

STUDY OF POLYETHYLENE BY AN EMANATION-THERMAL METHOD

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In this work, the emanation method was used to study polyethylene (degree of crystallinity 45%, melting point 118°).

In order to select the conditions of obtaining of the polytherms best reflecting the changes that occur during the heating of high-molecular compounds, we preliminarily estimated the influence of a change in the rate of heating and pressing of the sample upon the form of the emanograms, and the curves of cooling and repeated heating.

A hydrochloric acid solution of radiothorium (^{228}Th) with an activity of $0.5 \mu\text{Ci/ml}$ was used as the thorium source for the introduction of this isotope into the investigated solution. The powder was wet with this solution in portions and cautiously evaporated to dryness. In this case, the grains of the powder partially become sintered, and probably the radioactive equilibrium between ^{228}Th and ^{224}Ra is disturbed. To avoid sintering and achieve greater uniformity of distribution of the isotopes, the powder obtained was dissolved in hot toluene until a colloidal solution formed. After evaporation of the solvent, a powder remained, which was dried, and the fraction with diameter 0.25 mm collected.

In another method of activation, proposed by Jech, the introduction of radon was accomplished by bombarding the surface of the polyethylene powder with ions accelerated in a high-frequency Tesla discharge [1].

To prepare tablets, the polyethylene powder was saturated in a press mold heated to 140° and pressed at a pressure of 50 kg/cm^2 .

The melt was cooled without removing the pressure.

To obtain emanation polytherms, we used an emanation-thermal apparatus permitting recording of the activity of the liberated gas, the temperature, the differential temperature difference, the shrinkage and weight loss of the samples [2].

RESULTS OBTAINED

Figure 1 presents the emanation polytherms of powders activated by various methods. The maximum on the curve of the rate of evolution of radon, introduced into the surface layer according to Jech's method, lies at $45 \pm 4^\circ$ in the case of preparations obtained by evaporating an aqueous solution of radiothorium at $50 \pm 4^\circ$, and for a uniform distribution of activity over the volume (activation by the second method) at $60 \pm 4^\circ$. Above the melting point, the shape of the corresponding heating curves is the steepest for a uniform distribution of the label and the least in the case of bombardment by ions of radon (radon is entirely liberated from the sample at 140°).

The emanogram of first heating of the powder (Fig. 2) shows an increase in the emanation up to 60°, then the activity decreases as a result of sintering, and only after 80° does it rise again. The emanogram of first heating of a tablet (Fig. 2, curve 3) gives a smooth broad maximum at 80°, after which the activity increases to 120°; in the region of 95–104° there is a small plateau. The polytherms of the second heating lie below those for the first. The activity increases monotonically up to 120°, the plateau is retained in the interval 95–104° (tablet) and 105–114° (powder). After heating above the melting point, the initial activity drops by 15%. Pressing lowers the initial activity to half its value; exposure at a temperature above the melting point does not change the value of the initial activity.

In the case of slow cooling of a tablet ($0.5^\circ/\text{min}$), the melting peak (Fig. 3) becomes more distinct and is shifted in the direction of lower temperature. The number of peaks is unchanged, but they are smoothed out. On the rapid heating curve ($35^\circ/\text{min}$), there are two large peaks of pyrolysis, while the remainder disappear. Subsequently the experiments were conducted at rates of heating of $3\text{--}4^\circ/\text{min}$.

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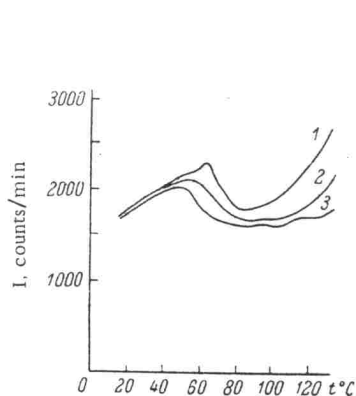


Fig. 1

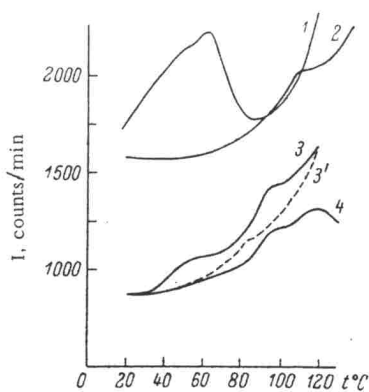


Fig. 2

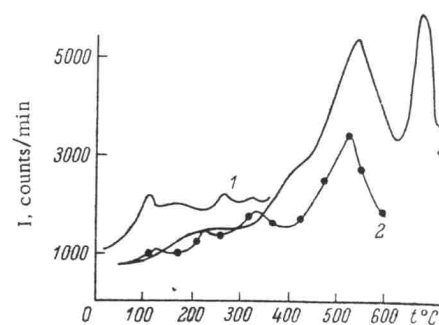


Fig. 3

Fig. 1. Emanograms of polyethylene powders activated by various methods. 1) Radioactive isotopes uniformly distributed over the volume; 2) radioactive isotopes are on the surface; 3) radon introduced in a high-frequency Tesla discharge.

Fig. 2. Emanation of polyethylene in repeated heatings. 1) 1st heating of powder; 2) 2nd heating of powder; 3) 1st heating of tablet; 3') cooling of tablet; 4) 2nd heating of tablet.

Fig. 3. Influence of the rate of heating on the emanation of polyethylene (tablet). Rate of heating: 1) 0.5°/min; 2) 4°/min; 3) 35°/min.

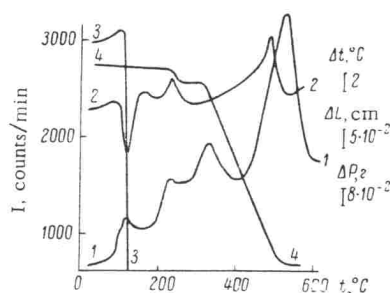


Fig. 4

Fig. 4. Pyrolysis of polyethylene (tablet). 1) Emanogram (ETA); 2) differential thermal analysis (DTA); 3) dilatometer (DLA); 4) weight loss curve (TGA).

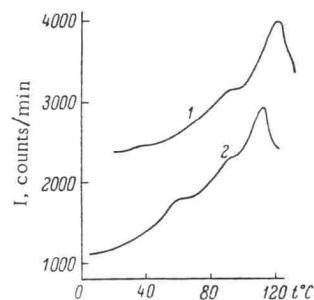


Fig. 5

Fig. 5. Crystallization of polyethylene. 1) Emanation of tablets prepared by rapid cooling; 2) emanation of tablet prepared by slow cooling.

In the heating of polyethylene within the interval 0-700°, there are four peaks on the curve of emanation of a tablet (Fig. 4). The first peak at $120 \pm 2^\circ$ (melting), the second at $230 \pm 4^\circ$ (formation of oxygen cross links), the third at $320 \pm 5^\circ$ (predominance of destruction of macrochains over oxidation of side groups), and the fourth at $520 \pm 10^\circ$ (oxidation and sublimation of all pyrolysis products).

The DTA curve has an endo-effect at $120 \pm 2^\circ$ (melting) and two exo-effects at $230 \pm 3^\circ$ and $480 \pm 4^\circ$. The dilatometer shows an increase in the linear dimensions up to 120° , after which the block breaks down. Up to 220° there is no decrease in the weight; then the weight decreases slightly, and after 320° a sharp loss of weight begins.

We are interested in studying the emanation of tablets of polyethylene depending upon the rate of preliminary cooling. For this purpose, samples of polyethylene were exposed for 30 min at the temperature 140° , and then part of the tablets were rapidly cooled to room temperature, while another part were slowly cooled ($0.1^\circ/\text{min}$). The initial activity of the tablet prepared by slow cooling had two plateaus within the intervals 60-65° and 95-100°. The peak at the melting point is shifted into the low-temperature region and is observed at 113° (Fig. 5).

The DTA curve registers an effect at 113°. The block of the dilatometer collapses at 114°.

DISCUSSION OF RESULTS

The emanation method well describes the processes that occur in polymers during heating, especially in the study of hot-pressed tablets. The evolution of gas is greatly influenced by the thermal prehistory of the samples; preparations produced by slow cooling (large degree of crystallinity) possess a lower emanation ability at room temperature. The emanation method gives information on the state of the surface layer of the tablet (thickness 3×10^{-3} cm). As is well known [3], crystallization under the conditions described leads to the formation of a surface layer consisting of narrow lamellae, oriented perpendicular to the surface. Therefore there is no unambiguous relationship between the gas evolution and the degree of crystallinity of the polymer.

The plateau at 60–65° on the emanation polytherm of a tablet produced by slow cooling from a melt may be caused by the more intense vibration of the chains in the amorphous region, which began at this temperature, and disrupts the surface of the well-formed lamellae, leading to the formation of defects that entrap thoron.

It is interesting to compare the emanograms with the data of differential thermal analysis. The plateau of the peak on the DTA curve permits us to judge the total amount of the crystalline phase, while the height of the peak gives information on the intensity of the process. On the heating curve of a sample produced by slow cooling, there is an exothermic effect within the interval 20–120°, while on the heating curve of a sample rapidly cooled to -70°, a smooth broad maximum is observed in the interval 30–80°, whereupon the entire amorphous mass remaining crystallizes. Melting of the crystallites occurs within a broad range of temperatures, and the sloping exothermic peak of crystallization turns directly into an endothermic minimum of melting. Quenched samples give doubled melting peaks, since the imperfect crystallites melt at temperatures favorable for further crystallization. As a result of the melting, together with the formation of an amorphous phase, higher melting more perfect crystals arise.

The superposition of the endothermic effect of melting and the exothermic effect of crystallization also leads to doubling of the peaks observed in the case of sufficiently slow rates of heating.

The emanograms of oxidative pyrolysis of polyethylene show that the emanation method permits a qualitative estimation of the regions of formation of oxygen cross links, destruction and oxidation. The data obtained correspond to the results of differential thermal and gravimetric analysis, obtained on the same samples under the same conditions.

CONCLUSIONS

1. A method of activation of polyethylene was developed for emanation investigations.
2. The effectiveness of emanation-thermal analysis for the study of crystallization, melting, and various kinds of structural transformations in polymers was demonstrated.
3. It was shown that emanograms of the pyrolysis of polyethylene reflect effects associated with destruction and oxidation of the macrochains of the polymers.

LITERATURE CITED

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