MECHANISM OF INTERNAL MASS TRANSFER IN DEEP DRYING OF POLYMER MATERIALS

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A mass-spectrometric method is used to study the drying kinetics of polyolefine. It is shown that the low rate of deep drying is associated with the removal of the solvent by diffusion through the solid phase of the polymer.

The removal of traces of moisture from polymer materials is particularly important, because when polymers are converted to the form in which they are to be used, for example, a film or a wire, the traces of moisture vaporize and produce bubbles, which are undesirable defects. There are two possible approaches: The traces of moisture are removed either at the extrusion stage or at the drying stage. In the latter case, it is necessary to investigate the mechanism of internal mass transfer, since this is the process that limits the removal of residual moisture and determines the length of the drying process as a whole.

One of the most important groups of polymer materials is that of the polyolefins (low-pressure polyethylenes, polypropylenes). Research by the Scientific-Research and Design Institute of Chemical Engineering (NIIKhIMMASh), in conjunction with the Kalinin Polytechnic Institute and Kiev State Pedagogic Institute, has shown that drying is sufficiently rapid if the mass content of moisture in the polyolefin is more than 1%. As shown by adsorptional investigation of the polyolefin structure, the diffusional resistance is negligible and is equivalent to the removal of solvent from pores of diameter between 1000 and 40 Å. The main difficulty is the removal of residual moisture of mass content from 1 to 0.1%, and hence attention will now be concentrated on this stage (deep drying).

In [1] a theory was developed for the isothermal deep drying of solid particles with small pores, using adsorption isotherms and the ideas of vapor diffusion in small capillaries. It follows from this theory that for the initial stages of drying ($U/U_0 \geq 0.5$)

$$U/U_0 = 1 - B\sqrt{\tau}, \tag{1}$$

where B is a constant depending on the parameters of the adsorption isotherm, the shape and size of the sample, and the effective diffusion coefficient D_i of the vapor in the small pores. It was shown in [1] that, for a linear adsorption isotherm and spherical particles of radius R_0, D_i may be determined from the equation

$$D_i = \pi B^2 R_0^2 \beta / 36. \tag{2}$$

For small pores ($r \leq 10^{-5}$ cm) Knudsen diffusion may be assumed. Then, if the pore is cylindrical, D_i is related to the pore radius as follows:

$$r = (3/8)\, D_i \sqrt{2\pi M/RT}\ . \tag{3}$$

Thus, if B is found from Eq. (1) using experimental data on the desorption kinetics, Eqs. (2) and (3) may be used to find the mean pore radius for the particles. In [1] such calculations were made for a series of silica-gel samples. The results obtained for the radius are in satisfactory agreement with the values r_c calculated from the desorption isotherm using the capillary-conduction equation and with the mean hydraulic pore radius $r_0 = 2m/S$.

The present paper gives the results of analogous investigations for a number of polymer materials. Deep drying was investigated in isothermal conditions. At low initial mass contents of moisture, the effect of shrinkage may be neglected, and hence the solutions in [1] may be used.

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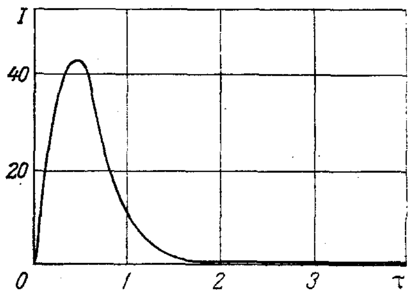

Fig. 1

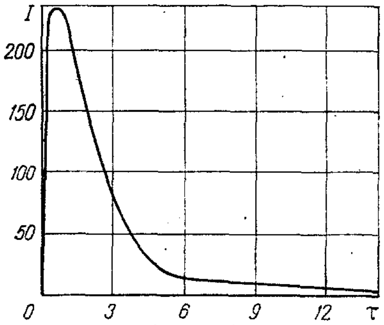

Fig. 2

Fig. 1. Calibration curve. Solvent: benzine with 11.3% isopropyl alcohol; P = 32 μg; t = 92°C. I, mm; τ, min.

Fig. 2. Dependence of intensity I, mm, of the peak m/e = 43 for benzine on the time of drying, min. Sample III: P = 100 mg; t = 105°C.

A mass-spectral method was developed for the experimental determination of the coefficients B characterizing the drying kinetics. The drying kinetics were investigated both in vacuo and in an atmosphere of inert gas (usually helium). For the vacuum experiments, the sample was sealed into an ampul, which was put into an auxiliary chamber of an MKh-1303 mass spectrometer. The chamber and all the passages leading to it were heated to a given temperature, and then the ampul was broken by means of a blade fitted in the chamber. The vaporizing material was fed to the mass spectrometer, which was tuned to a definite peak: If the vaporizing material was water, m/e = 17; if benzine, m/e = 43. Using an N37 loop oscillograph or an ÉPP-09 instrument, the dependence of the peak intensity I on the vaporization time τ was recorded. The amount of vaporizing material is proportional to the area s under the curve of I(τ). Graduated capillaries containing a known quantity P of water or organic solvents were used for standardization.

The investigation of drying kinetics in an inert-gas atmosphere was analogous. A KhÉP-01 chromatographic attachment was fitted to the mass spectrometer. The sample was not introduced in a sealed ampul but was placed in a flow of inert gas heated to a certain temperature; the gas flow carries the desorbed vapor to the mass spectrometer.

As an example, Fig. 1 shows the calibration curve for the vaporization of 32 μg of solvent (benzine with 11.3% isopropyl alcohol) from the capillary in an atmosphere of helium. The lack of sharpness of the peak is associated with the parabolic velocity distribution of the carrier gas in the tubes, adsorption of solvent molecules on the walls of the tube, and the finite rate of vaporization of the solvent from the capillary. The mean sensitivity of the equipment k = s/P for the different cases was as follows: in vacuo, $2.2\cdot10^9$ mm•sec/g for benzine and $5\cdot10^8$ mm•sec/g for water (multiplier potential 3.6 kV); in helium, $3.3\cdot10^8$ mm•sec/g for benzine and $6.3\cdot10^7$ mm•sec/g for water (multiplier potential 2.8 kV).

The advantages of the mass spectral method of investigating the drying kinetics in comparison with the existing gravimetric methods are that it is extremely sensitive, so that it is possible to use very small samples of material and low initial mass contents, and that it is possible to study separately the drying kinetics of each of the components (for example, water and benzine).

Table 1 gives the characteristics of the types of polyolefin sample investigated. One of the experimental curves of peak intensity I against time τ for benzine vaporizing from a type-III sample is shown in Fig. 2. Using this curve of I(τ) and the known value of the instrument sensitivity k, it is simple to plot the time dependence of the amount of adsorbate that has vaporized, $Q_0 - Q$.

Curves of the drying kinetics for various samples and temperatures are shown in Fig. 3. Using the linear portions of such curves (and not the sloping initial section, corresponding to preliminary heating of the samples), values of B may be obtained from Eq. (1), remembering that $U/U_0 = Q/Q_0$.

Table 2 gives the results for B. Table 3 gives values of the pore radius r obtained from Eqs. (2) and (3) using values of B and of the adsorption-isotherm parameter β for samples

TABLE 1. Characteristics of Polymer Samples

Sample type	Sample material and characteristics	U_0, %
I	Polypropylene, $2R_0 = 0.15$-0.3 mm	0.3
II	Copolymer of ethylene with α butylene, $2R_0 = 0.12$ mm, $i = 1$-2	0.23
III	Poly-4-methylpentene, $2R_0 = 0.2$ mm	3.5
IV	Low-pressure vanadium polyethylene, $2R_0 = 10\ \mu$, $i = 10.5$	0.197
V	Low-pressure polyethylene, $2R_0 = 10\ \mu$, $i = 5.0$	0.37
VI	Low-pressure vanadium polyethylene, $2R_0 = 10\ \mu$, $i = 7.9$	0.22

TABLE 2. Experimental Values of B

Liquid removed and conditions	t, °C	Type of sample					
		I	II	III	IV	V	VI
Benzine in vacuo	100				0,050	0,061	0,020
	80				0,020	0,017	—
	60				—	0,013	—
Water in vacuo	100				0,053	0,035	0,072
	80				—	0,031	—
	60				—	0,019	—
Benzine in helium atmosphere	120	—	—	0,06	—	—	—
	100	0,0013	0,045	0,03	—	—	—
	90	0,00032	0,042	—	0,02	—	—
	65	—	0,0048	—			

IV and VI. As is evident from Table 3, the pore radius is found to be many orders of magnitude smaller than the molecule itself. Corrections for the different forms of the isotherm at high temperatures and possible differences (even by a factor of 3-4) in the values of B cannot change this basic relationship. Therefore, it must be assumed that in the case of deep drying of the polymers there is internal diffusion of the water and benzine molecules dissolved in the polymer matrix (but not adsorbed in the small pores) and this is what leads to the extremely slow rates of deep drying, making the removal of the last traces of material very difficult.

Further confirmation of this conclusion is that the results obtained for D_i are close to the diffusion coefficients for dissolved material in a solid. In fact, according to [2], the value of D_i for low-pressure polyethylene (LPP) is around 10^{-8} cm^2/sec, which is of a similar order of magnitude to the present results.

To verify this hypothesis, additional pycnometric measurements of the density of LPP powders in various solvents were made. If the LPP particles contained a network of hollow channels, the sealing of air into these channels by the pycnometric liquid would lead to a density value different from that of solid blocks of LPP.

A 10-ml pycnometer suspended on ADV-200 weights was used. Acetone and tetradecane were the working liquids. The measurements were made in an ultrathermostat by the usual method. The results for the LPP particle density were as follows: in acetone, $\rho = 1.05 \pm 0.02$ g/cm^3; in tetradecane, $\rho = 1.02 \pm 0.02$ g/cm^3. These values hardly differ from the density of solid blocks of LPP. Thus, the pycnometric method does not indicate any significant internal porosity of the LPP particles.

Electron-microscopic observations also confirm that there is no network of capillaries in the polymer samples and that the transfer of adsorbed water and benzine is by diffusion through the polymer matrix.

To examine the samples in an electron microscope, drops of LPP suspension were applied to a slide and dried. By this method, it was possible to obtain a uniform distribution of LPP particles over the molecularly smooth surface of the slide. Then by vacuum sputtering a thin carbon film was applied to the slide with the layer of particles. The film, with the powder particles adhering to it, was removed from the slide by immersion in water.

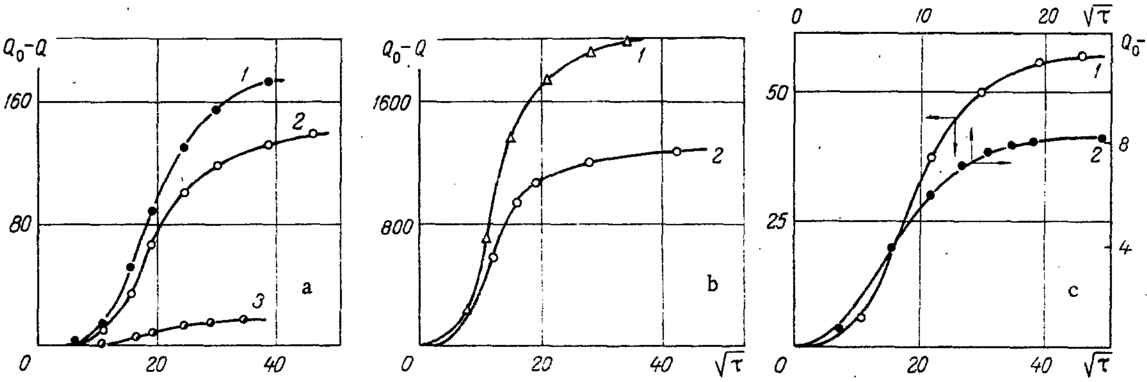

Fig. 3. Curves of the drying kinetics of various polyolefin samples containing traces of benzine: a) P = 100 mg, sample II in helium [t = 100°C (1), 87 (2), 65 (3)]; b) P = 100 mg, sample III in helium [t = 120°C (1), 105 (2)]; c) sample IV (P = 90 mg, t = 90°C) in helium (1) and (6.75 mg, 80°C) in vacuo (2). Q, μg; $\sqrt{\tau}$, $sec^{1/2}$.

TABLE 3. Calculation of Diffusion Coefficients and Pore Radius

Sample, adsorbate	Drying conditions	β (at 25°C)	B, $sec^{-1/2}$ (at 80-100°C)	D_i, cm^2/sec	r, Å
IV, benzine	vacuum	37*	0,05	$2{,}0\cdot10^{-9}$	$1{,}2\cdot10^{-5}$
VI, water	"	10^4	0,07	10^{-6}	$2\cdot10^{-3}$
IV, water	"	820	0,05	$4{,}5\cdot10^{-3}$	$1\cdot10^{-4}$
IV, benzine	helium	37*	0,02	$3{,}2\cdot10^{-10}$	$1{,}9\cdot10^{-6}$

*In calculating β, the saturation vapor pressure of benzine at 80°C was used.

The carbon film, mounted on a metal support, was studied in the electron microscope. The LPP particles appeared as a continuous structure, not containing pores larger than 10-20 Å (the limits of resolution of the electron microscope). The particles contained amorphous and crystalline sections and were no different, in appearance, from continuous finished polymer products.

It is of interest to note some of the characteristic features of the deep drying of polyolefin samples. First, water and benzine vaporized in approximately equal quantities from samples of types I and V (the industrial preparation of high-density polyethylene using titanium catalysts includes a washing stage and so the samples may contain not only benzine but also a certain amount of water). From samples of types II, III, IV, and VI only benzine vaporized; no water was observed (samples of type VI, prepared by a different method, are only contaminated by water on storage in air).

Second, for samples of all types, the curves of $Q_0 - Q = f(\sqrt{\tau})$ are close to linear up to a certain mass content (Fig. 3), the deviation in the initial sloping section being associated with the preliminary heating of the sample. This is in agreement with the theory of [1], although the diffusion coefficient does not characterize Knudsen diffusion through a pore but diffusion through the polymer matrix in a solid.

As is evident from Table 2, the rate of drying is rather higher in vacuo than in helium. In fact, for samples of type IV in helium B = 0.02 and t = 90°C, whereas in vacuo the same value of B is reached at a lower temperature (t = 80°C). This difference is significant, since for samples of type IV a particularly sharp change in B is observed in the range 80-100°C.

From Fig. 3 and other results, it is possible to estimate the time necessary for the sample to be dried to a given final mass content Q/Q_0. For example, at around 100°C the time required to reach $Q/Q_0 = 0.5$ (which corresponds to mass content U = 1.75% for type-III samples and U = 0.1-0.15% for the others) is as follows: in vacuo, 5-10 min for samples IV and V and 25 min for sample VI; in helium, 8 min for samples II and III, while for samples I and IV this level is not reached even after 1 h.

Now consider the temperature dependence of B. The most careful study has been made for type-II samples in helium (Table 2). With increase in temperature from 65 to 90°C, B rises by an order of magnitude, which is due to the increase in the internal-diffusion coefficient. Further rise in temperature leads to only slight increase in B, but there is an increase in the values of the difference $Q_0 - Q$ for which the linear dependence in Eq. (1) is valid. As a result, the drying time is significantly reduced. For example, after 15 min at $t = 90°C$, $Q/Q_0 = 0.5$ (final mass content $U = 0.11\%$), while, at $t = 100°C$, $Q/Q_0 = 0.3$ ($U = 0.07\%$). When the temperature is raised above the melting point, the drying rate falls sharply. This is because the individual particles run together on melting, which leads to increase in R_0 and hence in the time required for diffusion through the sample.

The lack of adsorption isotherms for samples I-III and also of solid-state diffusion coefficients means that it is impossible to compare all the results obtained for B with the theoretical values.

The sharp fall in the rate of vaporization at mass contents of less than 0.5-1% may be attributed to the transition from diffusion through a network of micropores to diffusion through the solid phase of the polymer. The change in the mechanism of internal mass transfer is responsible for the low rate at the deep-drying stage. Because of the low rate, it requires a great deal of time to remove the solvent at mass contents of 1-0.1%.

Removing the bulk of solvent at mass contents from 60 to 1% does not pose any particular problems, since it is not accompanied by any considerable diffusional resistance. Therefore, the drying of polyolefins is best carried out in two-stage equipment, the first stage for preliminary dyring of the material to a mass content of 1% and the second stage for drying to a residual mass content of 0.2-0.1%.

A suitable choice for the first stage would be a convective drier with active hydrocynamic conditions and in particular a cyclonic drier, the advantage of which is that it is simple in construction and relatively small. The second stage should be a drier,employing a fluidized bed or a vibrational fluidized bed, ensuring a high drying rate. The fluidized-bed drier should provide directed motion of the material.

However, the flow rate in the fluidized-bed drier is limited by the supply rate of the smallest polyolefin particles (5-10 m/sec) and the gas temperature by the softening point of polyolefin particles (90-110°C). As a result, the heat which may be transferred form the gas to the material in the drier is sinsufficient for fast drying of the polyolefins. The additional heat must be supplied to the material by other means. In the two-stage apparatus for drying polyolefins designed by NIIKhIMMASh, the additional heat supply in the second stage is provided by the vibrating surface of a heater fitted in the fluidized-bed drier itself [3]. The vibration increases the rate of heat transfer from the heated surface to the material and improves transfer in the drier.

Attempts to achieve further intensification of deep drying should concentrate on increasing the diffusion coefficient for the solvent in the solid phase of the polymer, for example, by increasing the temperature or producing radiational defects in the polymer. Other possibilities are to decrease the size of the particles to be dried or to create within them a network of relatively large pores. A multiple approach to this problem should be adopted. It seems desirable to change the method of preparation of the polymer materials so as to produce an optimum structure for drying.

NOTATION

U_0, U, initial and current mass content, g/g solid phase; τ, time, sec; R_0, particle (grain) radius of sample, cm; $\beta = da/dc$, adsorption-isotherm parameter; a, mass of adsorbed material per unit volume of porous body, g/cm^3; c, vapor mass in pore space per unit volume of porous body, g/cm^3; r, pore radius, cm; m, porosity; S, specific surface; M, mass of a mole of vaporizing material, g/mole; R, universal gas constant, erg/mole; T, absolute temperature, °K; t, temperature, °C; m/e, mass:charge ratio of ion; P, weight of sample introduced in mass spectrometer, g; Q_0, Q, initial and current content of vaporizing material, g; i, melt index, g/10 min.

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HIGH-TEMPERATURE CONDUCTION OF HELIUM—XENON MIXTURES

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An experimental method is described and is used to obtain new experimental data on the heat conduction of the mixtures 0.5He—0.5Xe and 0.9He—0.1Xe at high temperatures and near-atmospheric pressure.

Introduction

Most of the problems encountered in high-temperature engineering are associated with the heat transfer in a hot gas or from a gas to a wall, and require a knowledge of thermophysical characteristics, in particular, the transfer properties of heat carriers. The heat conduction is a very important property of a material but the determination of heat conduction at high temperatures is beset by considerable difficulties.

The rigorous molecular-kinetic theory of monatomic gases gives satisfactory theoretical results for the heat conduction of mixtures of monatomic gases at moderate temperatues, and the model of molecular interactions that is used has been experimentally verified at these temperatures. At high temperatures (on the order of 10^{3}°K), however, experimental verification of the theoretical calculations is lacking or incomplete.

Heat-conduction measurements at temperatures up to approximately 1500-2000°K are usually made by the fairly accurate steady-state heated-wire method and those at 6000-8000°K are made on the basis of the energy balance of a hot or quenching electric arc, measuring its characteristic and the radial temperature distribution in the arc column. The region between 1500 and 6000°K has had little methodical investigation; almost the only method that can be used is to investigate the nonsteady heat transfer in the temperature boundary layer of the gas heated by the reflected shock wave at the end of the shock tube. The advantage of the method is the purely thermal homogeneous preheating of the gas. The measurements are made by the contact method (the temperature at the end surface) or optically (the temperature profile in the temperature boundary layer of gas at the end of the tube).

2. Formulation of Problem. Method

With regard to both the procedure and the specific techniques of the experiment, determining the heat conduction by the shock-tube method is complicated, since it involves the investigation of a high-temperature medium in a thin (on the order of $\sim 10^{-4}$ m) temperature boundary layer with a large temperature gradient (of the order of 10^{6}-10^{7}°K/m) in an extremely short time interval ($\sim 10^{-7}$-10^{-4} sec).

In this interval, a number of physical and chemical processes that may affect the experimental results are occurring in the gas. It is customary, in dealing with these measurements, to make a number of a priori assumptions, which are found to be satisfactory for many gases over a sufficiently wide range of temperature and pressure; the heat-conduction data in the literature are based on these assumptions. They are as follows: that there is local thermodynamic equilibrium in the gas; that the heat transfer is one-dimensional; that the thickness of the temperature boundary layer is small in comparison with the length of the hot-gas column; that the pressure in the gas behind the reflected shock wave is constant; that the macroscopic velocity (flow) of the gas at the end of the tube is zero; that the radiation of the gas does not depend on the coordinate and is negligibly small; and that the accommodation of the gas energy at the wall is complete.

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