	$S_{\overline{\lg \rho}}$	ΔE (eV)	$S_{\overline{\Delta E}}$	n
3	200	11.981	0.10	1.90	0.10	4
4	250	12.403	–	1.80	–	1
5	300	14.257	0.05	2.78	0.16	2
6	350	14.199	0.72	1.33	0.48	2
7	400	10.599	–	0.45	–	1
8	450	7.484	–	0.12	–	1
9	600	5.560	1.05	0.30	0.10	2
	Pyrolysis in air					
10	180	13.431	0.19	2.28	0.16	2
11	200	13.807	0.52	2.21	0.13	4
12	300	14.103	0.45	1.53	0.28	2
13	350	14.419	0.52	0.85	0.22	2
14	400	12.485	0.31	0.85	0.0	2
15	450	8.493	0.44	0.50	0.32	4
16	500	8.729	0.48	0.53	0.16	2

Note: n—number of parallel determinations. $S_{\overline{x}}$—variance of the arithmetic mean.

(^{9}) are the absorption bands of carbon (740, 800, 872, 1440, 1586 cm^{-1}). Consequently, carbon begins to form after 300°, and as the pyrolysis temperature is increased carbon formation proceeds more intensively. The IR spectrum of the products of PVA pyrolysis at 500° gives a pattern characteristic of wood chars from carbohydrates (^{9}).

X-ray diffraction studies showed that the initial specimen (Fig. 2a) is a substance of a low degree of crystallinity (Fig. 2b), but during heat treatment at 200° there is a considerable increase in crystallinity (Fig. 2b), which, however, is not accompanied by any substantial change in the electrophysical properties (see Table 1). Treatment at a higher temperature leads to a decrease in the degree of crystallinity (Fig. 2c), and the pyrolysis product at 300° is completely amorphous (Fig. 2c). A further increase in the pyrolysis temperature leads to the appearance of a new structure (Fig. 2d). Pyrolysis at 450, 600, and 800° leads to an increase in the crystallinity of the substance, but with an entirely new structure. In the corresponding X-ray patterns (Fig. 2e, f, g) rings are visible that are characteristic neither of the initial state nor of the pyrolysis product at 350°.

Thus, in the process of thermal treatment of polyvinyl alcohol there is an increase in the degree of crystallinity, leading to the appearance of a comparatively highly ordered structure of the polymer (0–200°); in the temperature interval

Fig. 3. Dependence of the activation energy and the logarithm of the electrical resistivity of PVA pyrolysis products in a nitrogen atmosphere on the pyrolysis temperature

Figure 2: Fig. 3. Dependence of the activation energy and the logarithm of the electrical resistivity of PVA pyrolysis products in a nitrogen atmosphere on the pyrolysis temperature

Fig. 4. Activation energy and electrical resistivity of PVA pyrolysis products in air as a function of the pyrolysis temperature

Figure 3: Fig. 4. Activation energy and electrical resistivity of PVA pyrolysis products in air as a function of the pyrolysis temperature

250–350° a phase transition is observed, accompanied by passage through an amorphous state with complete loss of long-range order; further pyrolysis at 450–600° leads to growth in the degree of crystallinity of the new phase; probably, formation of the structure of carbon takes place. It should be noted that no difference was observed between specimens pyrolyzed in air and in an atmosphere of inert gas.

Thus, all three methods show (see Figs. 3 and 4) that at 300° a rearrangement of PVA molecules occurs. This corresponds to the maximum concentration of aliphatic conjugated double bonds, the minimum degree of crystallinity, and the maximum value of the logarithm of electrical resistivity. For specimens pyrolyzed in an atmosphere of inert gas, a maximum activation energy is also observed. For spec-

samples pyrolyzed in air, the course of the change in activation energy with pyrolysis temperature has a different character. At higher pyrolysis temperatures there is a sharp increase in electrical conductivity and a decrease in its activation energy. It is clear that this increase in electrical conductivity cannot be associated with an increase in the number of double bonds, since the appearance of such bonds at considerably lower temperatures is not accompanied by a noticeable change in electrical properties. The increase in electrical conductivity and the decrease in activation energy upon pyrolysis above 300° are probably associated with the appearance of carbon structures and an increase in their concentration, which are detected both by X-ray diffraction and spectroscopically.

Fig. 3. Dependence of the activation energy and the logarithm of the electrical resistivity of PVA pyrolysis products in a nitrogen atmosphere on the pyrolysis temperature

Fig. 4. Activation energy and electrical resistivity of PVA pyrolysis products in air as a function of the pyrolysis temperature

The maximum of resistance and activation energy observed for samples pyrolyzed at 300° is probably associated with the complete destruction of the initial structure of PVA and the disappearance of hydrogen-bond bridges, when carbon structures are still absent. These experimental facts correspond to the previously advanced assumption that the electrical conductivity of the original PVA is associated with the presence of hydrogen-bond bridges. We have found no relation between the presence of polyacetylene structures and electrical conductivity. It should be noted that polyacetylene obtained by the action of concentrated sulfuric acid on PVA [10] has electrophysical properties similar to those of PVA pyrolysis products at 400°, and a similar IR spectrum. It is possible that in the cited work the material studied was not polyacetylene, as the authors assumed, but a product carbonized to a considerable extent.

In conclusion, it should be noted that wherever carbon structures are mentioned in the article, what is meant is the formation of regions of large, highly condensed aromatic molecules.

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