THERMOPHYSICAL CHARACTERISTICS OF THE AMORPHOUS PHASE OF IRRADIATED POLYETHYLENE

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Using experimental data on heat capacity, thermal conductivity, and density of irradiated polyethylene obtained earlier, crystallinity values and thermophysical parameters of the amorphous phase are calculated as functions of dose absorbed and irradiation and measurement temperatures.

Earlier studies of the present authors [1, 2] have yielded data on the thermophysical constants of industrial polyethylene irradiated in a reactor at dosages of 0-5000 Mrad. Irradiation was performed at 80°C (series I) and 30°C (series II). Heat capacity c was measured for the series I polyethylene, and thermal conductivity λ and density ρ for series I and II.

This present study will utilize the experimental data obtained earlier to make a quantitative evaluation of the effect of dosage and temperature, as well as irradiation temperature, on the crystallinity x and thermophysical properties of the amorphous phase of polyethylene.

Various authors [3-5] have studied the contribution of the amorphous and crystalline fractions of unirradiated polyethylene to c and λ, although the structure of polyethylene differs significantly from an ideal two-phase system, and processes in the premelting region show a clearly expressed relaxation character. In [6] doubts were raised as to the distribution of the crystalline phase in an amorphous matrix, while the analysis of λ data and calculation of x in [4] is performed in a formal manner. However, no other models were proposed. On the basis of calculation we selected a two-phase model for polyethylene, and since the cross-linking process under radiation occurs basically in the amorphous phase, the thermophysical characteristics of the crystalline phase were taken unchanged. The temperature dependence of c of the crystalline phase c_c and amorphous phase c_a of polyethylene were calculated by Wunderlich [3], λ_c and λ_a by Eucken [7] and Eiermann [4], while ρ was calculated in [8].

For calculation of λ_a, Eiermann used specimens with a known degree of crystallization. Using Eiermann's method, we varied x by irradiation. x was determined either from c for series II specimens, or from ρ for series I specimens, since there were no c data for the latter. The values of $c_c = f(t)$ used are presented in [3-5], all being close to each other in value. The function $\lambda_c = f(t)$ used in the calculations [4] decreases with temperatures as 1/T, and was obtained by Eucken [7] for low-molecular-weight crystals.

The method for determination of c_a of the irradiated polyethylene consists of extrapolating experimental values of c for polyethylene rendered totally amorphous by irradiation to c_a values at D = 0. c_a values were obtained by Wunderlich [3] by extrapolation of heat capacity of polyethylene specimens of differing degrees of crystallization to zero crystallinity, and agree well with the data of [9, 10]. The dosage at which polyethylene amorphizes completely was determined by analysis of experimental data on

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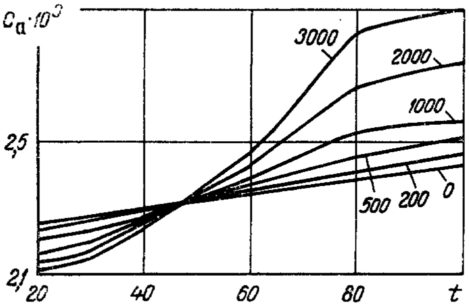

Fig. 1. Heat capacity of amorphous phase of polyethylene versus temperature for various irradiation doses, Mrad. $c_a \cdot 10^3$, J/kg•°C; t,°C.

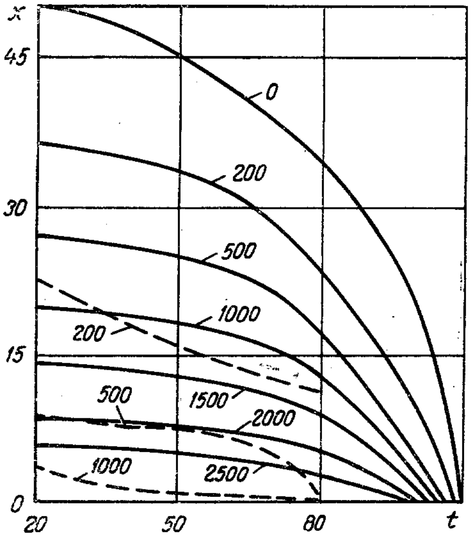

Fig. 2. Degree of crystallization versus temperature for various dosage, Mrad. Solid lines, series II; dashes, series I. x, %; t, °C.

the function c = f(t) for doses of 0-5000 Mrad [1]. The quite diffuse melting peak at D = 3000 Mrad and practical absence of change in c with doses above 3000 Mrad permitted us to set this dose at about 3000 Mrad, whence extrapolation was performed. The linear change of the curve $c_a = f(D)$ seems logical to us for the following reasons. First, in the amorphous phase at doses up to 3000 Mrad the cross-linking process predominates and heat capacity will decrease monotonically with dosage increase. Thus extremal values of c_a are hardly to be expected. Secondly, c_a values at D = 3000 Mrad are quite close to c_a at D = 0, so that the error in linear extrapolation will be small. Results are shown in Fig. 1 (abscissa is temperature). From Fig. 1 it is evident that, at temperatures up to 50°C, c_a decreases with dose due to the significant effect of cross-linking. At temperatures above 50°C the decrease in amorphous matrix rigidity upon crystal destruction begins to predominate.

Accurate determination of the degree of crystallinity x of polymers is quite difficult. A more accurate, but more complex, method of x determination is the use of calorimetric data and the formula

$$c = c_a(1 - x(t)) + c_c x(t) + \Delta H \frac{\partial x}{\partial t}. \qquad (1)$$

The majority of authors [3, 11] neglect the dependence of x on temperature, relying on the expression

$$c = c_a(1 - x) + c_c x,$$

which undoubtedly will lead to errors at high temperatures. The value of the heat of fusion of polyethylene ΔH has been determined quite accurately by a number of authors. Wunderlich [3] and Dole et al. [12] found ΔH = 66.3 cal/g; Billmeyr [13] found ΔH = 65.8; and Quinn and Mandelkern [14], 64.9 and 67.1 ± 2.1 cal/g. In our calculations we took ΔH = 66.0 cal/g. In [15], for calculation of the temperature dependence of x, Eq. (1) was utilized, but instead of solving a differential equation, the authors used the formulation

$$c = xc_c + (1 - x)\, c_a + bH,$$
$$x = a - b(T - T_D),\ b = -\frac{dx}{dt}.$$

In the differentiation the authors discarded the second derivative, which will have an effect at high temperature. As a result, the temperature for completion of crystal destruction was erroneously determined to be 80°C.

To determine x = f(D, t), we rewrote Eq. (1) in the form

$$\frac{\partial x(D,\ t)}{\partial t} + \frac{1}{\Delta H}\,[c_a(D,\ t) - c_c(t)]\, x(D,\ t) = [c_a(D, t) - c(D,\ t)]\,\frac{1}{\Delta H} \qquad (2)$$

with the boundary condition x = 0 at t = t_m = f(D).

TABLE 1. Effect of Porosity on Thermal Conductivity of Polyethylene $\left(1-\frac{\lambda_{ae}}{\lambda_a}, \%\right)$

t, °C	D. Mrad	
	1200	2300
20	6,0	16,0
40	5,8	13,0
60	5,3	11,4
80	4,1	9,8

Numerical integration of Eq. (2) by the Runge method was performed on an M-220 computer. Results of the computation are shown in Fig. 2. The curve for D = 0 agrees well with the data of other authors [16, 17], which confirms the validity of the approach and initial data. It is evident from the curve that the crystallinity of unirradiated polyethylene decreases monotonically, commencing at 30°C. The same method was used to calculate x of irradiated polyethylene (series II) as a function of temperature. The results are shown by the solid lines of Fig. 2.

The degree of crystallinity may also be determined by the densities or specific volumes of the individual phases, a method regarded as sufficiently reliable in the literature [17]. The expression for the degree of crystallinity by weight has the form

$$x=\frac{\rho_c}{\rho}\left(\frac{\rho-\rho_a}{\rho_c-\rho_a}\right) \tag{3}$$

by volume

$$\gamma=\frac{v-v_a}{v_c-v_a}, \quad x=\frac{\rho_c}{\rho}\gamma. \tag{4}$$

The specific volume of the amorphous phase is determined by extrapolation to room temperature of the specific volume value measured at temperatures above 115°C. By extrapolation to D = 0, Ross [18] found ρ_a for polyethylene irradiated to about 400 Mrad to be 0.877 g/cm^3, with unirradiated polyethylene being 0.853 at 20°C. The function $\rho_a = f(t)$ is presented in [8]. Since in the case of the series II polyethylene there were available data on x, obtained from heat capacity, using Eq. (3) it is possible to directly determine $x = f(D, t)$. For series I specimens, Eq. (3) is used by direct substitution. Values of ρ_a calculated from our experimental data for ρ of unirradiated polyethylene and calculated values of x agree well with the data of [8]:

t, °C	ref. [8]	our data
20	0,855	0,855
40	0,842	0,842
60	0,829	0,830
80	0,817	0,818

Calculated values of ρ_a for series II specimens are shown in Fig. 3 (solid lines). From Fig. 3 it is evident that ρ_a decreases with temperature for all radiation doses, with the temperature coefficient remaining practically constant at about $6\cdot10^{-4}$ deg^{-1}. With doses up to 1000 Mrad, ρ_a increases by 6%, then changes more slowly.

ρ_a of series I specimens was determined by extrapolation of experimental data to D = 0 from D = D*, corresponding to complete amorphization of the polyethylene. The value of D* determined by experimental data on ρ of series I samples [2] (commencement of linear change of ρ with dose) lies within the limits 1000-1500 Mrad, and according to data on ρ of these same specimens increases up to approximately 2000 Mrad. The difference in these figures does not affect the results of extrapolation because of the linear change in ρ with dose. The extrapolation is based on the premise that increase in irradiation temperature leads to: 1) acceleration of cross-linking and consequent increase in ρ_a; 2) acceleration of the crystal destruction process. Results of series I ρ_a determination are shown in Fig. 3 (dashed lines). A number of studies have examined the effect of irradiation temperature on the progress of radiochemical processes, in particular, on the amount of cross-linking. In [19, 20] it was shown that except

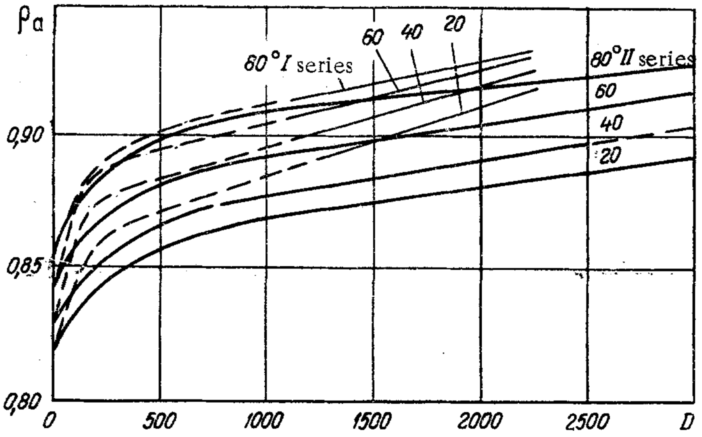

Fig. 3. Density of amorphous phase of polyethylene versus dosage absorbed at various temperatures, °C. Solid lines, series II; dashed lines, series I. ρ_a, g/cm^3.

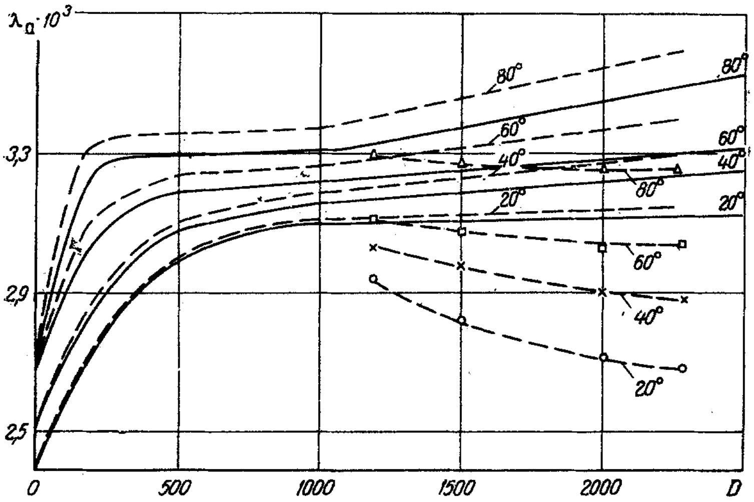

Fig. 4. Thermal conductivity of amorphous phase of polyethylene versus absorbed dose at various temperatures, °C. Solid lines, series II; dashed lines, series I; points, experiment.

for a narrow range near the melting point the degree of cross-linking does not change with temperature. At the same time in [21, 22] the amount of crosslinking changed by a factor of 4 for a change in irradiation temperature from -196 to +73°C.

The dependence of x on temperature (series I) calculated from Eq. (3) with extrapolated values of $\rho = f(D, t)$ is shown in Fig. 2 (dashed line). The degree of crystallinity decreases sharply with increase in radiation temperature.

The thermal conductivity of unirradiated polyethylene has been analyzed by a number of authors [4, 23-26]. The results have been contradictory. Eiermann used the Maxwell-Eucken equation for λ:

$$\lambda = \frac{2\lambda_a + \lambda_c + 2\gamma(\lambda_c - \lambda_a)}{2\lambda_a + \lambda_c - \gamma(\lambda_c - \lambda_a)}\lambda_a. \tag{5}$$

λ_a was determined by comparing two specimens with different degrees of crystallization, assuming that γ is independent of temperature. It was shown that λ_a increases with temperature to -20°C, decreasing slightly at temperatures above -20°C. This change in the temperature dependence was explained by the author by an assumption that x remained constant. But the λ_a calculated in [23] with consideration of the temperature dependence of x gives a similar $\lambda_a = f(t)$ curve. Hattori [24] studied the effect of molecular weight on λ in linear polymers, including polyethylene, and demonstrated a monotonic increase in λ in the interval 20-100°C. Hattori indicates that the vitrification temperature T_D may be considered to be the temperature at which microbrownian motion of the polymer molecules is excited. Sheldon [5], using a different model for the distribution of the crystalline phase in the amorphous matrix, obtained lower values of λ_a than in [4], while maintaining the same change in λ_a with temperature. Anderson [25] relates the decrease in λ_a with increase in temperature above T_D to increase in free molecular volume. Arutyunov [26] presents a generalized dependence of λ on the fraction of free volume f for amorphous polymers above T_D, giving a decrease in λ_a above T_D, using the data of [4] for polyethylene.

In our study, using the Maxwell model for the two-phase system, we attempted to evaluate the effect of irradiation on the value of λ_a. λ_a for unirradiated polyethylene was calculated from Eq. (5), with the use of γ from Fig. 2 and λ_c from [4]. Results of the calculation are presented in Fig. 4 (D = 0). Our data for the relative change of $\lambda_a = f(t)$ contradict those of [4, 5, 25] and agree with those of [24]. Evidently, the actual behavior of λ_a with t depends on the relationship of two processes — increase in free volume and microbrownian motion of portions of the polymer chains. We thus pose the question: what is the reliability of the results of λ_a behavior with temperature obtained by the different authors, considering experimental error? An analysis shows that with an error in λ measurement of ±4%, use of the Maxwell-Eucken equation does not give a reliable temperature dependence of λ_a, since the change in λ_a in the range 20-80°C (10-15%) lies within the limits of computation error. We thus consider that the question of temperature dependence of λ_a of polyethylene remains unanswered.

Results of calculation $\lambda_a = f(D, t)$ are presented in the same Fig. 4. It is evident that a sharp change (~15%) in λ_a occurs at doses up to ~500 Mrad, and that it changes more slowly thereafter. The behavior of $\lambda_a = f(D)$, obtained from calculations, is identical to that of $\lambda = f(D)$ of polyethylene at t = 110°C [2], i.e., practically amorphous.

In the case of series I specimens no similar calculations were performed, since the specimens proved to be porous, indicating the presence of a third phase. Thus $\lambda_a = f(D, t)$ was determined by another method. It was assumed that λ_a/ρ_a remained constant for one and the same dosage for change in the irradiation temperature, because of the identical mechanisms of their change with radiation. Data on ρ_a and λ_a for series II specimens and on ρ_a for series I specimens permitted determination of ρ_a for the series I specimens. The λ_a values obtained correspond to the thermal conductivity that would exist in the absence of porosity.

A method for estimating the effect of porosity on λ_a in polyethylene is presented in [4]. To use this method a detailed analysis of the pore microstructure is necessary, which analysis we did not perform. Consequently, a different approach was employed. Experimental data on λ of series I specimens at doses above approximately 1000-2000 Mrad, where the polyethylene is practically completely amorphized (λ_{ae}) permits determination of the effect of pores and fissues on λ_a.

The effect of porosity increases with dose and falls with measurement temperature, as was shown by us previously [2].

The quantitative estimates of the effect of radiation on thermophysical characteristics of the amorphous phase of polyethylene obtained here may prove useful in predicting the radiation stability of polyethylene and similar polymers.

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