

Analytic and experimental estimates are made of the contribution of photon heat conduction to the total heat transfer in polymers.

It is generally assumed that heat transfer in both crystalline and amorphous polymers is determined by phonon heat conduction. In transparent materials at elevated temperatures, however, an appreciable contribution may be made by radiative heat transfer in the infrared region of the spectrum, so-called photon transmission heat conduction. This contribution is made up of the direct flux from the heater to the backing through the sample and the internal photon flux resulting from the absorption of electromagnetic radiation in each preceding layer and the transmission of part of the energy into the next layer.

We estimate the role of photon thermal conductivity λ_p in polymers by investigating the effect of ionizing radiation on the overall thermal conductivity λ_T of polyethylene. It was found that λ_T in the temperature range 600–650°K was substantially increased by large (20–60 MR) radiation doses. The transparency of samples in the visible region of the spectrum was increased when irradiated with such doses. A possible reason for this behavior of λ_T may be an increased contribution of photon heat conduction to the overall value of the thermal conductivity in this temperature range.

The photon thermal conductivity of transparent glasses and ceramics was determined experimentally in [1], and the direct and internal components were estimated. It was found that these heat-transfer mechanisms begin to play a significant role above 650°K.

We have made approximate calculations of the upper limit of the fractional contribution of photon heat conduction to the total heat transfer. The calculations were made for a thin disk pressed between two plane parallel surfaces with emissivities $\varepsilon_1(\lambda)$ and $\varepsilon_2(\lambda)$ at temperatures T_1 and T_2 , respectively.

In the absence of temperature drops at the interfaces the total heat transfer Q through the sample is

$$Q = \lambda_T (T_1 - T_2) / \delta. \quad (1)$$

The radiative heat transfer from a surface with emissivity $\varepsilon(\lambda)$ through a medium with the spectral transmission coefficient $\tau(\lambda)$ is

$$E = \int_{\lambda_1}^{\lambda_2} I(\lambda) \tau(\lambda) \varepsilon(\lambda) d\lambda.$$

Neglecting reflection from the backing surfaces, the resulting heat transfer is

$$\Delta E = E_1 - E_2 = \int_{\lambda_1}^{\lambda_2} I_1(\lambda) \tau(\lambda) \varepsilon_1(\lambda) d\lambda - \int_{\lambda_1}^{\lambda_2} I_2(\lambda) \tau(\lambda) \varepsilon_2(\lambda) d\lambda. \quad (2)$$

For small values of $T_1 - T_2$ the effective emissivity at the temperature $T = (T_1 \cdot T_2)^{1/2}$, independent of the wavelength λ , can be used [2]. Then

$$\Delta E = \varepsilon_{\text{eff}} \left[\int_{\lambda_1}^{\lambda_2} I_1(\lambda) \tau(\lambda) d\lambda - \int_{\lambda_1}^{\lambda_2} I_2(\lambda) \tau(\lambda) d\lambda \right]. \quad (3)$$

Values of $I(\lambda)$ calculated from the Planck formula are tabulated in [3].

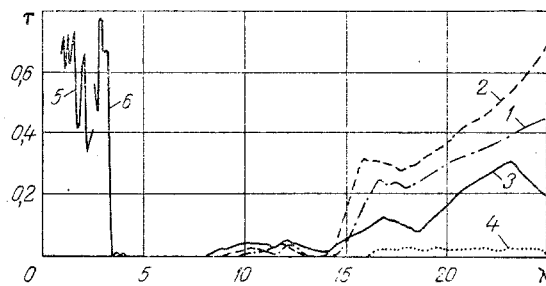


Fig. 1. Transmission spectra for low-density polyethylene measured with various spectrometers: 1) SPECORD IR75, sample diameter $D = 40$ mm; 2) UR-20, $D = 40$ mm; 3) SPECORD IR75, $D = 15$ mm, unirradiated sample; 4) same, irradiated sample; 5) FM-59, $D = 40$ mm; 6) data from [4], $\delta = 0.5$ mm. λ in μm .

The principal difficulties were related to the direct determination of the spectral transmission coefficients for the samples under study, since the data in the literature generally refer to films tens of microns thick. Measurements of $\tau(\lambda)$ for a sample of low-density polyethylene 40 mm in diameter and 1.5 mm thick with polished surfaces were made on UR-20 and SPECORD IR75 spectrometers in the wavelength range 4-25 μm . In the near infrared region (1-2.5 μm) $\tau(\lambda)$ was measured on an FM-59 spectrometer. Since the latter was designed primarily for work in the ultraviolet and visible regions, the values of $\tau(\lambda)$ in this wavelength region are less reliable.

The measured values of $\tau(\lambda)$ are shown in Fig. 1. Data from [4] obtained for a film 0.5 mm thick were used for the range 2.6-4.0 μm . It can be seen from the figure that most of the transmission is in the ranges 16-25 and 1-3.3 μm .

For numerical calculations Eq. (3) was not as convenient to use as the relative fractions L_i of the total blackbody radiant energy in the wavelength range from 0 to λ_i . The values of L_i for $T = 300$ -600°K shown in Fig. 2 were calculated from the dependence of ΔE on λT given in [2].

If L_i is the relative fraction of the total radiant energy in the wavelength range from 0 to λ_i , ΔL_i is the fraction in the range $\Delta\lambda_i = \lambda_{i+1} - \lambda_i$. The transmittance τ_i was assumed constant for $\Delta\lambda_i$. Then

$$\Delta E = \left[\sum_0^{\lambda_{\max}} \tau_i \Delta L_i \right] \Delta E_{\max}. \quad (4)$$

Here ΔE_{\max} is the maximum value of the radiant energy transfer for a perfectly transparent medium, calculated from the Stefan-Boltzmann law

$$\Delta E_{\max} = \sigma_0 \epsilon_{\text{eff}} \left[\left(\frac{T_1}{100} \right)^4 - \left(\frac{T_2}{100} \right)^4 \right]. \quad (5)$$

The values of the effective emissivity were calculated from the formula

$$\epsilon_{\text{eff}} = \frac{1}{1 + \left(\frac{1}{\epsilon_1} - 1 \right) \varphi_{12} + \left(\frac{1}{\epsilon_2} - 1 \right) \varphi_{21}},$$

where $\varphi_{12} = \varphi_{21} = 0.9$ are the irradiance coefficients for heat transfer between two plane parallel circular disks of diameter D ($D/\delta = 10$) [5].

It was assumed in the calculation that $\epsilon_1 = \epsilon_2 = 0.7$ for oxidized copper. The fractions of photon heat conduction m and m_{\max} were defined as follows: $m = \Delta E/Q \cdot 100\%$; $m_{\max}/Q \cdot 100\%$. The results of the calculation are listed in Table 1.

The values of m_{\max} correspond to heat transfer through a perfectly transparent sample. The values of m in the numerator of the fraction were calculated for total absorption in the range 1-2.5 μm , and those in the denominator for $\tau(\lambda)$ shown in Fig. 1 (curve 5). The abrupt decrease of the value of m in comparison with m_{\max} results from the fact that an overwhelming fraction of the energy of the latter is absorbed in the wavelength range 3.5-15 μm where the sample completely absorbs infrared radiation.

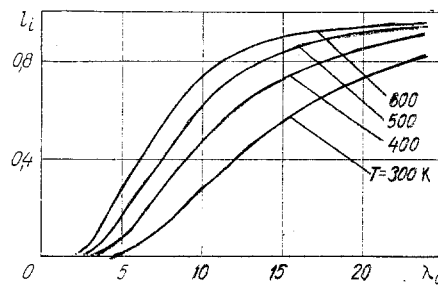


Fig. 2. Fraction of total blackbody radiant energy in the wavelength range from 0 to λ_i .

The values found for m_{\max} vary from 1 to 13%, and are in good agreement with data in [6] obtained for a polyethylene melt in that same temperature range.

The part of the infrared spectrum with $\lambda > 25 \mu\text{m}$ which was not taken into account does not have an appreciable effect on the values obtained for m , since the fraction L_i of the total radiant energy in this region is 4% for $T = 600^\circ\text{K}$, 5% for 500°K , and 8% for 400°K (Fig. 2).

The values of the transmittance τ_i were found for 20°C . With an increase in temperature there is generally a small reduction of the wavelength range in which the material is transparent. The value of the transmittance in this range is decreased [1]. The value $\epsilon = 0.7$ is the maximum for copper backing. For real emissivities the values of m must be smaller than those listed in the table.

Thus, the calculation shows that the contribution of photon heat conduction to the total heat transfer can be neglected.

There remains unanswered the question of the change of transmission in samples irradiated with ionizing radiation. To investigate this we used the SPECORD IR75 spectrometer to measure the transmission spectra for two samples of polyethylene 15 mm in diameter and 1.5 mm thick which were used for the thermal conductivity measurements. Since these small samples did not completely fill the cross section of the light beam, the transmission spectra (curves 3 and 4 of Fig. 1) are of a relative character and are presented for comparison with one another. Curve 3 is for the unirradiated sample, and curve 4 is for a sample bombarded with 9-MeV electrons to a dose of 40 MR. The irradiation led to practically complete absorption of infrared radiation, which is clearly a result of the polymer becoming completely amorphous, a state generally reached for a dose of 10-15 MR. The initial crystallinity of the low-density polyethylene was 50%. Hence, it follows that the contribution of photon heat conduction in irradiated polyethylene is still smaller than in the unirradiated polymer.

Experiments in [1] showed that internal photon heat conduction begins to contribute in quartz at $T > 600^\circ\text{K}$. Since the average absorption coefficient K_λ for polyethylene in the wavelength range in which the materials are transparent is ≈ 20 times larger than for quartz, the contribution of internal photon heat conduction to the total heat transfer through a polyethylene sample can be neglected.

The calculated results were tested experimentally. Measurements were made on an IT- λ -400 commercial type thermal conductivity apparatus in the temperature range 25 - 325°C . Two series of tests were performed for the same polymer sample. In the first series both backings (copper and copper plated with a thin layer of nickel) were in the initial state - partially oxidized during long operation at temperatures up to 400°C using a silicone lubricant. In the second series the backing surfaces were polished to a shine with boron carbide powder. In both cases the backing surfaces remained dry (without lubricant). For an appreciable contribution of the photon heat-transfer mechanism, the temperature dependence of the thermal conductivity curves should be different at elevated temperatures as a result of the change of the emissivity of the radiating surfaces. The absolute values of the thermal conductivities may also differ because of a change of the thermal resistances at the sample-backing interfaces as a result of the polishing. The experiments showed that the difference in the thermal conductivities in the two series did not exceed 1.4% (total error of the measurements was 5-6%) and did not correlate with the temperature.

TABLE 1. Relative Fraction of Photon Heat Conduction, m , %

| T , K | m_{\max} | m | T , K | m_{\max} | m |
|---------|------------|------|---------|------------|-----------|
| 300 | 1,5 | 0,12 | 500 | 7,0 | 0,32/0,35 |
| 400 | 3,6 | 0,21 | 600 | 11,5 | 0,39/0,58 |

Thus, it has been established both analytically and experimentally that heat transfer by electromagnetic radiation is negligibly small in polyethylene. From a comparison of the absorption spectra for polyethylene, polystyrene, polymethyl methacrylate, and Teflon given in [4] in the wavelength range 2.6-15 μm , it appears that this conclusion is true also for other polymer samples a millimeter or more thick.

NOTATION

λ_T , overall thermal conductivity, $\text{W/m}\cdot\text{K}$; λ_p , photon thermal conductivity, $\text{W/m}\cdot\text{K}$; λ , wavelength, m ; ϵ , emissivity; Q , total heat flux, W/m^2 ; δ , sample thickness, m ; $\tau(\lambda)$, spectral transmission coefficient; E , radiative heat transfer, W/m^2 ; $I(\lambda)$, spectral density of blackbody radiation; T , temperature, K ; \mathcal{L}_i , relative fraction of total blackbody radiant energy in the range 0 to λ_i ; σ_0 , Stefan-Boltzmann constant, $\text{W/m}^2\text{K}^4$; φ , irradiance coefficient; D , diameter of sample, m ; m , relative fraction of photon heat conduction; K_λ , absorption coefficient, cm^{-1} .

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APPROXIMATE CALCULATION OF THE ULTRAVIOLET RADIATION OF DIATOMIC MOLECULES AT LOW PRESSURE

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UDC 535.231.4

A method is given of calculating the emission bands of isolated lines for a rigid rotator based on summation of equivalent linewidths. A comparison of this method with the method based on the rotational structure-averaged absorption coefficient is carried out.

The conventional method of calculating the radiation of diatomic molecules in gases at temperatures of 2000-10,000°K in the visible and ultraviolet spectral regions is based on rotational structure averaging of the emission and absorption coefficients [1, 2]. It is assumed in this approach that the rotational lines of the electronic-vibrational bands of the molecule are distributed densely and are broadened sufficiently so that the lines overlap. This basic simplifying assumption is normally not valid at temperatures less than 2000°K and pressures lower than 1 atm. Estimates of the mean distance between lines in the UV region of the spectrum are shown in Table 1 for some molecular systems at temperature 2000°K. The estimates were made by computing the number of electronic-vibrational bands n with the emis-

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