OPTICAL PROPERTIES OF TEFLON AT HIGH TEMPERATURES

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When considering thermal decomposition of thermoplastics by a thermal flux, the case wherein radiation is the dominant heat-transfer mechanism is of special interest. The temperature field within the decomposing material is then described by equations of thermal conductivity and radiation transfer, for the solution of which a knowledge of the thermophysical and optical properties of the material over wide wavelength and temperature ranges is necessary. This present study is devoted to an examination of the optical properties of teflon, a crystalline polymer. Measurement of the true coefficient of absorption of highly dispersive media, including teflon, presents certain difficulties, so in the present case spectral reflection and transmission coefficients were measured, and scattering and absorption coefficients were calculated using the theory of multiple scattering. Measurements were made over the wavelength range 0.2-2.5 μ at temperatures of 20-400° C.

1. Measurements of spectral reflection and transmission coefficients were made with an MPS-50 L two-beam spectrometer, whose optical system is shown in Fig. 1a; 1) light source (tungsten and deuterium lamps); 2) monochromator; 3) beam splitter; 4) specimen and comparison chamber; 5) diaphragm; 6) specimen material; 7) radiation detector. Photomultipliers were used as light detectors in the visible and ultraviolet regions, and in the infrared a zinc-sulfide photocell was employed. In the spectrometer the distance between the specimen and the light-sensitive surface of the detector was reduced to a minimum. This allows recording of diffusely transmitted light with practically no losses. We note that the ratio of the area of the light sensitive detector surface to the area of the incident light beam was 10^3. The specimen was disk shaped with thickness significantly less than diameter. In this case it can be assumed that the detector receives all light passing through the specimen. Thus, the infinitely extended incident light beam model can be employed.

Spectral reflection characteristics were measured with the reflectometric attachment of the spectrometer by comparing the reflecting power of the specimen studied with that of a standard. The standard used was a precalibrated plate of MS-14 opal glass.

A sketch of the reflectometric attachment which was installed in the specimen chamber is shown in Fig. 1b. It is composed of four mirrors 2, arranged such that on the specimen 3 there falls a beam of light at an angle of 45°. The mirror component of the reflected light is absorbed by light detector 1. The diffusely reflected light from the specimen is detected by detector 4 over a solid angle of 0.6 π.

It was assumed that the angular distribution of diffusely reflected light from MS-14 opal glass and teflon was similar. Such an assumption is valid within the framework of approximate theory and has been confirmed experimentally [1] for materials with photon survival probability $\Lambda > 0.8$.

Also measured was the coefficient of mirror reflection of specimen and standard, which proved to be weakly dependent on wavelength, being 6-8% for opal glass, and 3-5% for teflon. The presence of mirror reflection was considered in determination of the reflective power of the teflon. To study optical properties

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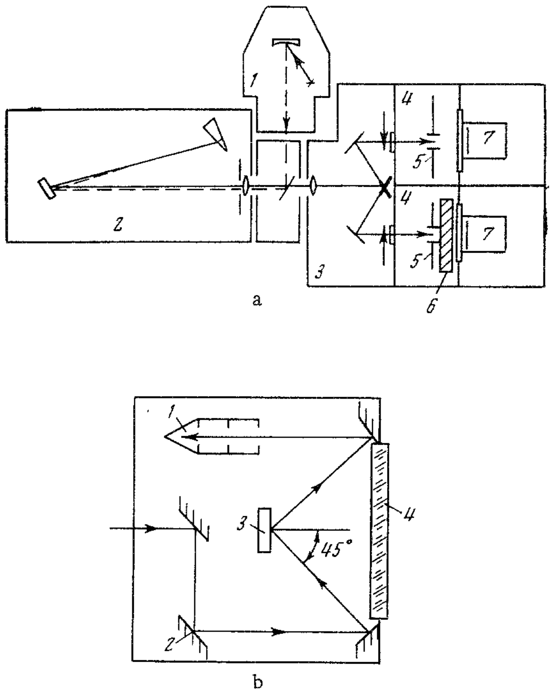

Fig. 1

at high temperature, a specially constructed vessel which allowed heating of the specimen to 400° C was employed. An electric heating element in the form of a resistance spiral sealed into an insulator was installed in the water cooled body. The heater was supplementally insulated from the body by asbestos. The teflon specimen was located in a metallic case, which ensured uniform specimen heating and the case was then installed within the electric heating element.

Light beam formation was accomplished by input and output diaphragms. The water cooled body protected the radiation detector from the thermal action of the heater element. Case temperature was measured by a chromel – alumel thermocouple 0.2 mm in diameter. It was found that temperature equilibrium was established between specimen and case in 10-15 min. The high temperature vessel was located within the specimen chamber, and to reduce errors to a minimum a similar vessel with no specimen was installed in the reference chamber.

As is well known, the intensity of light which does not undergo scattering depends on the optical density of the absorbing layer in the following manner:

$$I = I_0 e^{-\tau} \tag{1.1}$$

Here I_0 is the intensity of the incident light, $\tau = l(\sigma + \varkappa)$ is the optical density of a layer of thickness l, σ is the scattering coefficient, and $\varkappa$ is the coefficient of true absorption.

It follows from Eq. (1.1) that the optical density of the layer may be measured by the attenuation of direct light. The direct light is separated out by the diaphragm system. At high optical densities its intensity is quite low. Only diffusely scattered light passes through the specimen, and its angular distribution is assumed independent of wavelength. This assumption is also valid within the approximate theory.

To determine the total scattered light energy passing through the heated specimen the following equation was used:

$$\int_{\Omega} I(\Omega, \tau)\, d\Omega = \alpha(\Omega)\, \bar{I}(\tau) \tag{1.2}$$

Here $\alpha(\Omega)$, the fraction of the scattered light within a cone of solid angle Ω is dependent solely on system geometry. Using the method described above the quantity $I(\tau)$ was measured for the cold specimen. Thus the total light energy passing through the heated specimen can be determined by measuring the ratio of the scattered light energies passing through the heated and cold specimens.

At a temperature of 330° C a sharp change was noted in the teflon optical properties. The material became clear. Using the attenuation of direct light the optical density of the material was measured as a function of wavelength at 370° C.

2. Teflon is a highly dispersive material, and thus the theory of multiple scattering of light was used to determine its optical properties. Following [2], we will consider a plane-parallel plate of thickness l_0 with constant optical properties, upon which at an angle θ to the normal there falls a plane light wave of intensity πS.

The radiation field within the material is described by the transfer equation

$$\cos\theta\, dI(\tau,\theta,\varphi)/d\tau = -I(\tau,\theta,\varphi) + \frac{\Lambda}{4\pi}\int_0^{2\pi} d\varphi' \int_0^{\pi} I(\tau,\theta',\varphi) X(\gamma)\sin\theta' d\theta + (\Lambda/4) SX(\gamma) e^{-\tau\sec\theta} \quad (2.1)$$

Here $\Lambda = \sigma^0(\sigma + \varkappa)$ is the probability of photon survival, $X(\gamma)$ is the scattering indicatrix, γ is the angle between the incident rays and the scattered light, $I(\tau, \theta, \varphi)$ is the intensity of diffuse radiation at a depth τ in a direction characterized by the angle θ from the normal and an azimuth φ.

The term considering natural radiation of the medium has been omitted (in the experiments the teflon temperature did not exceed 400° C and thermal radiation of the medium was below the threshold sensitivity of the device).

The boundary conditions indicating absence of diffuse illumination of the upper and lower limits of the layer have the form

$$I(0,\theta,\varphi) = 0, \quad 0 \leqslant \theta < \pi/2; \quad I(\tau_0,\theta,\varphi) = 0, \quad \pi/2 < \theta \leqslant \pi \quad (2.2)$$

The solution of Eq. (2.1) is a complex problem. However, in the case where determination of the integral intensity distribution within the material is required, Eq. (2.1) may be replaced by a system of differential equations for intensity, averaged over the angular coordinates [2]

$$\begin{aligned} d\overline{H}(\tau,\xi)/d\tau &= -(1-\Lambda)\overline{I}(\tau,\xi) + (\Lambda/4) Se^{-\tau/\xi}\xi] \\ d\overline{I}(\tau,\xi)/d\tau &= -(3-\Lambda X_1)\overline{H}(\tau,\xi) + X_1(\Lambda/4) Se^{-\tau/\xi}\xi \end{aligned} \quad (2.3)$$

Here $\overline{I} = 4\pi^{-1}\int_0^{2\pi} d\varphi \int_0^1 I(\tau,\eta,\varphi)\, d\eta$ is the mean diffuse radiation intensity, $4\pi\overline{H} = \int_0^{2\pi} d\varphi \int_{-1}^{1} I(\tau,\eta,\varphi)\,\eta d\eta$ is the diffuse radiation flux, and $X_1 = {}^3/_2\int_0^{\pi} X(\gamma)\cos\gamma\sin\gamma d\gamma$ is the flux term in the expansion of the scattering indicatrix in Legendre polynomials, $\eta = \cos\theta$, $\xi = \cos\theta_0$, and c is the velocity of light. The boundary conditions for this system will have the form

$$2\overline{H}(0,\xi) = -\overline{I}(0,\xi), \quad 2\overline{H}(\tau_0,\xi) = \overline{I}(\tau_0,\xi) \quad (2.4)$$

This system is not exact, but for values of $\Lambda > 0.8$ its solution differs from that of the exact equation by not more than 10%.

The solution of Eq. (2.3) has the form

$$\begin{aligned} \overline{I} = \frac{\Lambda}{4} S\xi(1-K^2\xi)^{-1} \Big[& \frac{1}{e^{K\tau_0}(1+b)^2 - e^{-K\tau_0}(1-b)^2} \times \{[2+3\xi+(1-\Lambda)X_1\xi(1+2\xi)][e^{K(\tau_0-\tau)}(1+b) - \\ & - e^{K(\tau-\tau_0)}(1-b)] + [2-3\xi-(1-\Lambda)X_1\xi(1-2\xi)]e^{-\tau_0/\xi} \times [e^{-K\tau}(1-b) - e^{K\tau}(1+b)]\} - \{3+(1-\Lambda)X_1\}\xi e^{-\tau/\xi}\Big] \\ \overline{H} = \frac{\Lambda}{4}\frac{S\xi}{1-K^2\xi}\Big[& \frac{K/3-\Lambda X_1}{e^{K\tau_0}(1+b)^2 - e^{-K\tau_0}(1-b)^2}\{[2+3\xi+(1-\Lambda)X_1\xi(1+2\xi)][e^{K(\tau-\tau_0)}(1+b) + e^{K(\tau-\tau_0)}(1-b)] + \\ & + [2-3\xi-(1-\Lambda)X_1\xi(1-2\xi)]e^{-\tau_0/\xi}[e^{-K\tau}(1-b) + e^{K\tau}(1+b)]\} - \{1+(1-\Lambda)X_1\xi\}e^{-\tau/\xi}\Big] \\ K = \sqrt{(1-\Lambda)(3-\Lambda X_1)}, & \quad b = 2\sqrt{(1-\Lambda)(3-\Lambda X_1)^{-1}} \end{aligned} \quad (2.5)$$

From Eq. (2.5) for the total transmission and reflection (albedo) coefficients we have

$$\begin{aligned} V = \frac{2}{S\xi}\overline{I}(\tau_0,\xi) + e^{-\tau_0/\xi} = (\Lambda/2)1/(1-K^2\xi^2) \times \\ \times \Big\{ \frac{1}{e^{K\tau_0}(1+b)^2 - e^{-K\tau_0}(1-b)^2} [2b[2+3\xi+(1-\Lambda)X_1\xi(1+2\xi)] + \\ + [2-3\xi-(1-\Lambda)X_1\xi(1-2\xi)]e^{-\tau_0/\xi}[e^{-K\tau_0}(1-b) - \\ - e^{K\tau_0}(1+b)]] - [3+(1-\Lambda)X_1]\xi e^{-\tau_0/\xi}\Big\} + e^{-\tau_0/\xi} \end{aligned} \quad (2.6)$$

$$A = 2 / S\xi I(0,\xi) = \frac{\Lambda}{2} 1 / (1 - K^2\xi^2) \left\{ \frac{1}{e^{K\tau_0}(1+b) - e^{-K\tau_0}(1-b)} [2 + 3\xi + (1-\Lambda) X_1 \xi (1 + 2\xi)] \times \right. \tag{2.7}$$

$$\left. \times [e^{K\tau_0}(1+b) - e^{-K\tau_0}(1-b)] + [2 - 3\xi - (1-\Lambda) X_1 \xi (1 - 2\xi)] 2be^{-\tau_0/\xi}] - [3 + (1-\Lambda) X_1] \xi \right\}$$

Assuming $\tau_0 = \infty$ we obtain an expression for the albedo of a semiinfinite plate

$$A_\infty = (\Lambda / 2) \ \ 2 - 3b\xi + (1-\Lambda) X_1 \xi (2\xi - b) / (1+b) \ \ (1 - K^2\xi^2) \tag{2.8}$$

Equations (2.6-1.8) make possible calculation of the scattering coefficient σ, the coefficient of true absorption $\varkappa$, and the coefficient X_1, which characterizes the deviation of the scattering indicatrix from spherical, from experimentally measured transmission and reflection values of plates of various thickness.

3. Results of spectral reflection and transmission coefficient measurements for teflon plates of various thickness are shown in Fig. 2. Here curves 1-3 correspond to coefficients of reflection for plates 15, 2, 0.13 mm in thickness. The experiments with plates of different thickness, showed that the coefficient of reflection shows practically no variation for thickness greater than 10 mm. It may be assumed that the results of curve 1 (Fig. 2) correspond to the case of a semiinfinite plate.

Transmission coefficients for plates 2 and 0.13 mm thick as functions of wavelengths are shown by curves 4 and 5 of Fig. 2. Using Eqs. (2.6)-(2.8), these experimental results permit calculating the scattering coefficient σ the coefficient of true absorption $\varkappa$, and the quantity X_1 as functions of incident light wavelength. The results of these calculations, performed with an electronic computer, are shown in Fig. 3, curves 1, 3, and Fig. 4, curve 1. The calculated transmission coefficient V as a function of optical density behaves as follows:

V	0.91	0.78	0.6	0.4	0.25	0.2	0.16	0.11
I/I_0	0.85	0.73	0.55	0.37	0.25	0.2	0.18	0.12
τ	0.37	0.75	1.5	3	5	6	7.5	10

Also shown are results of measurement of the coefficient of transmission I/I_0 for plates of various thickness at wavelength 0.7 μ.

The results shown are taken from measurements made under normal conditions with specimen temperature 20° C.

The dependence of scattering coefficient on temperature is shown in Fig. 5, curves 1-3 for wavelengths of 0.29, 0.5, and 1.65 μ, respectively. With heating of the teflon from 20 to 400°C, the scattering coefficient initially increases proportionally to temperature, and then at 330° C drops sharply almost to zero. This behavior may be explained as follows. Under normal conditions teflon is a crystalline polymer with a 70–80% degree of crystallization. Light scattering in such structures takes place on internal inhomogeneities such as density and crystal orientation fluctuations.

As was demonstrated in [3, 4], the scattering coefficient is proportional to the mean square of these fluctuations. Upon heating of the teflon, the decrease in density of the crystalline phase is less than that of the amorphous phase. This leads to an increase in mean density fluctuations in the material, which in turn leads to an increase in the scattering coefficient. At a temperature of 327° C melting of the crystallites occurs. The material transforms to an amorphous phase and scattering decreases sharply.

The total attenuation coefficient of clarified teflon is shown in Fig. 4 (curve 3). Comparing curves 1 and 3 (Fig. 4) we note that in the long wave portion of the spectrum the absorption coefficient of clarified teflon is less than the true absorption coefficient of the cold specimen. This is all the more valid because attenuation of light passing through the teflon is produced by both absorption and scattering. In the visible region comparison of curves 1 and 3 (Fig. 4) is complicated, since the fraction of light scattered increases, leading to a significant increase in the coefficient of total attenuation.

To obtain a teflon specimen with a different degree of crystallization under normal conditions the quenching method [5] was used. In this method a specimen is cooled rapidly from the crystal melting point of 327° C to a temperature below 250° C. The crystallization rate at temperatures below 250° C is insignificant. According to the data of [5] the quenched teflon is 50% crystallized. Its optical properties differ somewhat from these of the material in the original state. The spectral coefficients of reflection and transmission for a plate of quenched teflon are presented in Fig. 2, curves 6 and 7. Using these values the scattering coefficient and true absorption of quenched teflon were calculated, and these values are presented in curve 2, Figs. 3, 4.

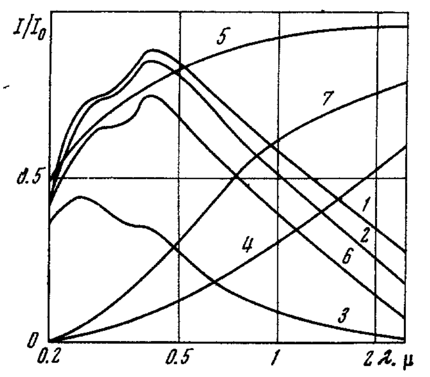

Fig. 2

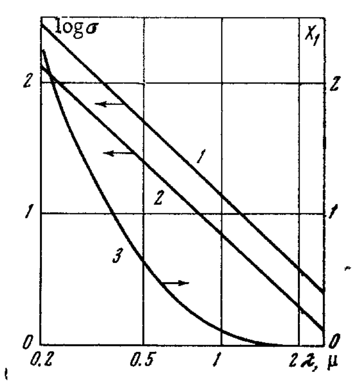

Fig. 3

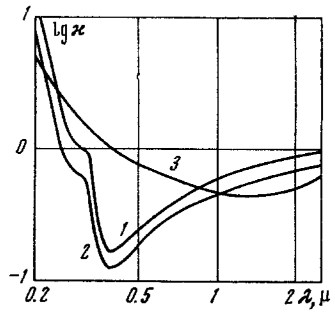

Fig. 4

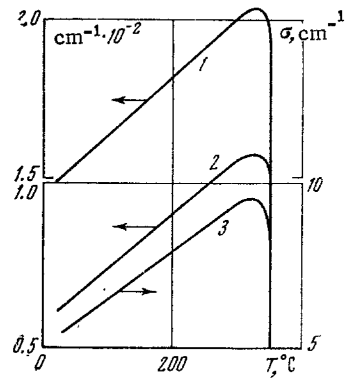

Fig. 5

In calculation, the quantity X_1 was assumed to be the same as in the original state. This assumption is valid for the case where the crystallite geometry is preserved, and only their concentration is changed. As is evident from Fig. 3, scattering is proportional to the degree of crystallization of the material.

Comparison of curves 1 and 2, Fig. 4 shows that the coefficient of absorption of teflon in the amorphous phase is less than in the crystalline phase. This has been supported by measurement of the coefficient of total attenuation of clarified teflon.

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