ANALYSIS OF THE HEAT-RADIATION CHARACTERISTICS OF HERMETIZING POLYMER SYSTEMS BY THE MIRROR HEMISPHERE METHOD

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The mirror hemisphere method with a single-beam spectrometer was used on epoxide resin and phenolformaldehyde resin specimens to obtain the heat-radiation characteristics and the indicatrices of reflected infrared radiation for such hermetizing polymer systems.

The external and the internal heat and mass transfer in hermetizing polymer systems cannot be calculated without data on the spectral characteristics of heat radiation (transmittivity T_λ, reflectivity R_λ, and absorptivity A_λ), because such systems belong into the category of selectively absorbing and scattering systems.

By the mirror hemisphere method described in [1-14, 17] one can determine the transmittance and the reflectance of a test object with scattering taken into account. It is to be noted that, for the type of materials considered here, the scattering of infrared rays in hermetizing polymer coatings occurs as a result of interaction between the radiation flux and mainly the particles of inert filler and dye "suspended" among polymer molecules.

The transmittivity and the reflectivity of polymers under study were measured with a mirror hemisphere attached to an IKS-12 spectrometer. A specimen was exposed to a monochromatic modulated radiation flux during the measurement of R_λ and T_λ, making it possible to eliminate the effect which intrinsic radiation from the specimen and from the surrounding medium would have on the instrument readings. The source temperature was maintained constant by a precise stabilization of the supply voltage. High precision in mounting the test specimens and the reference specimen in the same position during measurements was ensured by an appropriate design of this instrument attachment.

The optical system of the attachment with a mirror hemisphere and the ISK-12 spectrometer is shown in Fig. 1. For measuring R_λ one uses arrangement A, where the spherical mirror 3 and the plane mirrors 2, 4 are set so that the radiation flux from the slit of monochromator 1 passes through the 20 mm (diameter) aperture in the hemisphere 5 and impinges on the test (or reference) specimen 6 placed at one of the conjugate points in the equatorial plane of the 164 mm in diameter hemisphere. Radiation diffusively reflected from the specimen is gathered in the hemisphere, where it is picked up at the receiver pad of a nickel bolometer 7 [16].

For measuring T_λ one uses arrangement B, where the spherical mirror 3 and the plane mirrors 2, 4 are set so that the radiation flux focuses on the specimen 6. Radiation which has passed through the specimen is gathered in the hemisphere 5, where it is picked at the receiver pad of bolometer 7.

The modulated signal of infrared radiation, after having been picked up by the bolometer, was amplified in a model IMÉIK-2 low-energy measuring instrument and then recorded on an automatic model ÉPP-09 plotter. We had modified the IMÉIK-2 instrument somewhat, in order to increase the signal-to-noise ratio. The bridge circuit including the bolometer was redesigned according to the procedure shown in [15, 16]. This made it possible to increase the signal at the preamplifier input for the same given radiation level at the bolometer.

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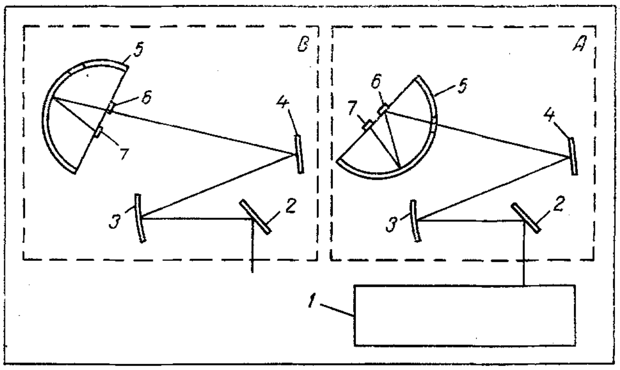

Fig. 1

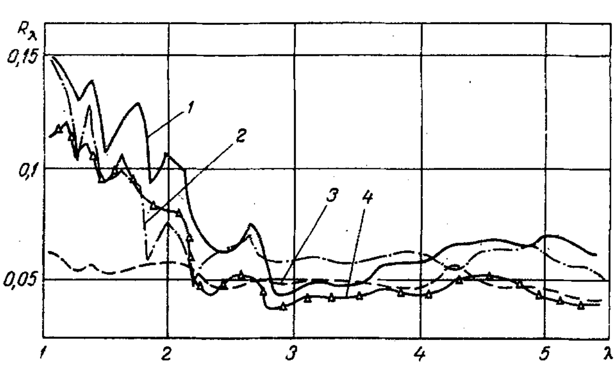

Fig. 2

Fig. 1. Optical system of the infrared spectrometer for measuring the reflectivity and the transmittivity of materials which scatter radiation.

Fig. 2. Reflectivity R_λ of various polymer systems, as a function of the wave length λ, μ: 1) high-filler polymer system 1; 2) low-filler polymer system 1; 3) grade ÉD-5 epoxide resin; 4) high-filler polymer system 2.

The use of a mirror hemisphere does not ensure, however, that the absolute values of transmittivity and reflectivity will be obtained, as had been assumed in the first studies on diffusive reflection in materials [1, 2]. The general trend of the curves is correct, but the values obtained for these coefficients are lower than their true values – because not all the transmitted or reflected energy is picked up by the receiver.

The radiation losses through the aperture in the hemisphere depend on the indicatrix of reflected or transmitted radiation, respectively. Therefore, for every test object one must determine the magnitude of the given type losses according to the formula:

$$\Delta I_R = \frac{s_1 \cos\alpha}{l^2 \int\limits_{2\pi} \frac{I(\theta)}{I(\theta_1)}\, d\omega} I_R . \tag{1}$$

The indicatrix of a test specimen must be plotted for the particular incidence angle of radiation at the specimen in the mirror hemisphere.

The effect of aberations in the mirror hemisphere was reduced to a minimum by observing the condition $r \leq 0.1\rho$ [4, 5].

In order to determine the reflectivity and the transmittivity of the materials under study here, we first measured the relative values of these coefficients. The true values of R_λ and T_λ were then determined according to formulas which relate these true values to those determined experimentally.

The measured reflectivity and transmittivity are, respectively:

$$R_\lambda^* = \frac{k_1 R_\lambda (1 - k_2^2 R_\lambda R_s^2 R_r)^{-1}}{k_2 R_e (1 - k_2^2 R_e R_s^2 R_r)^{-1}}, \tag{2}$$

$$T_\lambda^* = k T_\lambda (1 - k^2 R_\lambda R_s^2 R_r)^{-1} . \tag{3}$$

It must be noted that the factor k, which signifies what fraction of the reflected radiation is picked up by the receiver (some radiation is lost through the aperture in the hemisphere and by the shielding effect of the receiver housing), depends on the indicatrix of reflected or transmitted radiation. For materials which scatter radiation diffusively, as in our case, k = 0.66.

The reflectivity of the receiver over the entire tested band of infrared radiation was $R_r \approx 4.5\%$.

We analyzed the heat-radiation characteristics of three polymer systems with a high-filler content: system 1 on a grade ÉD-5 epoxide resin base, system 2 based on a mixture of grades ÉD-5 and ÉD-L epoxide resin, and system 3 on a phenolformaldehyde resin basis, also their compounds and bases with a low filler content. It is to be noted here that the quantity of inert inorganic filler in the polymer systems with a low filler content was many times smaller than in the corresponding polymer systems with a high-filler content.

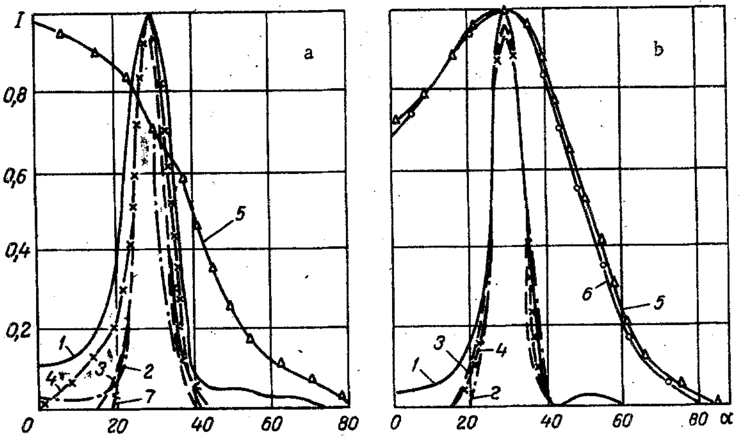

Fig. 3. Indicatrices of radiation reflected from polymer systems at an incidence angle of $\theta_1 = 30°$: a) with $\lambda = 2\ \mu$; b) $\lambda = 5\ \mu$; 1) high-filler polymer system 1; 2) low-filler polymer system 1; 3) grade ÉD-5 epoxide resin; 4) high-filler polymer system 2; 5) high-filler polymer system 3; 6) diffusively scattering reference mirror; 7) phenolformaldehyde resin.

The reflectivity spectra of the high-filler polymer system 1, its low-filler modification, and of grade ÉD-5 epoxide resin, also the reflectivity spectrum of the high-filler polymer system 2 are all shown in Fig. 2. The thicknesses of the test specimens, except that of the grade ÉD-5 epoxide, corresponded to the thickness of an optically infinitely thick layer.

The reflectivity reference was a mirror with an aluminum coating deposited on the outside glass surface, considering that the indicatrices of reflected radiation for the polymer systems under study were very elongated – almost like mirror indicatrices – as measured with an IPO-12 attachment to an IKS-11 spectrometer. For this reason, the radiation losses through the aperture in the hemisphere and by the shielding effect of the receiver housing were associated only with second and subsequent reflections of the radiation from the specimen in a multiple hyperreflection pattern between specimen and receiver. It must also be noted that radiation entering the hemisphere impinged on the specimen at a 30° angle. Consequently, in this case the factor k would appear only in those terms of expression (2) which account for multiple reflections.

As curves 1, 2, 3 in Fig. 2 indicate, the spectrum of reflected radiation from the high-filler polymer system 1 depends largely on the inert inorganic filler. An increase in the percent filler content affects appreciably the magnitude of the reflectivity R_λ, as can be seen from an analysis of curves 1, 2 (Fig. 2), especially within the 1-3 μ range of the radiation spectrum. The selective character of the reflectivity spectrum is not in evidence for grade ÉD-5 epoxide resin, because superficial reflection is always superposed on diffusive reflection along the entire specimen layer and it distorts the spectrum.

In Fig. 4 are shown the reflectivity spectra for high-filler and low-filler polymer systems 3, also the transmittivity spectrum for grade ÉD-5 epoxide resin and phenolformaldehyde resin. It can be seen here that both resins strongly absorb radiation beyond the 2.5 μ wavelength. In these cases the reflectivity references for high-filler and low-filler polymer systems 3 were: magnesium oxide deposited on a glass substrate for the 1-2.5 μ range, where reflection at these substances is diffusive, and a spherical mirror made up of a glass plate for the 2.5-5.0 μ range of the spectrum. One side of that special glass mirror had been treated with polishing powder. The rough side had been coated with aluminum. The reflectivity of the plate was checked against that of another polished plate which had been aluminum coated together with the reference plate. The indicatrix of radiation reflected from such a reference mirror had the same shape as the reflection indicatrix for high-filler and low-filler polymer systems 3.

The indicatrices of reflection from surfaces of high-filler polymer system 3 and from the reference mirror are shown in Fig. 3 (curves 5, 6). Since the references and the test substances produced identical reflection indicatrices, hence the factor k in the formula for R appears only with those terms in expression (2) which account for multiple reflections.

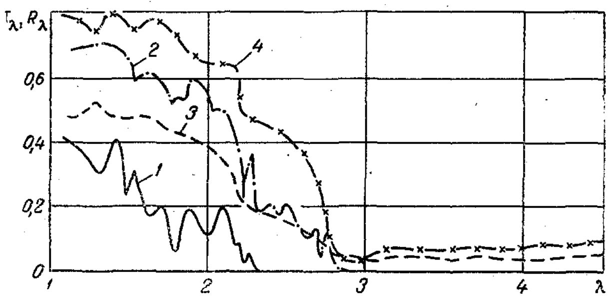

Fig. 4. Spectral transmittivity and reflectivity of polymer systems, as a function of the wavelength λ, μ: 1) T for grade ÉD-5 epoxide resin d = 3 mm; 2) T for phenolformaldehyde resin d = 0.25 mm; 3) R_λ for low-filler polymer system 3; 4) R_λ for high-filler polymer system 3.

For determining the reflectivity and the transmittivity of these test substances, the spectral width of the spectrometer aperture was varied from 38 to 8 cm^{-1} on LiF.

Curves 3, 7 in Fig. 3 show that the indicatrices of reflected radiation from grade ÉD-5 epoxide resin and from phenolformaldehyde resin are distinctly of the mirror type, which means that there is very little scatter in these cured resins. It is evident, then, that the scattering of infrared radiation in polymer systems studied here occurs at particles of the inert filler. Since epoxide and phenolformaldehyde resins strongly absorb infrared radiation in the spectrum range beyond 2.5 μ, hence the sharp increase in the reflectivity of polymer systems 1, 2, and 3 within the 1-2.5 μ range is explainable by the high transmittance of the matrices in these systems and by the scattering of infrared radiation at particles of the inert filler. All this is confirmed by the spectral characteristics of R_λ for each of the test substances and by the shape of the respective indicatrices. It is to be noted further that the scattering of reflected radiation by high-filler and low-filler polymer systems 3 (Fig. 4, curves 3, 4) within the range beyond 2.5 μ can, apparently, be explained by the surface structure of these systems (roughness) and by the more than twice as high percent content of inert filler material as in the other polymer systems 1 and 2.

In order to check the measurements, we also plotted the heat-radiation characteristics of polyethylene. The results agree with the values of reflectivity and transmittivity obtained for polyethylene in [18].

NOTATION

R_λ, T_λ, A_λ	are the reflectivity, transmittivity, and absorptivity of a layer of finite thickness;
$I(\theta)$	is the radiation intensity reflected by a specimen under angle θ, counted from the normal to the specimen surface;
s_1	is the area of the aperture in the hemisphere;
l	is the distance from the center of the aperture in the hemisphere to the point at which radiation impinges on the specimen;
α	is the angle between the direction of l and the normal to the aperture area;
θ_1	is the incidence angle of radiation on the specimen;
ρ	is the radius of the hemisphere;
r	is the distance from the center of the hemisphere to the specimen;
ω	is the solid angle;
d	is the thickness of the test specimen.

Subscripts

λ	refers to spectral radiation;
s, r	refer to the coatings of the hemisphere and of the bolometer receiver pad, respectively.

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