7. Yu. A. Buevich, "Fluctuations of number of particles in dense dispersed systems," Inzh.-Fiz. Zh., 14, 454-459 (1968).
8. Yu. A. Buevich, "Statistical model of linear polymers in the amorphous state," Zh. Prikl. Mekh. Tekh. Fiz., No. 1, 58-74 (1969).
9. T. L. Hill, Statistical Mechanics, McGraw-Hill, New York (1956).
10. E. Copson, Asymptotic Expansions, Cambridge Univ. Press, London (1965).
11. J. Batchelor, "Brownian diffusion of particles with hydrodynamic interaction," in: Hydrodynamic Interaction of Particles in Suspensions [IR], Mir, Moscow (1980), pp. 84-123.
12. Yu. A. Buevich and I. N. Shchelchkova, "Rheological properties of homogeneous finely dispersed suspensions. Steady-state flows," Inzh.-Fiz. Zh., 33, 872-879 (1977).

EFFECT OF IRRADIATION ON DENSITY OF POLYMERS

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UDC 678.742:046

A survey is made of available data on the effect of irradiation on the density of several polymers. Results of measurements are presented pertaining to the density of polyethylene, polystyrene, polymethyl methacrylate, and polytetrafluoroethylene at temperatures from −196 to +100°C.

The few available published data on the density of irradiated polymers pertain to the temperature range of +20°C and higher. It seems appropriate to separate the data pertaining to crystalline substances from those pertaining to amorphous ones, inasmuch as irradiation affects them through different mechanisms.

In crystalline polymers (polyethylene, polypropylene, polytetrafluoroethylene, etc.) the change of density is related to amorphization (or with increasing crystallinity, as in the case of polytetrafluoroethylene, with fragments of molecules aligning together and forming small crystals during the process of radiative decomposition) and to cross-linkage of polymer chains occurring principally in the amorphous phase. The change of density in amorphous polymers (polystyrene, polymethyl methacrylate, etc.) is determined by the competing processes of radiative linkage and decomposition. Amorphization of polymers lowers their density, since $\rho_c > \rho_a$ (densities of crystalline phase and amorphous phase respectively) over the entire temperature range. As a result of radiative linking, the density of a polymer increases on account of the decreasing free space. Decomposition has, as a rule, the opposite effect.

In many cases radiative macroeffects involving density, viz., those associated with pore and crack formation as a result of gas evolvement during irradiation, must also be taken into account. Such effects depend overridingly on the irradiation temperature and on the power of the absorbed radiation dose.

The data in Fig. 1 represent results of density measurements made for high-density polyethylene at +20°C [1-3]. The parameter here is the irradiation temperature t_0. At relatively low irradiation temperatures t_0 (20-30°C) the amorphization of high-density polyethylene resulting in a decrease of density is largely compensated by radiative linking. Consequently, the density either hardly changes or slightly increases over a wide range of absorbed radiation doses. As the irradiation temperature t_0 is raised, the amorphization of high-density polyethylene accelerates rapidly [4] while the radiative-chemical linkage yield changes little. Accordingly, the density of high-pressure polyethylene decreases until the radiation dose reaches a certain level of the order of D = 5-7 MgR at which the crystallinity level in the polymer is already low (reduced from 50 to 5-7% at t_0 = 80°C and measured at t_m = 20°C) and then increases as a result of further linking. Measurements of HPPE (high-pressure polyethylene) density ρ at temperatures t_m up to 80°C, not published in report [1], have revealed that the trend of the $\rho = f(D)$ curves remains the same as in Fig.

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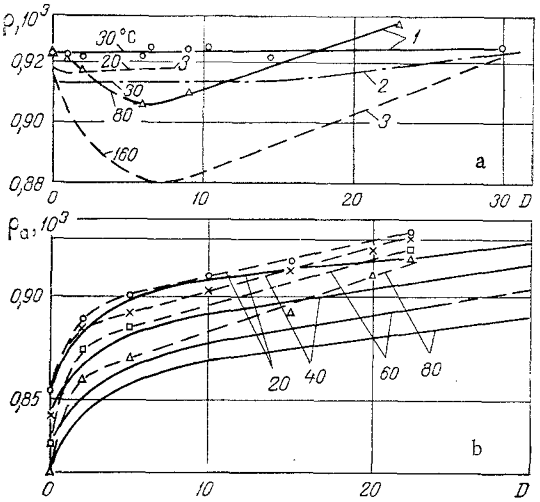

Fig. 1. Dependence of the density of high-pressure polyethylene (a) and of its amorphous phase (b) on the absorbed radiation dose: (a) numbers next to curves are irradiation temperatures (°C), 1) data from [1], 2) data from [2], 3) data from [3]; (b) numbers next to curves are measurement temperatures (°C), solid lines correspond to irradiation temperature t_0 = 30°C, dash lines correspond to irradiation temperature t_0 = 80°C; ρ, ρ_a (kg/m³), D (MgR).

1a for t_m = 20°C, except that the density minimum corresponding to t_0 = 80°C gradually flattens. An explanation for this is that the difference $\rho_c - \rho_a$ decreases as the temperature of specimens increases.

The existence of a minimum on the $\rho = f(D)$ at $t_0 = 160°C > T_{melt}$ is, apparently, related to partial recrystallization of a specimen during cooling after irradiation. Analogous results were obtained in another study [5] with use of mixed gamma-neutron radiation (t_0 = 80°C). Another study [6] has established that irradiation of high-pressure polyethylene with doses up to 20 MgR results in the appearance of a minimum on the $\rho = f(D)$ curve at D = 5 MgR (t_m = 20°C) and a monotonic increase of density at t_m = 150°C. An explanation for the latter trend is that the dependence of density ρ of molten high-pressure polyethylene on the radiation dose relates to radiative linking only.

The trend of the $\rho = f(D)$ curves for low-pressure polyethylene (ρ = 960 kg/m³) [3] is analogous to that for high-pressure polyethylene (ρ = 920 kg/m³).

The density characteristics of polypropylene were also studied [7]. Amorphization of polypropylene (reduction of the degree of crystallinity from 60% in an original specimen to 9% after irradiation with a dose of 18 MgR) was found to lower the density from 907 to 889 kg/m³ at t_m = 20°C. Data on the effect of irradiation by γ-quanta from a ^{60}Co source on the density ρ and the crystallinity X of polytetrafluoroethylene (measurements made at t_m = 20°C) are given in Table 1. As has been said before, a characteristic feature of polytetrafluoroethylene is that irradiation increases the degree of crystallinity and this causes its density ρ to increase with increasing radiation dose.

One of these authors (B. A. Briskman) participated in studies of several amorphous polymers in which data on polystyrene [1] and on the amorphous phase of high-density polyethylene [4] were obtained. The low radiative yield of linkages in polystyrene was what caused the density to hardly change with irradiation in doses up to 27 MgR. The recorded increment of density was 0.6% at t_m = 20°C.

The situation is different with the density ρ of the amorphous phase of high-pressure polyethylene [4]. Its density $\rho_a = f(D, t_m)$ for t_0 = 30°C was calculated from data on the

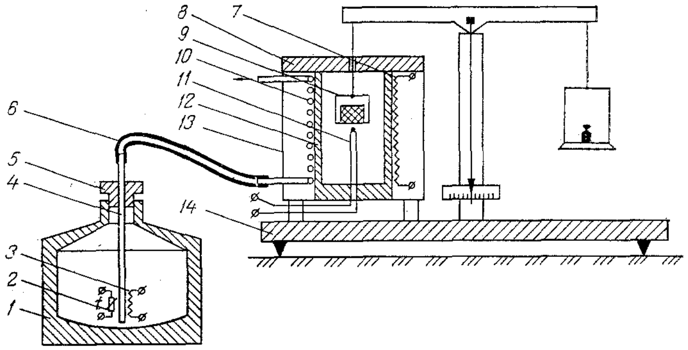

Fig. 2. Schematic diagram of measuring apparatus: 1) dewar flask; 2) thermistor in circuit for automatic regulation; 3) electric heater—evaporator; 4) metal tube for nitrogen feed; 5) stopper (foam plastic); 6) hose for nitrogen feed; 7) electric heater; 8) lid of test cell; 9) suspension; 10) copper coil; 11) thermocouple; 12) test cell beaker; 13) outer jacket with thermal insulation; 14) model VLA-200 balance.

TABLE 1. Dependence cf Density and Crystallinity of Polytetrafluoroethylene

Adsorbed dose, MgR	[1]			[8]			[9]		
	0	0,17	1,26	0	0,047	1,90	0	0,02	1,0
$\rho\cdot 10^{-3}$, kg/m^3;	2,155	2,234	2,246	2,154	2,198	2,222	2,180	2,221	2.248
X, %	62	72	82	54	67	74	—	—	—

Adsorbed dose, MgR	[9]			[10]*			[10]†		
	0	0,001	0,01	0	0,01	0,04	0	0,01	0,1
$\rho\cdot 10^{-3}$, kg/m^3;	2,156	2,166	2,183	2,16	2,21	2,24	2,19	2,28	2,29
X, %	—	—	—	50	65	80	60	92	95

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*Irradiation in vacuum.

†Irradiation in air.

crystallinity of irradiated high-pressure polyethylene, those data based on values of the specific heat. The density ρ_a of HPPE specimens irradiated at the temperature $t_0 = 80°C$ was determined through linear extrapolation of experimental data on the density of this material from D = 10-15 MgR to D = 0. The results are shown in Fig. 1b. Over the entire range of radiation doses, up to 30 MgR, the density ρ_a increases by 8-10% as a result of radiative linking. The temperature coefficient of density is almost independent of the radiation dose and equal to $6\cdot 10^{-4}$ $(°C)^{-1}$ (at $t_0 = 30°C$) over the entire $20 < t_m < 80°C$ range of measurement temperatures. The values of density ρ_a at $t_m = 20°C$ agree closely with the data in study [5] on high-pressure polyethylene irradiated with doses up to 4 MgR. The increase of ρ_a with higher t_0 is, apparently, related to a higher radiative yield of linkages, which, according to other data [11, 12], changes by a factor of 4 as the irradiation temperature is increased from −196 to +73°C.

The preceding survey of available experimental data on the effect of irradiation on the density of several representative polymers is limited, as a rule, to the +20°C measurement temperature. Only in two or three studies were data obtained at higher temperatures, and then only for polyethylene. The complete absence of data on the subzero temperature range greatly inhibits, for instance, further studies of the mechanism of radiative effects with regard to thermal conductivity of polymers. There is evidence that such a correlation exists also between the specific heat and the density of linear polymers [13].

In this connection, these authors have studied the density of several representative polymers (polyethylene, polystyrene, polytetrafluoroethylene, polymethyl methacrylate) at temperatures from −196°C to t_{max}, the upper temperature limit depending on the melting point of the material and on the radiation dose. Following are the data on the density of nonirradiated specimens.

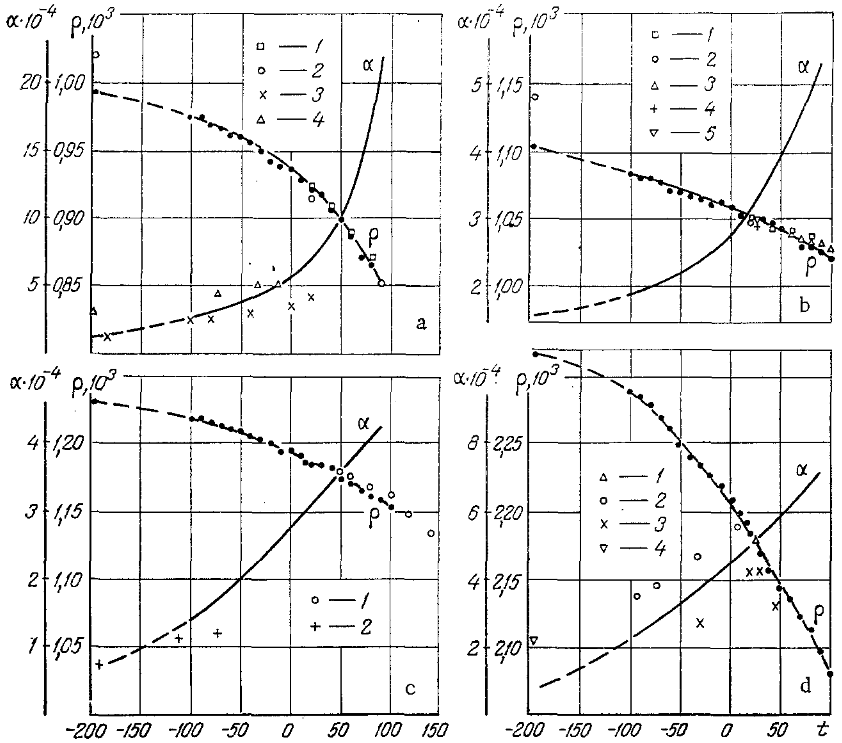

Fig. 3. Temperature dependence of the density ρ and the volume expansion coefficient α: (a) high-pressure polyethylene; (b) polystyrene; (c) polymethyl methacrylate; (d) polytetrafluoroethylene; (a) 1) data from [1], 2) data from [15], 3) data from [19], 4) data from [20]; (b) 1) data from [1], 2) data from [15], 3) data from [16]; 4) data from [17], 5) data from [18]; (c) 1) data from [16], 2) data from [21]; (d) data on ρ from [9], 2) data from [20], 3) data from [22], 4) data on α from [23]; dark dots represent data of this study; α (K^{-1}), ρ (kg/m^3), t (°C).

The density was measured by the method of hydrostatic weighing in the dynamic mode (Fig. 2). The test cell was replaced by one of the pans of a model VLA-200 analytical balance. The test cell was equipped with an electric heater and a copper coil for pumping nitrogen vapor from a dewar flask, with an electric heater inside, also a thermistor for automatic disconnection of the heater when the level of liquid nitrogen has dropped by a certain amount. The density at —196°C was measured indirectly in a special dewar flask with liquid nitrogen in lieu of the test cell. As working fluids for pouring into the test cell beaker were used standard iso-octane (Government Standard 4374-48) at temperatures from —100 to +30°C, water bidistillate at temperatures from 10 to 30°C, and nonane (pure) at temperatures from 20 to 150°C. The density data for these fluids were taken from a monograph on this subject [14]. The maximum systematic error of measurements, according to standard formulas for the error of results of indirect measurement, was 0.4%. The random error, based on a 0.95 confidence interval, did not exceed 0.1%. Intense evaporation of nonane at temperatures above 100°C limited the range of measurements to that temperature and not higher. Use of dodecane (t_{boil} = 210°C) and nonodecane (t_{boil} = 300°C) is suggested for further studies.

The results of density measurements made on specimens of polyethylene, polystyrene, polymethyl methacrylate, and polytetrafluoroethylene, as well as already published data, are presented in Fig. 3. The maximum discrepancy does not exceed 0.8% for any of the polymers, except at —196°C. Here the difference between the results of this study and the results in study [15] is 2% for polyethylene and 3% for polystyrene, with the maximum error of measurements in study [15] estimated at ±1%. Possible causes of such a discrepancy are: difference in the composition of original specimens (a small difference of crystallinity in the case of polyethylene), fundamentally different methodological approaches (hydrostatic weighing in this study, attenuation of α-particle flux in the specimen in study [15]). At the 20°C temperature, meanwhile, the difference between results of both studies does not exceed 0.5%.

On the basis of the data on density ρ at temperatures from −100 to +100°C, these authors have calculated the volume expansion coefficient α according to the relation

$$\alpha = \frac{1}{v_0} \frac{dv}{dt},$$

where v is the specific volume and v_0 is the specific volume at 0°C. Approximate values were also obtained for α at temperatures in the vicinity of 77°K. The results of these calculations are shown in Fig. 3. A comparison with published data was made with the aid of results of dilatometric measurements for determining the linear expansion coefficient β of polyethylene [19, 20], polymethyl methacrylate [21], and polytetrafluoroethylene [20, 22, 23], all these results collected together in one reference [24]. The calculations are based on isotropy of polymer properties, i.e., on the assumption that $\alpha = 3\beta$.

It is to be noted that the values of β in study [15] refer to the true linear expansion coefficient

$$\beta = \frac{1}{L_t} \frac{dL}{dt}.$$

The values of β obtained for polytetrafluoroethylene correspond to crystallinity X at 20°C, in one case $X_{20} = 83\%$ [22] and in another case $X_{20} = 50\%$ [20]. The crystallinity of specimens in this study was calculated according to the relation $\rho = 2.0 + 0.3X$, which yielded 62%. The agreement between the results of this study with those of studies [20] and [22] is entirely satisfactory, inasmuch as the linear expansion coefficient β of polytetrafluoroethylene in the low-temperature range is known [22] to decrease with increasing crystallinity. Several studies, [24] for instance, have revealed a sharp peak of β within the vicinity of +20°C, a peak associated with a phase transformation of the first kind involving change of the elementary lattice from a triclinic to a hexagonal one. This study did not reveal such a transition, possibly because of the dynamic mode of density measurement during heating as well as during cooling at rates of ≈ 1-2°C/min.

In a monograph on this subject [25] are given values of β, mean over temperatures from −80 to +45°C, for polystyrene and polymethyl methacrylate. The corresponding values of α are $2.32 \cdot 10^{-4}$ and $2.28 \cdot 10^{-4}$ $(°C)^{-1}$, respectively. The mean-integral values of density ρ over the same temperature range are $2.57 \cdot 10^3$ and $2.51 \cdot 10^3$ kg/m³, respectively. Considering the averaging mode, one must regard a deviation of 10% as acceptable.

We conclude, therefore, that the method of hydrostatic weighing in the dynamic mode yields sufficiently reliable data on the density of polymers and supplementary data on the volume expansion coefficient. The next stage of this study will cover the density of irradiated polymers over the same temperature range.

LITERATURE CITED

1. V. D. Bondarev, B. A. Briskman, and V. P. Savina, "Effect of γ radiation on thermal conductivity and density of certain polymers," Plast. Massy, No. 7, 7-10 (1973).
2. J. N. Tomlinson, D. E. Kline, and J. A. Sauer, "Nuclear radiation influence on polyethylene heat conductivity," Trans. SPE, 5, No. 1, 44-49 (1965).
3. D. Heinze, "Behavior of high-molecular polymers under high-energy radiation," Kolloid Z., 210, No. 1, 45-53 (1966).
4. B. A. Briskman and V. P. Savina, "Thermophysical properties of amorphous phase of irradiated polyethylene," Inzh.-Fiz. Zh., 27, No. 5, 804-809 (1974).
5. M. Ross, "Change in physical properties of polyethylene for in-pile irradiation at 80°C," Report M/R 1401 AERE (1954).
6. T. S. Nikitina, E. S. Zhuravskaya, and A. S. Kuz'minskii, Effect of Ionizing Radiation on Polymers [in Russian], Gosizd. Khim. Liter., Moscow (1959).
7. J. N. Tomlinson and D. E. Kline, "Effect of γ radiation on the thermal conductivity of polypropylene," J. Appl. Polym. Sci., 11, No. 10, 1931-1940 (1967).
8. K. L. Hsu and D. E. Kline, "Thermal conductivity of irradiated PTFE," J. Appl. Polym. Sci., 9, No. 11, 3567-3574 (1965).
9. A. Ferse, W. Koch, and L. Wuckel, "Effect of γ radiation on polytetrafluoroethylene," Kolloid Z., 219, No. 1, 20-26 (1967).

10. A. Ferse, W. Koch, and L. Wuckel, "Effect of γ radiation on polytetrafluoroethylene," Kolloid Z., 224, No. 2, 33-35 (1968).
11. R. N. Black, "Radiation yields of hydrogen for polyethylene," Nature, 178, 805-812 (1956).
12. A. Charlesby, Nuclear Radiation and Polymers [Russian translation], IL, Moscow (1962).
13. K. E. Perepelkin, "Correlation between molecular mass, density, and specific heat of linear polymers," Vysokomolek. Soedin., 11B, No. 12, 902-903 (1969).
14. N. B. Vargaftik, Handbook of Thermophysical Properties of Gases and Liquids [in Russian], Gosizd. Fiz. Mat. Liter., Moscow (1963).
15. H. Rauch and P. Tenor, "Measuring of polyethylene and polystyrene density at 77 and 4.2°K," Atomkernenergie, 12, No. 5/6, 163-168 (1967).
16. M. Takahashi, M. C. Shen, R. B. Tailor, and A. V. Tobolsky, "Master curves for some amorphous polymers," J. Appl. Polym. Sci., 8, No. 4, 1549-1551 (1964).
17. J. E. Karasz, J. E. Bair, and J. M. O'Reilly, "Thermal properties of atactic and isotactice polystyrene," J. Phys. Chem., 69, No. 8, 302-306 (1965).
18. I. Abu-Isa and M. Dole, "Specific heat of synthetic high polymers, Part 12: Atactic and isotactic polystyrene," J. Phys. Chem., 69, No. 8, 2668-2675 (1965).
19. J. L. Zakin, L. Simha, and H. C. Hershey, "Low-temperature thermal expansivities of polyethylene, polypropylene, and polystyrene," J. Appl. Polym. Sci., 10, No. 10, 1455-1473 (1966).
20. H. L. Laquer and E. D. Head, "Low-temperature thermal expansion of plastics," Report AECD-2161, Oak Ridge Tenn. (1952).
21. R. A. Haldon and R. Simha, "Dilatometric measurements for polymethyl methacrylate," Macromolecules, 1, No. 4, 340-343 (1968).
22. I. E. Leksina and S. I. Novikov, "Thermal expansion of polytetrafluoroethylene at low temperatures," Fiz. Tverd. Tela, 1, No. 3, 504-511 (1959).
23. M. van de Voorde, "Thermal expansion of polytetrafluoroethylene," IEEE Trans. Nucl. Sci., 20, No. 3, 693-697 (1973).
24. I. I. Perepenko, Properties of Polymers at Low Temperatures [in Russian], Khimiya, Moscow (1977).
25. Yu. K. Godovskii, Thermophysical Methods of Polymer Research [Russian translation], Khimiya, Moscow (1976).

THERMAL CONDUCTIVITY OF COLLOIDAL CAPILLARY POROUS BODIES IN THE PROCESS OF STRUCTURE FORMATION

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UDC 66.047

The article presents the results of the experimental investigation of the thermal conductivity of a solidifying system in the process of formation of a capillary porous structure.

The thermophysical processes occurring in colloidal capillary porous bodies have a substantial effect on structure formation and on the eventual physicomechanical properties of materials. For instance, the structure formation of binder-based disperse systems is directly connected with the regularities of heat and moisture transfer in them. Investigation of the thermal conductivity of such systems in the process of their solidification in the course of a long time is therefore very important for the study of problems of the interrelation between the structural, thermal, and strength characteristics of binders.

The present work represents the first investigation of the thermal properties in the process of formation of a capillary porous structure of the solidification of a modeling monomer binder, viz., gypsum.

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