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Thermophysical Properties of Irradiated Polymers

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The effect of ionising radiation on the specific heat, thermal conductivity, thermal diffusivity, and density of partially crystalline (polyethylene, polypropylene, polytetrafluoro-ethylene) and of amorphous polymers (polystyrene, poly(methyl methacrylate)) is discussed. Analytical models of the mechanism of heat conduction, and the development of anisotropic thermal conductivity in amorphous polymers, are examined. The influence of ionising radiation on the thermophysical properties of composite materials is analysed. 79 references.

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I. INTRODUCTION

Information about the influence of ionising radiation on the thermophysical characteristics of polymeric materials is important, for two reasons. Firstly, because the thermal state of constructional materials used in the new technologies in the presence of powerful ionising radiations is determined by the thermal constants of these materials, and secondly because the structure of the polymer can be inferred from the temperature and dose dependence of the thermal conductivity and (even more directly) of the specific heat. Thus information on the phonon mechanism of energy transfer in polymers and on the phase composition of the partially crystallised materials can be obtained from the changes in thermal conductivity λ. Measurements of the specific heat c_p of solid polymers have been used to study molecular mobility, relaxation processes, phase transitions, etc.; the high precision of calorimetric methods over a wide temperature range ensures that the information is unambiguous.

In spite of the importance of the influence of ionising radiation on the thermophysical properties of polymers, very few experimental data have been published on this topic (compared, for example, with the number of data on radiation effects on the mechanical and dielectric properties of the same materials). This may be due to the practical difficulty of measuring λ, c_p, and the thermal diffusivity coefficient a, and to the shortage of apparatus offering adequate precision. Another reason is that marked changes in thermophysical properties are observed only for very high absorbed doses of radiation (up to tens of Mrad). This causes practical difficulties and necessitates the use of fairly powerful radiation sources.

Results so far reported indicate a large difference between the radiation effects in crystalline and in amorphous polymers. Published data on the effects of ionising radiation on the specific heat c_p, the thermal conductivity λ, the density ρ, the degree of crystallinity x, and the melting point will therefore be reviewed separately for partially crystalline and for amorphous polymers.

II. PARTIALLY CRYSTALLINE POLYMERS

There are two important differences between simple solids and solid linear polymers: the chemical structure of the polymers is far more complex, and their physical structure is often metastable, and variable for a given chemical structure. This makes the thermal properties of the polymers a function of the thermal history of the sample, and also of the heating rate (in dynamic experiments). Because of the strong influence of the thermal history on the structure of polymers, both amorphous and crystalline, most of the discrepancies in published data on radiation interaction with polymers can be explained by differences in morphology between the different samples.

1. Polyethylene

a) *Specific heat of polyethylene.* Though the specific heat of polyethylene (PE) has been studied over a wide range of temperature in many laboratories (see, for example, reviews in Refs.1 and 2), relatively little work has been done on the effect of irradiation on c_p[3-5]. Radiation effects on c_p have been studied only above 20 °C. Thus, PE of PE-500 grade with an initial density of 915 kg m^{-3} and c_p = 1.91 kJ kg^{-1} K^{-1} has been irradiated[4] with γ quanta from a ^{60}Co source up to a dose of 6.1 Mrad. The irradiation temperature T_i and the measurement temperature T_m were both ~ 30 °C. As the dose was increased, c_p fell monotonically to 1.45 kJ kg^{-1} K^{-1}. This decrease in specific heat was ascribed[4] to the formation of cross-links between the linear macromolecules, which lowers the number of internal degrees of freedom.

High-pressure PE (c_p = 918 kg m^{-3}) was irradiated[5] in air with ^{60}Co γ quanta at a dose rate of 7.5 rad s^{-1} and T_i = 40 °C to give a range of absorbed dose up to 50 Mrad. Each sample was subjected to at least two heating runs (heating rate ~ 1K min^{-1}). The temperature dependence of c_p between 20 and 70 °C was linear for the PE samples which had not

been irradiated. Beyond this range the increase of c_p becomes much steeper, suggesting the onset of melting of the crystalline phase. The melting point (T_f) was found to be 110 °C. In the range 110–113 °C a large exothermic effect was observed, and c_p fell steeply from ~ 11.0 to ~ 1.6 kJ kg^{-1} K^{-1}. Further heating to 120 °C increased c_p to 2.5 kJ kg^{-1} K^{-1}. Repeated heating of the same sample (using the cycle: first heating to 90 °C, cooling, second heating to 140 °C) lowers the melting peak (observed in the second heating period) by 2 K. In the region of 95 °C a pre-melting effect occurs during the second heating: a sharp increase in c_p from 3.7 to 6.5 kJ kg^{-1} K^{-1} followed by a decrease to 5.1 kJ kg^{-1} K^{-1}. Very similar effects are observed for c_p in irradiated samples (Fig. 1a–1c). The position of the c_p maximum on the successive curves of the repeated heating cycle coincides with the maximum heating temperature of the preceding run. This phenomenon persists until all the crystals initially present in the sample have been melted.

A large number of melting peaks on the curve of c_p against T for PE was reported also in Ref. 6. An increase in the absorbed dose caused a marked decrease in the height of the main melting peak: at 30 Mrad the peak became diffuse, and at 50 Mrad it disappeared completely. The pre-melting peaks disappeared at doses greater than 10 Mrad, and the 110–120 °C exothermic effects disappeared at doses greater than 5 Mrad. At the same time as the heat of melting, the melting point T_f also decreases (as shown by the coordinate of the specific heat maximum).

The initial model used to explain the changes in thermophysical properties of partially crystalline polymers is usually the classical two-phase model[7–9], even though the structure of polyethylene is quite different from that of an ideal two-phase system, and the presence of marked relaxation processes in PE (pre-melting region) is well recognised. Godovskii[10] has criticised the hypothesis of a crystalline phase embedded in an amorphous matrix.

According to published data on the temperature dependence of c_p, the melting processes can extend over the temperature region 80–113 °C. This is evidence of a wide range of crystallite sizes, each crystalline formation having its own melting point. The "boundary melting" effect discussed in Ref. 11 may also be partly responsible for the wide melting range of these materials.

The nature of the non-equilibrium melting process is determined by the previous history of the sample: the situation is further complicated by the possibility of new partial crystallisation at a stage during the melting process when the temperature is quite high and the relative amount of crystalline phase is substantially decreased. This possibility is confirmed by the exothermic effects in the pre-melting region of both the irradiated and the non-irradiated PE.[5] When the system reaches a high enough temperature all the crystals suddenly melt. A similar phenomenon was observed in a study[12] of the thermodynamic behaviour of PE single crystals. The gradual flattening out of the $c_p = f(T)$ curve with increase in the absorbed dose is obviously caused by a

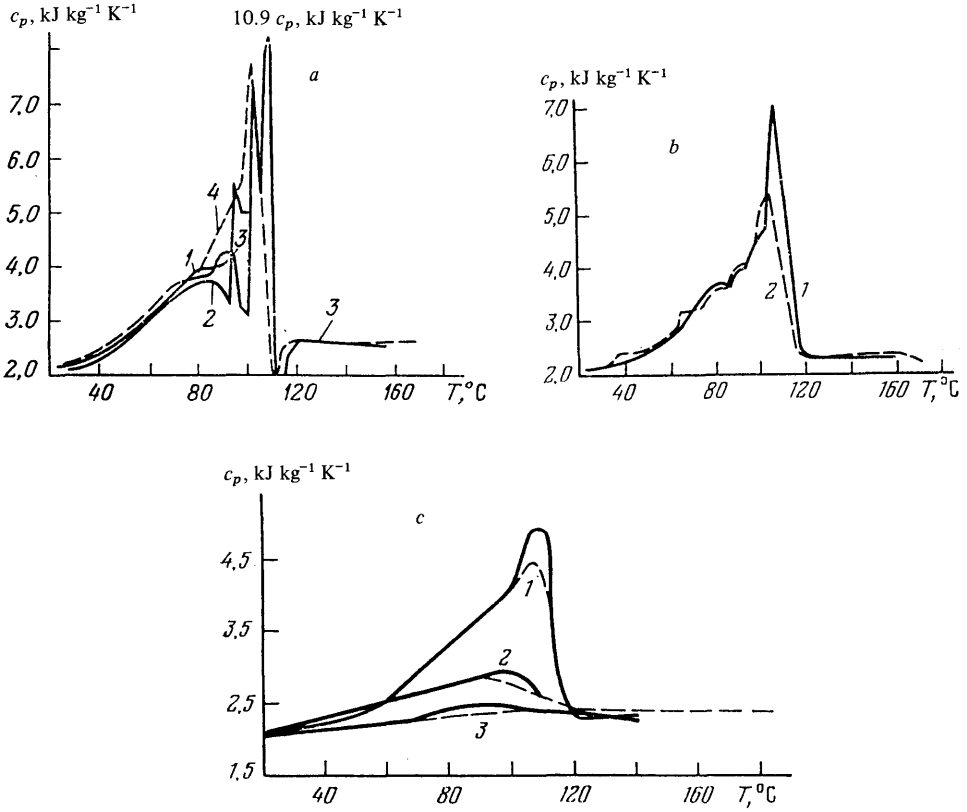


Figure 1. Temperature dependence of the specific heat of high-pressure polyethylene. (*a*) 2 Mrad dose, heated to different temperature: 1) 90, 2) 100, 3) 150, 4) 160 °C. (*b*) 5 Mrad dose: 1) first heating, 2) second heating. (*c*) different doses: 1) 10, 2) 30, 3) 50 Mrad (full lines denote first heating, broken lines second heating[5]).

decrease in crystallinity. The characteristic decrease in T_f and in the c_p maximum observed in all the samples subjected to heating cycles may be due to a decrease in size of the crystallites formed in the polyethylene during the cooling period.

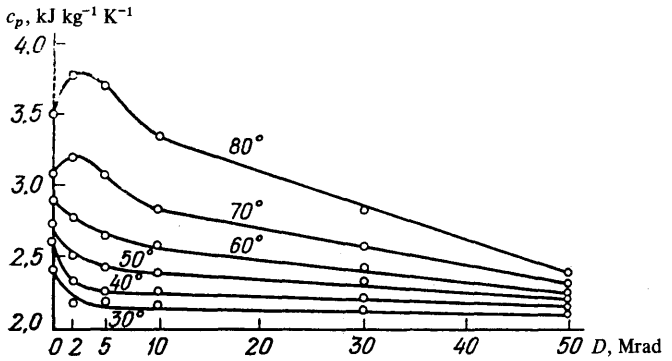


Figure 2. Dependence of the specific heat of high-pressure polyethylene on the dose of radiation for different measurement temperatures[5].

Plots of c_p against the absorbed dose are shown in Fig.2 for different measurement temperatures T_m.[5] In the 30–50 °C temperature range the parameter c_p decreases monotonically as the dose increases, but at and above 70 °C it goes through a maximum at D = 2 Mrad. Since c_p is higher for an amorphous than for a crystalline PE phase[13], the decrease in crystallinity produced by the irradiation should make the specific heat vary in the same sense as the dose. However, when the PE molecules become cross-linked the increased rigidity of the system (or, in other words, the loss of internal degrees of freedom) causes c_p to decrease. Evidently, at 30–50 °C the cross-linking process predominates over the amorphisation process for the whole range of doses. At T_m = 70 °C (and above) the intensification of the melting process increases the relative amount of amorphous phase, and the specific heat can therefore increase for doses up to ~ 2 Mrad, but at higher levels of cross-linking c_p begins to decrease with increasing dose.

Some of the published data on the effect of radiation-induced cross-linking on T_f in PE crystals are contradictory. Both a decrease in T_f with increase of dose[14] and an almost constant T_f[15] have been reported. Ushakov and co-workers[16] irradiated low-pressure PE samples (LPP) in the solid state (T_i = 45–50 °C) and as melts (T_i = 130–140 °C). In the solid samples T_f fell from 135 to 118 °C for a dose of ~ 5.5 Mrad, rising again to 124 °C at a dose of 11 Mrad, whereas irradiation in the melt lowered T_f to 50 °C even at a dose of 5.5–6 Mrad. For high-pressure polyethylene (HPP) at T_i = 45–50 °C the melting point T_f goes through a minimum as the dose increases (~ 107 °C for D = 6 Mrad), and then rises again to its original value (113 °C for D = 11 Mrad). As was stated above, T_f for HPP has been found[5] to decrease from 110 to 106 °C as the dose is increased to D = 10 Mrad. The maximum T_f value for the diffuse endothermic peak at a dose of 30 Mrad was 100 °C.

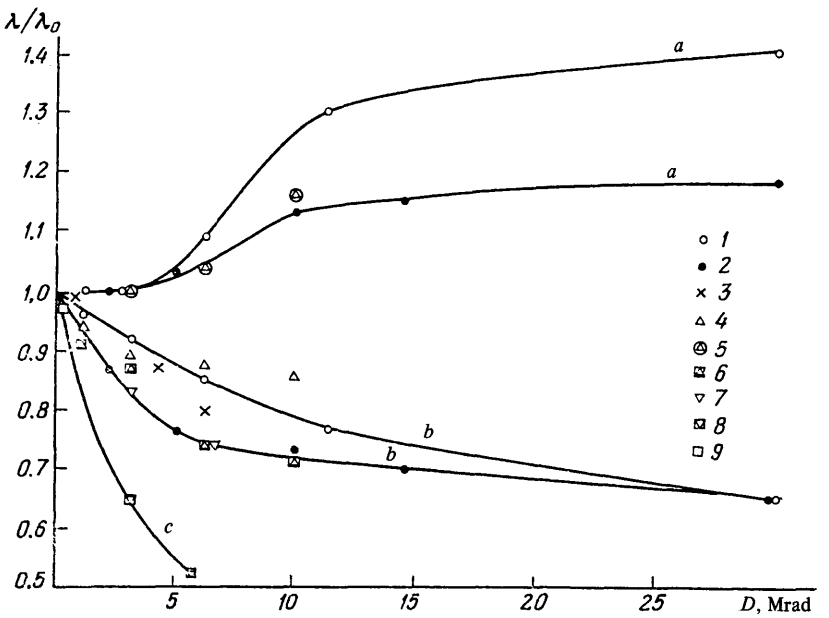


Figure 3. Relative thermal conductivity of polyethylene as a function of dose of radiation for different measurement temperatures [30 °C (*a*), 150 °C (*b*), and −150 °C (*c*)]. HPP: 1) from Ref.17, 2) from Ref.19, 3) from Ref.4, 4) from Ref.18, 5) from Ref.18, 6) from Ref.18; LPP: 7) from Ref.18, 8) from Ref.18, 9) from Ref.9.

Radiation-induced cross-linking causes a decrease in the degree of crystallinity and in the size of the crystallites, which lowers T_f, but on the other hand it also imposes some molecular order within each crystal, as shown by measurements of double refraction in spherulites of irradiated PE.[16] This local ordering effect causes an increase in T_f. As a result, the real behaviour of T_f in particular samples of PE becomes a function of the initial crystallinity and of the irradiation temperature.

The decrease in T_f to 105 °C in the second heating run (mentioned above) is practically constant for doses up to 10 Mrad.[5] PE has a "memory", and when the sample is cooled new crystals are formed on the original sites, but these are smaller as a result of cross-linking in the crystalline phase and they melt at lower temperatures. Since the thermal conditions for recrystallisation are approximately the same in different samples, we can expect constant values of the crystallite size and therefore also of T_f.

b) Thermal conductivity and density of polyethylene. As in the case of the specific heat, the effect of irradiation on the thermal conductivity λ of polyethylene is largely determined by the irradiation conditions and by the initial crystallinity of the polymer. Studies of radiation effects on λ in PE are mentioned in several papers[3,4,9,17-19]. Since λ is higher in a crystalline than in an amorphous phase (the mean free path of phonons being longer in crystals than in amorphous phases, where it is limited by the disordered arrangement of the atoms to a value of the same order as the interatomic distance) we can expect a decrease in λ in irradiated polyethylene. But at the same time the cross-linking of the molecular chains increases the packing density of the macromolecules, thus increasing the effective mean free path of the phonons, i.e. increasing λ. As a result, the behaviour of the thermal conductivity in irradiated samples depends on the relative magnitude of these competing processes.

Data on the relative changes in λ for HPP and LPP as a function of dose of radiation are shown in Fig.3. Some workers[4,9] irradiated their samples with γ quanta at T_i = 30 °C, others[18] used an electron beam (E = 1 MeV) giving a dose rate of 1.7 krad s^{-1} and absorbed doses up to 10 Mrad. In Refs.17 and 19 mixed radiation from a reactor was used at T_i = 80 °C. In Fig.3 curves *a* and *b* are drawn through the experimental points of Refs.17 and 19 for T_m values of 150 and 30 °C respectively, and curve *c* is drawn through the points of Ref.9 (T_m = −150 °C, LPP). The difference between the results from Refs.17 and 19 may be due to differences in the crystallinity of the initial samples. In the range of measurement temperatures (T_m) from −150 to 80 °C the λ value of polyethylene decreases as the absorbed dose is increased to ~ 20 Mrad (see Fig.4 below), indicating amorphisation of the polymer by the radiation. A gradually increasing contribution from radiation-induced cross-linking effects eventually stops the changes in λ, assisted by the increasing contribution from degradation processes. At the higher measurement temperatures ($T_m > T_f$) the crystallinity of the sample is low (or zero). Therefore the changes in λ due to radiation-induced cross-linking become more marked. However, the processes responsible for changes in λ are gradually inhibited by polymer degradation effects.

The influence of dose on λ at $T < T_f$ is more marked below the glass transition temperature (T_g) than in the region $T_g < T < T_f$. From the standpoint of the two-phase model this is explained by the strong temperature dependence of the thermal conductivity of the crystalline phase ($\lambda_{cr} \propto 1/T$) as compared to that of the amorphous phase (λ_a). As a result, the difference $\lambda_{cr} - \lambda_a$ increases sharply as the temperature falls. Under these conditions the effect of the dose of radiation, which lowers the crystallinity, becomes much stronger.

The effect of the irradiation temperature T_i on the changes in λ in polyethylene is shown in Fig.4, using data from Ref.19. We should note that a visual examination of the cross-section of samples irradiated at T_i = 80 °C (dose rate P = 200 rad s^{-1}) revealed small pores when the dose exceeded 2 Mrad, whilst at higher doses even cracks were observed. The number and size of these defects increased with the dose, suggesting gas evolution during irradiation. At T_i = 30 °C (P = 13 rad s^{-1}) the gaseous hydrolysis products can diffuse into the surroundings without producing large internal stresses. It is clear from Fig.4 that though the curves for two series of measurements at different irradiation temperatures have the same shape, the absolute values of λ are 15–20% lower for T_i = 80 °C than for T_i = 30 °C. This is due to differences in crystallinity and porosity between the samples. As the temperature of the sample increases, the degree of crystallinity decreases, and the thermal resistance of the pores decreases because of the increasing contribution from radiative heat transfer[20]. The net result is a decrease in the difference between the λ values for two series of experiments as a function of dose for T_i above 80 °C. Thus for T_i = 30 °C and a dose of 23 Mrad the difference between the λ values is 19%, and for T_i = 100 °C it is 8%.

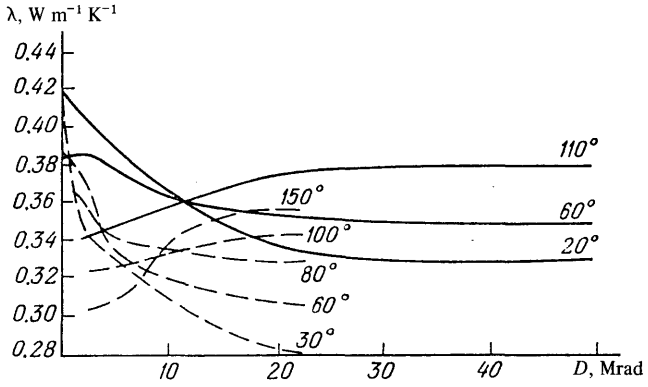


Figure 4. Dependence of the thermal conductivity of high-pressure polyethylene on the dose of radiation for different measurement temperatures (full curves for T_i = 30 °C, broken curves for T_i = 80 °C[19]).

A high initial crystallinity results in a steeper dose dependence of the λ value of polyethylene. Thus[9] even at a dose of 0.3 Mrad the λ value of polyethylene of density ρ = 947 kg m^{-3} is decreased by 3%. The difference in the behaviour of λ between HPP and LPP is clearly shown in Fig.3.

The thermal conductivity of polymers is known to be closely correlated with their density, since an increase in density causes an increase in the phonon mean free path, and hence in λ. Evidently, changes in density induced by radiation should also depend on the irradiation temperature. It has been shown[21] that irradiation of HPP with doses of up to 20 Mrad produces a minimum on the $\rho = f(D)$ curve at D = 5 Mrad (T_m = 20 °C), while the density increases monotonically from ρ = 780 to ρ = 890 kg m^{-3} at D = 20 Mrad (T_m = 150 °C). Data[17,19,22] on the effect of irradiation temperature (T_i) on the shape of the $\rho = f(D)$ curves for HPP are shown in Fig.5. In every case the temperature of the sample during the measurement (T_m) was 20 °C.

Analogous results were obtained[23] by using mixed (gamma and neutron) radiation at T_i = 80 °C. In this case the density minimum was obtained at a dose of 4–5 Mrad. On the other hand, measurements for T_i = 30 °C gave a monotonic increase in ρ with dose of radiation[4] from the initial value of 915 kg m^{-3} to 1005 kg m^{-3} for D = 6.1 Mrad.

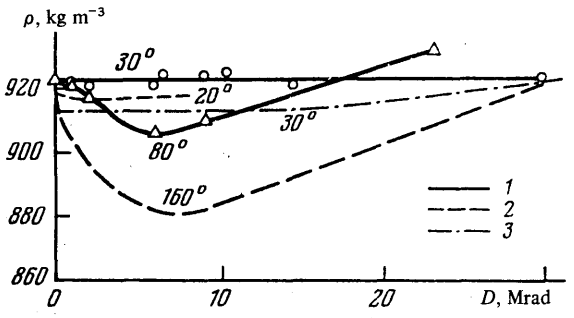


Figure 5. Density of high-pressure polyethylene against dose of radiation for different irradiation temperatures: 1) from Ref.19, 2) from Ref.22, 3) from Ref.17.

The mechanism of the change in density of polyethylene is exactly the same as that described above for the thermal conductivity. For relatively low values of T_i (20–30 °C) the amorphisation of the PE (which causes ρ to decrease, since $\rho_{cr} > \rho_a$) is largely compensated by the radiation-induced cross-linking. Under these conditions ρ either remains constant over a wide range of doses or increases slightly. An increase in T_i causes a large increase in the rate of amorphisation without a proportionate increase in cross-linking. The result is a decrease in ρ for polyethylene irradiated with doses up to 5 Mrad, followed by an increase.

The presence of a minimum on the $\rho = f(D)$ curve for T_i = 160 °C (T_f) is due to partial recrystallisation of the sample during the cooling period after irradiation. A monotonic increase in density with dose of radiation for T_i = 150 °C can be obtained[21] by very slow (near-equilibrium) cooling of the sample after irradiation, or by using a preliminary anneal.

Table 1. Thermal diffusivity of irradiated polyethylene[19].

D, Mrad	$10^7 a$, m^2 s^{-1}			D, Mrad	$10^7 a$, m^2 s^{-1}		
	20° C	40° C	80° C		20° C	40° C	80° C
0	2.00	1.71	1.13	10	1.90	1.88	1.21
2	1.99	1.85	1.15	20	1.74	1.79	1.33
5	1.94	1.91	1.18	30	1.69	1.74	1.41

c) Thermal diffusivity of polyethylene. Table 1 gives the thermal diffusivity values (a) of irradiated PE, calculated by the formula $a = \lambda/c\rho$ from the results of Ref.19 for T_i = 30 °C. According to Samoilov[4], radiation-induced changes in the thermal diffusivity of PE measured at $T_m \approx 20$ °C are undetectable for doses up to 6 Mrad. This is not inconsistent with the previous results[19], since the change in a found for the same range of radiation doses with T_m = 20 °C was less than 5%. The dependence of a on the absorbed dose is determined mainly by the behaviour of the thermal conductivity characteristics.

d) Thermophysical properties of the amorphous phase, and crystallinity of polyethylene. Our calculations of these properties[24] were based on the two-phase model of PE. Since cross-linking under the influence of radiation occurs mainly in the amorphous phase, the thermophysical characteristics of the crystalline phase were assumed to be constant.

The temperature dependence of the specific heat of the crystalline phase (c_{cr}) and of the amorphous phase (c_a) in non-irradiated PE was calculated as in Ref.8; the corresponding values of λ_{cr} and λ_a have been reported previously[25,7], and also those of ρ_{cr} and ρ_a.[26] The calculations of λ_a were carried out[7] with samples having different initial levels of crystallinity (x). In our experiments[24] changes in x were carried out by irradiation, using published data[5,19,20].

The parameter x was measured[24] either from the specific heat of polyethylene irradiated at T_i = 30 °C or from the density of PE for T_i = 80 °C. The values of $c_{cr} = f(T)$ used in the calculations[24], taken from Refs.7–9, are internally consistent and very reliable.

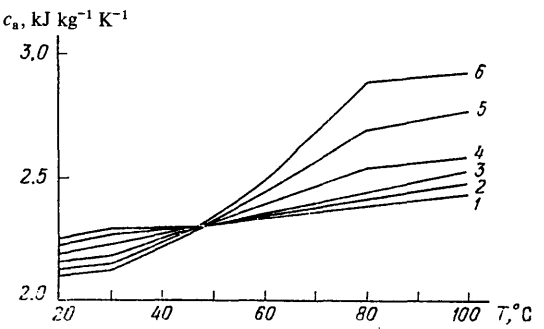


Figure 6. Temperature dependence of the specific heat of the amorphous phase of polyethylene for different doses of radiation[24]: 1) 0, 2) 2, 3) 5, 4) 10, 5) 20, 6) 30 Mrad; T_i = 30 °C.

The method of determining the specific heat c_a of irradiated PE consisted in a linear extrapolation of the experimental plot of c_p for PE samples fully amorphised by irradiation to the value c_a for D = 0.[8] The dose of radiation corresponding to full amorphisation of polyethylene was taken to be 30 Mrad. It was found (Fig.6) that in the range of doses between 0 and 30 Mrad and for T_m less than ~ 50 °C the c_a values decrease with dose as a result of radiation-induced cross-linking (by 10% at T_m = 20 °C). For T_m = 50–100 °C on the other hand the c_a values increase with dose (by 20% at T_m = 100 °C). In this region of temperature the predominant role is played by the decreased rigidity of the amorphous matrix resulting from the breakdown of the crystals.

Exact determination of the degree of crystallinity x of polymers is often difficult. The most accurate (though laborious) method is the calculation of x from calorimetric data, using the expression

$$c = c_a[1 - x(T)] + c_{cr}\, x(T) + \Delta H \partial x/\partial T, \quad (1)$$

where ΔH is the heat of melting of the polymer. Most workers[8,27] ignore the dependence of x on T and use the simplified expression

$$c = c_a(1 - x) + c_{cr} \cdot x,$$

which can lead to serious errors at high temperatures. Shimchuk and co-workers[28] used Eqn.(1), but they avoided solving the differential equation by making the substitution

$$c = c_{cr}\, x + (1 - x)c_a + b\Delta H$$
$$x = a - b(T - T_f);\ b = -\mathrm{d}x/\mathrm{d}T\ .$$

In the differentiation of the expression for x the non-linear terms were ignored[28], because their effect is appreciable only at high temperatures. Because of these assumptions the melting point of the crystals was incorrectly calculated as 80 °C.

To determine $x = f(D,T)$ we have re-written Eqn.(1) as[24]

$$\frac{\partial x(D,T)}{\partial T} + \frac{1}{\Delta H}[c_a(D,T) - c_{cr}(T)]\, x(D,T) = [c_a(D,T) - c(D,T)]\frac{1}{\Delta H} \quad (2)$$

with the boundary condition $x = 0$ for $T = T_f = \phi(D)$. The parameter ΔH for PE was found to be 277 J g^{-1} (according to Refs.8 and 29), 275 J g^{-1} (Ref.30), and 271 or 280 ± 9 J g^{-1} (Ref.31). In the solution of Eqn.(2) a value of $\Delta H = 276$ J g^{-1} was used.

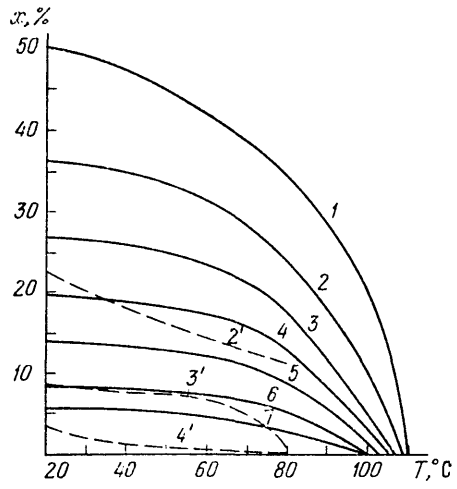


Figure 7. Temperature dependence of the crystallinity of polyethylene for different doses of radiation: 1) 0, 2) and 2') 2, 3) and 3') 5, 4) and 4') 10, 5) 15, 6) 20, 7) 25 Mrad (full lines T_i = 30 °C, broken lines T_i = 80 °C[24]).

The results (Fig.7) of our numerical integration[24] of Eqn.(2) show that the degree of crystallinity of PE decreases at temperatures above T_m = 30 °C (full curves, T_i = 30 °C). The behaviour of x for $D = 0$ is consistent with earlier results[32,33] and confirms the general validity of our method[24].

The $x = f(D)$ dependence shown in Fig.7 agrees on the whole with the results[21] obtained by Nikitina for 20 °C. The only exception is the dose for full amorphisation, which Nikitina gives as 20 Mrad.

It has been reported[34] that when HPP with an initial crystallinity of 50% is irradiated with a dose of up to 2 krad the x value falls to 33%, rising again to 50% for a dose of 1 Mrad before decreasing once again. The temporary restoration of the crystallinity during irradiation is ascribed to the photochemical breaking of the distorted bonds in the keto groups formed by irradiation in air. It is suggested[34] that in this case some of the units can be accommodated in the crystalline lattice. However, this hypothesis is not confirmed by our results.

The degree of crystallinity can be calculated from the densities ρ or from the specific volumes v of the separate phases: the crystallinity by weight is given by the formula

$$x = \frac{v_a - v}{v_a - v_{cr}} = \frac{\rho_{cr}}{\rho}\frac{\rho - \rho_a}{\rho_{cr} - \rho_a} = \frac{1 - \rho_a/\rho}{1 - \rho_a/\rho_{cr}}$$

and the crystallinity by volume by the formula

$$\gamma = \frac{\rho - \rho_a}{\rho_{cr} - \rho_a} = \frac{\rho}{\rho_a}\, x \quad (3)$$

Table 2. Density of the amorphous phase of polyethylene.

T_m, °C	ρ_a, kg m^{-3}	
	(Ref.24)	(Ref.26)
20	855	855
40	842	842
60	830	829
80	818	817

The density of the amorphous phase ρ_a can be determined by extrapolating to room temperature the ρ values measured at $T > T_f$. Ross[23] obtained a ρ_a value of 877 kg m^{-3} at T_m = 20 °C for HPP irradiated to D = 4 Mrad by extrapolation to $D = 0$, and 853 kg m^{-3} for non-irradiated HPP. By using Eqn.(3) for T_i = 30 °C, and data on crystallinity obtained in Ref.24, we have calculated[24] the $\rho_a = f(D,T)$ dependence (see Fig.8, full lines). Over the whole range of radiation doses (up to 30 Mrad) ρ_a increases with dose as a result of radiation-induced cross-linking. The increment $\Delta\rho_a$ for a dose of 30 Mrad is 8–10%. In the range of T_m = 20–80 °C the parameter ρ_a decreases monotonically with temperature for all doses of radiation, and the temperature coefficient is practically independent of the dose (~ 6 × 10^{-4} K^{-1}). The ρ_a value for non-irradiated PE agrees very well with published data[26] (see Table 2). The results of Ross mentioned above[23] on the ρ_a value of irradiated HPP are also consistent with our calculation[24], confirming the validity of the proposed method for calculating crystallinity and for determining the $c_a(D)$ relationship[24].

To calculate the ρ_a values of HPP irradiated at T_i = 80 °C we used[24] a linear extrapolation of the experimental densities ρ for D = 10–15 Mrad (corresponding to complete amorphisation of the PE) to $D = 0$. The ρ_a values obtained in this way (Fig.8, broken curves) are higher than the ρ_a values for T_i = 30 °C, the largest difference corresponding to the measurement temperature T_m = 80 °C. This dependence of the density ρ_a on the irradiation temperature is probably due

to an increase in the yield of radiation-induced cross-links, which has been found[35,36] to increase four-fold as the irradiation temperature is varied from −196 to +73 °C.

By combining these values of ρ_a with Eqn.(3) we calculated the degrees of crystallinity $x(D,T)$ for T_i = 80 °C (shown in Fig.7 as broken curves). As could have been expected, the crystallinity of PE decreases steeply as the irradiation temperature is increased.

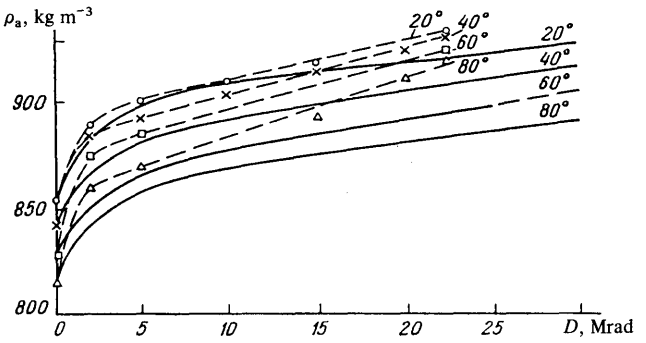


Figure 8. Density of the amorphous phase of polyethylene against dose of radiation for different measurement temperatures: full lines for T_i = 30 °C, broken lines for T_i = 80 °C[24].

The thermal conductivity λ_a of the amorphous phase of non-irradiated PE has been discussed in many papers[7,37-40], usually in terms of the two-phase Maxwell–Eucken model:

$$\lambda = \frac{2\lambda_a + \lambda_{cr} + 2\gamma(\lambda_{cr} - \lambda_a)}{2\lambda_a + \lambda_{cr} - \gamma(\lambda_{cr} - \lambda_a)}\lambda_a \quad . \qquad (4)$$

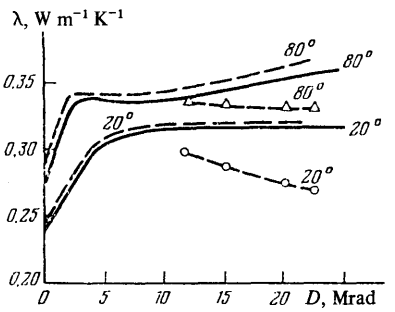


Figure 9. Thermal conductivity of the amorphous phase of polyethylene against dose of radiation for different measurement temperatures: full lines for T_i = 30 °C, broken lines for T_i = 80 °C. The broken lines with experimental points are for samples containing pores (T_i = 80 °C)[24].

Some workers[41,42] have used the Bruggeman model[43] and the Cheng–Vachon model[44] to determine the thermal conductivity of two-phase solid systems. It has been shown[7] that λ_a increases with temperature up to the glass transition temperature T_g = −20 °C, and decreases slightly at higher temperatures. This type of temperature dependence of λ_a has been explained by postulating[7] a constant value of the volume crystallinity γ. However, the same type of $\lambda_a = f(T)$ dependence is obtained[37] even allowing for the temperature dependence of γ. A different model[9] of the disposition of the crystallites in the amorphous matrix gave λ_a values lower than those of Ref.7 without affecting the shape of the temperature dependence. The decrease of λ_a with increase of temperature above T_g is explained[39] in terms of the increased free volume of the molecules. A proposed[40] generalised relationship between λ_a and the fractional free volume for amorphous polymers at temperatures above T_g implies a decrease in λ_a with increase in temperature (we note that data from Ref.7 were used for PE in these calculations). On the other hand, Hattory found[38] that λ_a for PE increases monotonically in the range 20–100 °C, and he explained this by postulating excitation of micro-Brownian motion of the polymer molecules at temperatures above T_g. Similar conclusions were reached by other workers[45,46].

We have calculated[24] the effect of irradiation on λ_a for irradiation temperatures of 30 and 80 °C, using the Maxwell–Eucken model [Eqn.(4)] with the x values given in Fig.5 and λ_{cr} values from Ref.7. Increasing the dose to 5 Mrad produced a marked increase in λ_a (15%). Beyond this point λ_a increased more slowly (see Fig.9). The $\lambda_a = f(D)$ curve is identical in shape to $\lambda = f(D)$ for almost completely amorphous PE at T_m = 110 °C (see Fig.4).

Table 3. Effect of porosity on the thermal conductivity of amorphous polyethylene[24].

T_m, °C	$(1 - \lambda_{ae}/\lambda_a) \times 100$, %	
	D = 12 Mrad	D = 13 Mrad
20	6.0	16.0
40	5.8	13.0
60	5.3	11.4
80	4.1	9.8

The λ_a values for T_i = 80 °C could not be determined by this method because the samples of irradiated PE were found to be porous. It was argued[24] that for a given dose of radiation the ratio λ_a/ρ_a must be independent of the irradiation temperature, since the same mechanism was assumed to apply to both radiation-induced changes. The λ_a values obtained in this way were 2–4% higher than those for T_i = 30 °C: they correspond to the thermal conductivity which would be observed in samples without pores. By comparing these results with experimental data for λ_a (T_i = 80 °C) obtained at doses greater than ~ 10–12 Mrad (λ_{ae}), and therefore with almost fully amorphised PE, the influence of pores and cracks on λ_a was determined (see Table 3). The effect of porosity increases with dose of radiation and decreases with temperature.

It follows from those results[24] that an increase of T_m from 20 to 80 °C increases λ_a by 10%, which agrees with some published results[38,45,46] but not with others[7,9,37,39]. Evidently, in practice the dependence of λ_a on T_m is determined by the relative importance of two processes: the increase in free volume and the micro-Brownian motion of the sections of the polymer chain.

We have calculated the reliability of these results by allowing for the experimental error. Our analysis showed that if the measurement error of λ is ±4% the Maxwell–Eucken model

(like many other models) cannot give a reliable indication of the variation of λ_a with temperature, since the changes in this parameter between 20 and 80 °C are only 5–15% and lie within the uncertainty limits of the calculation. We must therefore conclude that the nature of the temperature dependence of λ_a in PE is still a live issue.

Nevertheless the gradual damping of the increase of λ_a produced by an increase in the absorbed dose[24] seems to support the micro-Brownian motion mechanism, since an increase in the number of radiation-induced cross-links should suppress this motion more rapidly than it lowers the molecular free volume.

2. Polytetrafluoro-ethylene

a) Density and crystallinity of polytetrafluoro-ethylene. Polytetrafluoro-ethylene (PTFE) is a partially crystalline polymer in which the degree of crystallinity (unlike that of PE) is increased by irradiation, even with small doses. This behaviour is explained by assuming the formation of molecular fragments (during the radiation-induced degradation) which can combine to form small crystallites[74,48]. Quantitative results on the increase in crystallinity caused by irradiation have been published by various workers[19,49–52]. The following dependence of the density ρ (kg m^{-3}) on the crystallinity x has been proposed[53]

$$\rho = 2000 + 300\,x \ .$$

Table 4. Density and crystallinity of polytetrafluoro-ethylene.

D, Mrad	ρ, kg m^{-3}	x, %	Refs.	D, Mrad	ρ, kg m^{-3}	x, %	Refs.
0	2155	62	[19]	0	2156	—	[51]*
0.17	2234	72	[19]	0.001	2166	—	[51]*
1.26	2246	82	[19]	0.01	2183	—	[51]*
0	2154	54	[49]	0	2160	50	[52]**
0.05	2198	67	[49]	0.01	2210	65	[52]**
1.90	2222	74	[49]	0.04	2240	80	[52]**
0	2180	—	[51]	0	2190	60	[52]***
0.02	2221	—	[51]	0.01	2280	92	[52]***
1.00	2248	—	[51]	0.10	2290	95	[52]***

* Data for two samples with different initial densities.
** Irradiated *in vacuo*.
*** Irradiated in air. Density measured by i.r. spectroscopy.

Data on the effect of irradiation with γ quanta from ^{60}Co on the density and crystallinity of PTFE (for $T_m \cong 20$ °C) are given in Table 4. According to Ferse and co-workers[52] the volume of the pores produced in the samples by the irradiation was 0.57% for a dose of 10 krad and 1.4% for a dose of 40 krad. The melting point of PTFE decreases (as the dose of radiation is increased) from 340 °C for $D = 0$ to 334 °C for $D = 10$ krad and 314 °C for $D = 1$ Mrad[51]. This decrease in T_f is discussed by the authors in terms of an increase in the density of radiation-induced cross-links.

b) Thermal conductivity of polytetrafluoro-ethylene. Radiation-induced change in λ for PTFE have been observed[19,49]. It was found[49] that λ is practically independent of T_m between 10 and 180 °C, with a value close to 0.27 W m^{-1} K^{-1}. Small changes in λ were observed at $T_1 = 20$ °C and $T_2 = 125$ °C, and ascribed to a phase transition of the first kind in the crystal lattice of PTFE (T_1) and to relaxation processes in the amorphous phase (T_2). Irradiation with γ quanta from ^{60}Co to a dose of 1.9 Mrad (dose rate ~ 24 rad s^{-1}) gave a decrease in λ by 8%. At the same time T_1 fell by 1 K for $D = 0.05$ Mrad and by 14 K for $D = 1.9$ Mrad, while T_2 increased.

The changes in λ in PTFE can be explained by the two-phase model of a polymer. The λ value for the crystalline phase increases with temperature[7], since in complex crystals (like those of PTFE) the mean free path of phonons L is comparable to the mean free path for the amorphous phase. This can explain[7] the similarity between the temperature dependences of λ_{cr} and of λ_a. The relationship between λ_{cr} and λ_a for PTFE has been expressed in terms of the corresponding densities[54] as

$$d\lambda/\lambda = 5{,}8\ d\rho/\rho \ .$$

Since $\lambda_{cr} > \lambda_a$, the λ values for PTFE should increase with the degree of crystallinity, as has indeed been reported[53]. A decrease in λ on irradiation, accompanied by an increase in crystallinity, has been ascribed to porosity effects[49].

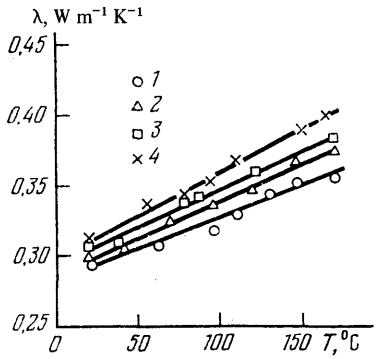


Figure 10. Temperature dependence of the thermal conductivity of polytetrafluoro-ethylene for different doses (D, Mrad): 1) 0, 2) 0.04, 3) 0.17, 4) 1.26[19].

A 6–12% increase in λ, depending on the measurement temperature, has also been observed[19] (as expected) in PTFE irradiated with γ quanta from ^{60}Co to a dose of 1.26 Mrad at a dose rate of ~ 8 rad s^{-1}. At the same time, and in contrast to earlier work[49], a monotonic increase of λ by 20–25% in the temperature range 20–170 °C was observed[19] in both non-irradiated and irradiated samples (Fig.10).

The problem of the temperature dependence of λ in polytetrafluoro-ethylene is not yet fully resolved. Some workers[45,49,55,56] found λ to be practically independent of temperature, whereas others[19,57,58] noted an increase of λ with temperature above 0 °C. Irradiation produces an increase in λ.

3. Polypropylene

Tomlinson and Kline[59] have reported the effect of γ radiation (^{60}Co) on the density and specific heat of isotactic polypropylene (PP) at temperatures between 0 and 160 °C, doses up to 18 Mrad, and a dose rate of 26 rad s^{-1}. The initial crystallinity of the samples (x_0) was 60%.

The λ value of non-irradiated PP samples increases from 0.188 W m^{-1} K^{-1} at 0 °C to 0.200 W m^{-1} K^{-1} at 80 °C before decreasing monotonically to 0.130 W m^{-1} K^{-1} at 160 °C (Fig.11). Melting occurs in the range 127–167 °C; the melting peak corresponds to a temperature of 161 °C.

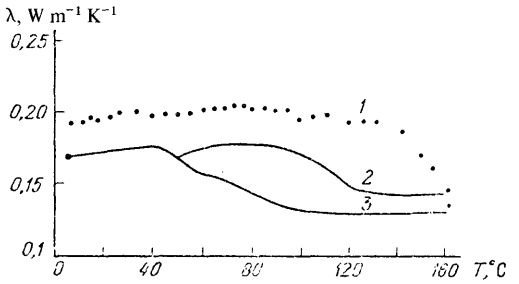


Figure 11. Temperature dependence of the thermal conductivity of polypropylene for different doses (D, Mrad): 1) 0, 2) 6, 3) 18[59].

Irradiation of PP causes breakdown of the crystals. The crystallinity is determined from the area under the exothermic melting peaks as x = 44% for D = 6 Mrad and x = 9% for D = 18 Mrad. Repeated heating does not affect the x value for D = 0, but it lowers the crystallinity from 44 to 14% for D = 6 Mrad and from 9% to 0 for D = 18 Mrad. These changes in crystallinity suggest a decrease in the size of the crystallites with increase in the dose of radiation, and this hypothesis is confirmed by the shift of the melting peak from 161 to 105 °C for D = 6 Mrad and to 63 °C for D = 18 Mrad. The density of PP at 20 °C decreases from 907 for D = 0 to 889 kg m^{-3} for D = 18 Mrad.

As in polyethylene, the λ value of PP decreases with dose of radiation. The maximum change in λ is 30%, and occurs at ~ 100 °C. At temperatures above T_m = 120 °C the thermal conductivity of irradiated samples becomes practically independent of temperature.

III. AMORPHOUS POLYMERS

The extent of radiation-induced changes in the thermophysical characteristics of amorphous polymers is determined mainly by the relative rates of radiation-induced cross-linking and degradation processes respectively. In polymers with a low radiation yield of cross-links, like polystyrene, we cannot expect marked changes in thermal properties. Polymers which suffer degradation under the influence of radiation, like poly(methyl methacrylate), will show changes in these properties: for example, a decrease in thermal conductivity.

1. Polystyrene

a) Specific heat of polystyrene. The specific heat of polystyrene (PS) at helium temperatures has been studied[60] with 2–16 Mrad doses of radiation consisting of 80 MeV electrons. In the calculation of the radiation-induced changes by the continuum model the effect expected from the deformation of the acoustic phonon spectrum was less than 0.5%: the effect actually found amounted to 25%.

The following is a possible mechanism for the change in c_p under the influence of irradiation. An important contribution to the low-temperature specific heat of amorphous polymers comes from low-frequency constrained vibrations of chain segments in regions of the sample where the density is less than the average value. The contribution from these vibrations may be decreased by radiation-induced cross-linking either through a decrease in the number of the segments or through an increase in their average vibration frequency. The radiation effect calculated by adopting this mechanism was 35%, i.e. fairly close to the experimental value.

We have studied[5] the effect of radiation on the specific heat of atactic PS at 30–200 °C with doses of up to 50 Mrad of mixed gamma and neutron radiation at a dose rate of 36 rad s^{-1}. At least up to 80 °C the specific heat of PS was found to be independent of the absorbed dose. The dispersion of the specific heat values for a confidence level of 95% was 0.7% at 30 °C and 1.8% at 80 °C. This result is not unexpected in view of the small distortion of the acoustic phonon spectrum.

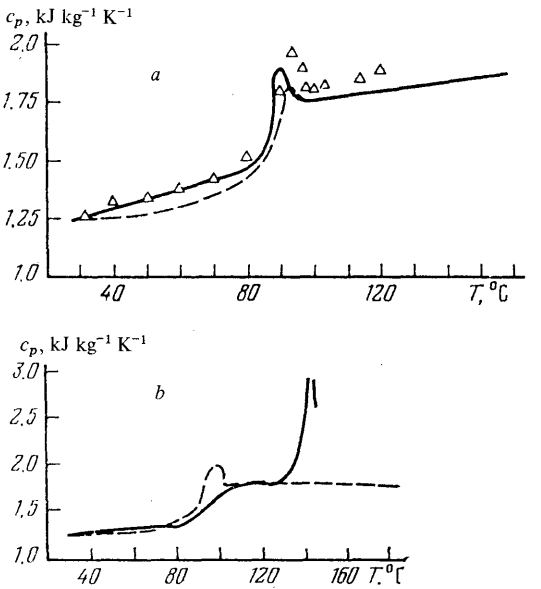


Figure 12. Temperature dependence of the specific heat of polystyrene: (*a*) D = 0, full curve first and second heating, broken curve third heating[5], experimental points from Ref.61; (*b*) D = 2.5 Mrad, full curve first heating, broken curve second heating[5].

Large radiation effects were obtained in the region of the thermal phase changes. Non-irradiated PS shows a sharp rise in c_p from 1.48 to 1.90 J g^{-1} K^{-1} at the glass transition temperature T_g = 87 °C (the average temperature of the glass formation region). These results[5] are fully consistent with earlier reports[61] (see Fig.12*a*). Other reports[62,63] of relaxation transition in the region of 50 °C were not confirmed[5,61].

Irradiation with a dose of 2.5 Mrad (Fig.12*b*) converts the maximum of c_p into a sharp break in the $c_p = f(T)$ curve, and increases T_g from 87 to 93 °C. Further irradiation produces a further increase in T_g (see Table 5).

Clearly defined high-temperature transitions, similar to the endothermic melting peak, were found[5] in samples irradiated with doses greater than 2.5 Mrad. The temperature (T_t) of these effects increased with dose (Table 5). In repeated heating runs the high-temperature effects had disappeared, and they could not be restored by any form of heat treatment.

Table 5. Temperatures of phase transitions in polystyrene[5].

D, Mrad	0	2.5	4.4	10	21	27	50
T_g, °C	87	93	90	97	94	97	102
T_t, °C	—	142	144	146	174	178	192

The presence of this transition in atactic non-irradiated PS was demonstrated[64] by various physicochemical methods including dilatometry, calorimetry, and X-ray diffraction. The transition temperature T_t lies between 115 and 225 °C, depending on the molecular weight of the PS. The appearance of the transition depends also on the heating rate. At low heating rates the transition may be shifted towards T_g, and overlap the glass formation process. In some samples of PS[5,61,65] this transition was not detectable for $D = 0$ because of the low heating rate used (≤ 1 K min^{-1}).

Boyer has pointed out[64] that T_t corresponds to the transition from one amorphous state (characterised by constrained rotations, due to interactions with neighbouring polymer chains) to another amorphous state (in which rotations are relatively free). This type of transition should be present in all amorphous polymers. At low molecular weights the two transitions (T_g and T_t) merge into one, and they can be resolved only if the molecular weight is of the order of 10^4. Unlike the glass formation process, which involves polymer segments of 50–100 carbon atoms, the high-temperature transition relies on the displacement of a whole polymer chain, made possible by the increase in the free volume and in the mobility of the polymer chains produced by changes in the position of their centre of gravity. In support of this model Boyer quotes the fact that the transition is suppressed by cross-linking the polymer (for example, in natural rubber or in polybutadiene).

The observation[5] of the high-temperature transition in irradiated PS at low heating rates, and of the disappearance of this transition in duplicated heating runs, is incompatible to some extent with the Boyer model. We suggest the following possible explanations: 1) the breakdown of relatively dense ordered regions of the quasi-crystal type formed during irradiation, whose size (and melting point) increase with dose, causing the transition temperature to increase; 2) relaxation of the mechanical stresses produced by the irradiation and therefore increasing with dose; 3) evaporation of liquid radiolysis products or the sudden ejection of gaseous products, whose diffusion is hindered under normal conditions.

A surprising analogy is noted between the dependence[5] of T_g and T_t on the dose of radiation (Table 5) and their dependence on the molecular weight of the PS[66]. Fox and Flory have shown[66] that T_g and T_t increase monotonically with the molecular weight, reaching values of $T_g = 100$ °C and $T_t = 192$ °C for $M = 360000$. Thus the radiation-induced cross-linking of PS appears to be equivalent to an increase in molecular weight from the point of view of the mechanism of the high-temperature transitions.

b) Thermal conductivity and density of polystyrene. According to the Klemens theory[67] of the thermal conductivity of amorphous materials the coefficient λ at low temperatures in these materials is determined by longitudinal acoustic phonons, whose mean free path L is determined by scattering phenomena associated with the elastic disordering of the amorphous solid structure. At low temperatures the characteristic wave lengths of the emitted phonons (and therefore also the L values) are much greater than the size of the disordered regions. From this point of view the formation of transverse bonds in the PS as a result of radiation-induced cross-linking will only produce additional point defects in an already disordered structure, and it should not have a marked effect on λ, as long as the average distance between cross-linking points remains greater than the wave length of the phonons (~ 10 Å).

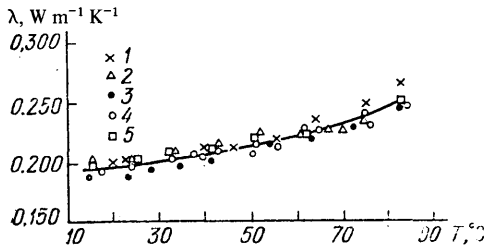


Figure 13. Temperature dependence of the thermal conductivity of polystyrene for different doses (D, Mrad): 1) 0, 2) 2.5, 3) 10, 4) 21, 5) 27[19].

Since the radiation yield of cross-links is small in PS, large changes in λ cannot be expected, even for large doses. Thus, no changes in λ could be detected (within experimental error) with doses of 2–16 Mrad at helium temperatures[60] and with a dose of 27 Mrad at 16–85 °C.[19] On the other hand, an increase in temperature from 16 to 85 °C increases the λ value of polystyrene by 24% (Fig.13). A small increase in the density of PS (by 0.6% at 20 °C) has been noted[19]: clearly, this cannot cause a large change in λ. The distortion of the spectrum of acoustic phonons caused by the transition from helium temperatures to the region of 50–100 °C is clearly insufficient to make the L value comparable with the distance between cross-linking points.

2. Poly(methyl methacrylate)

Poly(methyl methacrylate) (PMMA) is one of the polymers which are degraded by radiation. Therefore we can expect (from the above considerations) relatively small changes in λ for fairly high doses of radiation.

Knappe and Yamamoto[18] studied λ in PMMA by using samples cross-linked with triallyl cyanurate (TAC) or samples of PMMA irradiated to doses of 20 Mrad at a dose rate of 17 krad s^{-1}. For a 10% weight fraction of TAC the molecular weight of PMMA fell from 3.2×10^4 to 8.2×10^3 and the density rose from 1184 to 1191 kg m^{-3}, giving a maximum increase in λ of 10%.

Irradiation of the PMMA to a dose of 1 Mrad had no effect on λ. At a dose of 2 Mrad and T_i = 25 °C the λ value fell by 5–6%. The degradation of the polymer is shown by the decrease in molecular weight (22800 at a dose of 1 Mrad and 10700 at a dose of 2 Mrad). This decrease in molecular weight increases the number of end-groups of macromolecular chains, corresponding to an increase in the relative number of van der Waals bonds, i.e. to a decrease in λ.

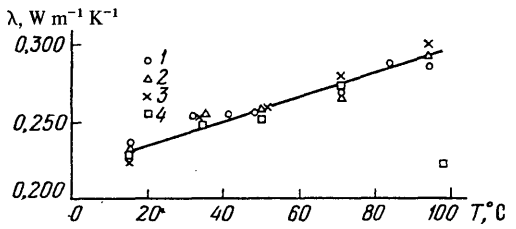


Figure 14. Temperature dependence of the thermal conductivity of poly(methyl methacrylate) for different doses (D, Mrad): 1) 0, 2) 0.1, 3) 0.3, 4) 0.6[19].

These results were confirmed by measurements in our laboratory[19], in which PMMA was irradiated with γ quanta from ^{60}Co to doses of 0.09 and 0.57 Mrad at a dose rate of 3.6 rad s^{-1}. The λ values measured at 18–98 °C increase with temperature by 25% and are independent of dose (Fig.14). At 98 °C a dose of 0.57 Mrad produces marked frothing which causes a sharp drop in λ.

IV. ANALYTICAL MODELS OF HEAT CONDUCTION MECHANISMS

In order to predict radiation effects on the thermophysical properties of polymers we need analytical models which adequately describe the observed changes in these properties.

In some early descriptions[68,69] of the thermal conductivity of amorphous materials the polymer was treated as a series network of elementary thermal resistances corresponding to chemical and to van der Waals types of bonding between atoms. The standard Debye formula for phonon heat conduction was used. According to the elastic constants of these bonds, the thermal conductivity along the main polymer chain is 10 times greater than between chains.

For a series network of thermal resistances equivalent to a cross-linked polymer with n carbon atoms in the chain between the cross-linking points the parameter λ_c can be expressed as

$$\frac{1}{\lambda_c} = \frac{1}{3}\left(1 + \frac{r}{2}\right)\frac{1}{\lambda_1} + \frac{1}{3}\left(2 - \frac{r}{2}\right)\frac{1}{\lambda_2} + \frac{1}{3n}\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right),$$

where λ_1 and λ_2 are the coefficients for the thermal conduction along the chain and between chains respectively, and $r = (M_n/M_c - 1)/n$ is the cross-linking parameter. (M_n is the number-average molecular weight before cross-linking, and M_c is the molecular weight of the chain portions between cross-links.)

For a cross-linked polymer it seems more logical to postulate a series–parallel equivalent network of thermal resistances. If we assume that the radiation effects appear mainly in the cross-links between polymer chains we can confine the changes in thermal resistance to the direction perpendicular to the chains. Under these conditions we can write[18]

$$\lambda_c = 3\frac{\frac{r}{4}\lambda_1 + \left(1 - \frac{r}{4}\right)\lambda_2}{\left(\frac{r}{4} + 2\right)\lambda_1 + \left(1 - \frac{r}{4}\right)\lambda_2}\lambda_1 . \qquad (5)$$

A comparison[18] of calculation and experiment for irradiated polyethylene above the melting point of the crystals and for poly(methyl methacrylate) chemically cross-linked with triallyl cyanurate showed that the λ_c values given by the formulae for series or parallel connection lie well below the experimental values. Calculation by formula (5) gives much better agreement with experiment, though the discrepancy increases with the degree of cross-linking.

One possible reason for the discrepancy is the use of too rough an approximation for the parameter r, by taking the limit

$$r = \lim_{n\to\infty}\left(\frac{M_n/M_c - 1}{n}\right) = \frac{M_g}{M_c},$$

where M_g is the molecular weight of a monomer unit in the chain. It could be useful to determine the absolute values of λ_1 and λ_2 from experimental data for both irradiated and non-irradiated polymers, and to use these values in tests of the various models of thermal conductivity.

V. ANISOTROPY OF THERMAL CONDUCTIVITY

It is clear from the above discussion that crystalline or partially crystalline polymers can show changes in thermal properties on irradiation as a result of changes in phase composition. For amorphous polymers, or for the amorphous phase of partially crystallised polymers, the radiation effect depends on the number of the resulting radiation-induced cross-links and on the extent of degradation of the material. When the yield of cross-links is quite high, for example in the amorphous phase of polyethylene, the radiation effects are substantial. When the yield of cross-links is low (for example, in polystyrene) radiation-induced changes in thermal conductivity are not detected, and in easily degraded materials (for example, poly(methyl methacrylate) and thermal conductivity decreases. At the same time chemical cross-linking of the polymer chains causes λ to increase.

It is interesting to compare the effect of transverse links between the polymer molecules on the λ value of the polymer with anisotropy effects in the thermal conductivity of polymers. The basic reason for anisotropy in the thermal properties of polymers is the difference between the transport of heat along the macromolecular chains and the transport between the chains. Thermal vibrations in the macromolecule are transmitted much more rapidly along the main covalent bonds than along the side bonds. Intermolecular heat transfer in an amorphous polymer is characterised by a definite potential barrier (or thermal resistance) which opposes the transfer of thermal impulse created by the van der Waals interaction forces.

Experimental data (for polystyrene, poly(methyl methacrylate), poly(vinyl chloride), and polycarbonate) on the stretch (η) of oriented polymers gave the following relationship between λ and the thermal expansion coefficient β[2]:

$$\frac{\lambda_\eta}{\lambda_0} = 0.8\frac{\beta_\eta}{\beta_0} + 0.2,$$

where the subscript "η" denotes a stretched polymer. As η is increased, both λ and β increase linearly in the stretch direction, and in the transverse direction both parameters

decrease. The smallest anisotropy is found in polystyrene, and the largest in polycarbonate. The longer (or bulkier) the side-groups in the main chain, the less marked is the anisotropy.

By interpreting the cross-linking of polymer chains as an increase in size of the side-groups in the macromolecule we can establish an analogy between the radiation-induced cross-linking and the mechanical deformation of a polymer, i.e. we can compare the absence of radiation effects on the λ value of an amorphous polymer with the absence of anisotropy in its properties. Conversely, strong radiation effects on λ suggest that anisotropy can be expected. Thus, the anisotropy of λ and β is found[2] to be much more marked in PMMA than in PS. Similar effects from cross-linking (radiation-induced in PS[19,60] and chemical in PMMA[18]) have been obtained for the thermal conductivity of these materials.

If our hypothesis is valid it offers a practically useful corollary: dilatometric measurements of the linear expansion coefficient of non-irradiated polymers could be a valuable tool in studies of radiation effects in the thermal conductivity of polymeric amorphous materials. Clearly, in the absence of substantial anisotropy in the β values the need for radiation experiments disappears.

VI. COMPOSITE MATERIALS

Whereas the polymers considered above are to some extent model materials, for which an analysis of the radiation effects can be fairly reliable, in the case of the practically very important composite materials a comparable analysis is often impossible in our present knowledge of the mechanism of physicochemical phenomena in polymers. The main difficulties arise from the structural complexity of the polymers, from the frequent lack of information on the properties of the separate components, from the non-additivity of those properties, etc.

Dosimetry can present a very difficult problem in composite systems. If the particle size of the components is of the order of a tenth of a millimetre or less in a system where electronic equilibrium is not reached, irradiation with γ quanta or with fast electrons[70] leads to a substantial redistribution of the absorbed energy between substances with different effective atomic number Z, while retaining the overall balance: the dose absorbed by the substance with the smaller value of Z increases, and the dose absorbed by the substance with the larger value of Z decreases. As a result the conventional calculation of average radiation dose can be seriously misleading, since some components of the composite are almost invariably "over-irradiated" while others are "under-irradiated". The magnitude of this effect can reach several tens of per cent, and in some cases 100%, depending on the type (and spectrum) of the radiation.

Evidently, the only prospect of a realistic prediction of radiation-induced changes in the thermophysical properties of composite materials lies in an extensive study of model substances, in the characterisation of the radiation-induced changes in these substances, and in the development of a unified theory of radiation effects on thermophysical properties, followed by application of the results to composite materials and detailed experimental tests of theoretical predictions.

Published experimental data on radiation effects in the thermophysical properties of these materials relate to the thermal conductivity of the composites VK-9 and Kriosil[71]. The VK-9 resin is a compound of the epoxide oligomer ED-20 and polyamide PO-300, and Kriosil consists of the organosilicon polymer DFMKr, the low-molecular polyamide L-20, boron nitride, and Aerosil. Irradiation was carried out with γ quanta from ^{60}Co at 30 °C in air, or in a reactor at 50 °C. The results of our study of VK-9 are summarised in Table 6, those for Kriosil in Table 7.

The radiation-induced changes in these composites were analysed by the two-phase model for partially crystalline polymers, using Eqn.(4). In order to establish whether the decrease in the thermal conductivity of VK-9 on irradiation is due to amorphisation of the partially crystalline polyamide or to degradation of one or both polymers we calculated the λ and λ_a/λ values of the polyamide from published data[72].

Table 6. Thermal conductivity of VK-9, W m^{-1} K^{-1}.[71]

D, Mrad	−100° C	0° C	100° C	180° C
0	0.210	0.231	0.260	0.289
1	0.202	0.224	0.251	0.282
3	0.197	0.219	0.248	0.276
10	0.188	0.219	0.245	0.269
20	0.151	0.186	0.224	0.248

Table 7. Thermal conductivity of Kriosil, W m^{-1} K^{-1}.[71]

D, Mrad	−100° C	0° C	100° C	180° C
0	0.570	0.728	0.810	0.859
1	0.514	0.686	0.748	0.796
2.2	0.500	0.656	0.720	0.756
6.6	0.479	0.600	0.665	0.693
10	0.431	0.576	0.632	0.659
20	0.369	0.479	0.528	0.583

The experimentally observed change in λ for VK-9 at a dose of 20 Mrad is 1.3–2.3 times greater than the change corresponding to full amorphisation of the polyamide (allowing for its proportion by weight in the compound). An analysis of the density of different polyamides as a function of crystallinity, and a study of the changes in density of VK-9 as a function of dose, showed that the amorphisation of the polyamide is far from complete even at a dose of 20 Mrad. It follows that the degradation of the VK-9 resin under the influence of radiation makes a significant contribution to the observed changes in λ. However, further work is needed to determine whether both polymers are degraded or only one, and to what extent.

At temperatures near −50 °C the $\lambda = f(T)$ curves show maxima which gradually decrease as the dose is increased. These maxima disappear at a dose of 20 Mrad. They appear to be related to the glass transition in the components of the polymer. This suppression of a phase transition of the second kind has been observed previously, for example in the specific heat of irradiated polystyrene[5]. A possible explanation is the formation of micro-inhomogeneities during irradiation, each new structure having its own glass transition temperature. The result is a "smearing out" of the phase transition in temperature.

The amorphous polymers (organosilicon polymer and polyamide) in Kriosil are typical of the polymers which are degraded by irradiation. We know[73] that in filled polymers the rate of radiation-induced degradation is much higher than in unfilled organosilicon vulcanised materials, possibly as a result of the stress concentration on the chains in contact with the filler particles. It is clear from the decrease of the

λ value of Kriosil with increase in the dose of radiation (Table 7) that in this system the cross-linking processes cannot compete with the degradation processes. The monotonic decrease in density of Kriosil with dose of radiation (by 12%) is also consistent with the degradation hypothesis.

We note that whereas in Kriosil the magnitude of the radiation effects is almost independent of the temperature at which λ is measured, in the case of VK-9 the change in λ at -100 °C is almost double that at +100 °C. This may be due to the large difference between λ_{cr} and λ_a for the polyamide ($\lambda_{cr}/\lambda_a = 2.0$ at -100 °C and 1.68 at +50 °C), or to a difference in their temperature dependence. Whereas the relationship obtained by Eucken[25] for low-molecular crystals ($\lambda_{cr} \propto 1/T$) applies in our case, the parameter λ_a increases with temperature up to the glass transition point and then slowly decreases.

In both composites the radiation effects were unaffected by the type of radiation used.

VII. REVERSIBLE EFFECTS ON THE THERMOPHYSICAL PROPERTIES

Reversible effects include changes in the properties of polymers initiated by irradiation but which disappear as soon as the irradiation is stopped. These effects can be very strong in the dielectric (and in some of the mechanical) properties of polymers, but as far as the writer is aware no such observations have been reported for the thermophysical properties. This may be due, at least in part, to the practical difficulty of this type of work.

Indirect evidence for the absence of reversible effects in the thermal conductivity of polyethylene comes from our relaxometer[70] study of the components of the absorption from nuclear reactors. The detector of the relaxometer was a rectangular polyethylene prism 50 × 50 mm in cross-section and 150 mm long. From the thermal conductivity coefficients of polyethylene measured after irradiation the temperature fields in the cross-section of the prism were calculated: the results agreed well with those of irradiation experiments at 50–100 °C with doses of up to 10 Mrad and dose rates between 13 and 55 rad s^{-1}.

Radiation-induced gas evolution is a possible reason for the appearance of reversible effects in the specific heat of polymers. At high enough dose rates the pressure of gaseous radiolysis products (mainly hydrocarbons) in the microvolumes of irradiated samples can reach several MPa. On reaching a particular pressure, depending on the mechanical strength of the polymer, the irradiation temperature, etc., the sample develops microscopic cracks and pores. This process continues as long as the absorbed dose continues to increase. The polytropic emission of radiolysis gases involves a decrease in temperature according to the laws of thermodynamics, and therefore it should lead to a change in the "apparent" specific heat of the material. This mechanism may be more easily observed for irradiation temperatures below 0 °C, when the polymers are less plastic.

No reversible effects were noted within experimental error (±5%) in our recent measurements of the specific heat of polyethylene and Kriosil irradiated at 20–90 °C and dose rates of 5.5–11 rad s^{-1} to a dose of 2 Mrad. According to our model these effects (if they exist) can be expected only for doses and dose rates an order of magnitude higher than those used in these experiments†.

† Essentially reversible effects were observed in very recent experiments on the specific heat of polyvinylformal (see B.A.Briskman. et al., Vysokomol.Soed., in press).

VIII. STORED ENERGY OF IONISING RADIATIONS

The analytical prediction of the effect of radiation on the properties of polymers, including their thermophysical properties, requires a knowledge of the energy balance of the interaction between the ionising radiation and the substance.

During the interaction of γ quanta, electrons, or neutrons with the substance being irradiated most of the energy of the secondary electrons or charged heavy particles is dissipated through intermediate forms of excited or ionised atoms and molecules. In the majority of materials the ionisation energy is rapidly converted into heat by recombination processes. However, some of the energy absorbed during irradiation is not converted into heat: this is usually called the stored energy ΔW. Storage can occur, for example, by the formation of crystal defects. In polymers a very important form of energy storage is the generation of cross-links between polymer chains.

Most of the published experimental data on ΔW are estimates of the upper limit of this parameter, obtained from dosimetric measurements directly within the material. The following is a list of the relative values of ΔW for polyethylene (as a percentage of the total energy absorption) obtained in different laboratories: ΔW (%) = 3,[74] 2,[75] 3.7,[76] 0.7,[77] 4,[78] and 3.8%[79].

Weimer[78] found that in polyethylene and for doses up to 1 krad the predominant reaction is exothermic, with a maximum heat evolution at the beginning of the irradiation which accounts for more than 20% of the energy in the absorbed dose. At doses in the region of 1 krad the exothermic reaction is replaced by an endothermic reaction (with energy storage); at a dose of 2 krad the parameter ΔW reaches 4%, and stays constant at higher doses. Polystyrene also shows a characteristic exothermic reaction[78], but when the dose exceed 2 krad, $\Delta W = 0$. In a plastic equivalent to biological tissue with effective atomic number Z proton irradiation gave[76] $\Delta W = 4.2 \pm 0.3\%$. Sabel and co-workers[79] used X-radiation of 30 keV energy and obtained the following values of ΔW: 2.31 ± 0.78% for poly(methyl methacrylate), 6.95 ± 0.94% for polyamide, 2.01 ± 0.68% for poly(vinyl chloride), and 4.08 ± 0.55% for Shonka-plastic. The exothermic effect reported[78] for PE was not observed in this work[79], but it was observed for PMMA.

Differences in stored energy for different types of radiation have not been reported. Though the selectivity of the interaction of different types of radiation with the thermophysical properties of polymers has not been specifically examined, we have no reason to expect any marked differences, especially at temperatures above 0 °C.

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From this analysis of the work published so far we may conclude that further studies of the thermophysical properties of irradiated polymers should be aimed at the following problems: 1) the creation of a basic theory of the effects of radiation on the thermophysical properties; 2) the study of likely reversible effects in these properties; 3) the study of the selectivity of interactions with different types of radiation; 4) the extension of the range of model polymers and of the range of characteristics for which detailed information is available. In particular, we need data on the behaviour of the linear thermal expansion coefficients.

The solution of these problems should allow the prediction of the after-effects of radiation on the thermophysical properties of polymers, including composite materials, which is currently of interest in both pure and applied science.

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