SOLIDS

PHOTOTHERMOACOUSTIC EFFECT IN LAYERED POLYMER FILMS—PIEZOELECTRIC STRUCTURES

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We have studied theoretically and experimentally the photothermoacoustic (PTA) effect in polymer films with the piezoelectric registration of informative signals in the following polymers: polyurethane, polypropylene, and nylon. It is shown that the PTA effect in the layered polymer—piezoelectric structure in the form of a thin plate may be used for measuring some elastic and thermal parameters at low frequencies of modulation of the light flux. We defined experimentally the reduced Young modulus and the thermal diffusion coefficient of the above-mentioned polymers.

At present, the physics of polymers is the frontier of material science. It requires the expansion of implementation of different physical methods of study (especially the nondestructive ones) that allow us to obtain the relevant information on the substance properties. First of all, we could refer to the acoustic methods that are widely used in studies of polymer materials [1—2]. As a rule, these methods impose some restrictions on the geometric parameters of samples. In particular, the typical sizes of the solid polymer samples have to be of the order of a few or tens of centimeters. Unfortunately, it is difficult to manufacture such samples because polymer materials usually have the form of thin plates or films.

Last years, studies of substances in different aggregate states were performed with the help of the PTA effect [3—5]. In this method, the substance under investigation is illuminated by the modulated light flux. The absorbed light heats the substance and excites thermal waves. The amplitudes and phases of thermal waves contain the information on optical and thermal properties of the substance. Registering the thermal waves by one or another method, we could obtain the corresponding information. At the moment, the most reliable methods of registration of thermal waves are the acoustic methods. In the sample and in the environmental gas, the temperature field of thermal waves generates, due to the thermoelastic effect, the acoustic vibrations and waves that could be registered. At this, there are no severe constraints imposed on the geometry of samples. In the case of the piezoelectric registration of photoacoustic vibrations, the samples could be manufactured in the form of thin plates [6]. As far as we know, there were no systematic studies of the PTA effect in polymers. We could refer to only separate papers [7, 8]. The present paper studies the PTA effect in thin plates of polymer materials by using the piezoelectric registration.

We consider a layered structure in the form of a thin plate (see Fig.1). Let the piezoelectric be a crystal of the $6mm$ class or piezoceramic. We accept that the thermomechanical properties of the crystal are isotropic. Let the piezocrystal polar axis coincide with the z-axis. The surface of the polymer sample ($z = 0$) is illuminated uniformly by the modulated light flux with frequency ω:

$$P = \frac{1}{2}P_0(1 + \cos\omega t), \tag{1}$$

where P_0 is the light flux intensity.

The light absorbed by the sample heats it with varying temperature and generates the thermal waves that propagate along the z-axis. Due to the thermoelastic effect, the acoustic waves emerge in the system as well. We consider a case of comparatively low modulation frequencies of the light flux when the wavelength of acoustic waves is much larger of the typical linear size of the structure. This allows us to neglect the absorption of acoustic vibrations by the polymer sample (quasistatic approximation). In this

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case, only two components of the elastic tensor, T_{11} and T_{22}, are nonzero. They are equal, $T_{11} = T_{22} \equiv T$, and may be presented in the form [9]

$$T = \tilde{E}(C_1 - C_2 z - \alpha_T \theta). \tag{2}$$

Here, $\tilde{E} = \frac{E}{1-\sigma}$ is the reduced Young modulus (E is the Young modulus, σ is the Poisson's coefficient), α_T is the linear heat expansion coefficient, and θ is a temperature of the sample (piezogage). The constants C_1 and C_2 are determined from the following boundary conditions: the resultant force and the resultant moment per unit length of the structure contour are equal to zero [9]

$$\int\limits_0^h T\, dz = 0, \quad \int\limits_0^h Tz\, dz = 0, \quad h = h_1 + h_2. \tag{3}$$

The acoustic vibrations and the thermal waves in the plate result in the electric polarization of the piezoelectric sample. The normal component of the electric induction vector D_z in our case could be defined as

$$D_z = \varepsilon_{33} E_z + 2d_{31} T_{\mathrm{PE}} + p\,\theta_{\mathrm{PE}}, \tag{4}$$

where ε_{33} is the dielectric permittivity, d_{31} is the piezomodulus, p is the pyroelectric constant, T_{PE} and θ_{PE} are the elastic stress and a temperature of the piezoelectric, respectively.

Now we calculate a potential difference $\hat{U}$ that appears in the layer of width Δh at the coordinate z (Fig.1)

$$\hat{U} = -\int\limits_{z-\Delta h/2}^{z+\Delta h/2} E_z\, dz. \tag{5}$$

The quantity E_z could be found from (4) provided that $D_z = 0$ since there are no external electric fields and the normal component of the electric induction is continuous.

To find the distribution of a varying component of the temperature as a function of z in the sample, it is necessary to solve simultaneously the heat conductivity equation for both the sample and the piezoelectric with the following boundary conditions: continuity of both the heat flux and temperature at the interfaces.

When solving this problem, we assume that the sample absorbs completely the light flux. The energy of light goes completely for a heating of the sample, and
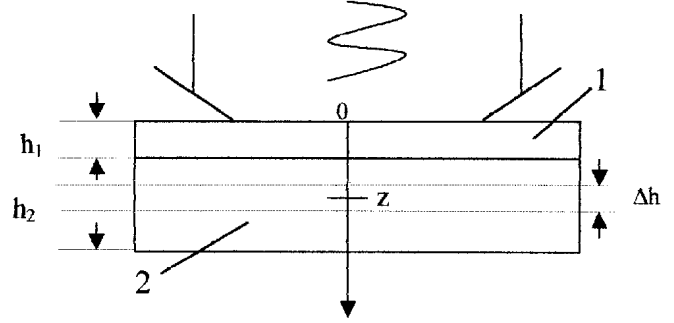

Fig.1. The scheme of the problem. 1 — polymer, 2 — piezoelectric

the thermal wave does not reach the surface $z = h$. The final result reads

$$\hat{U} = \frac{2d_{31}\tilde{E}_{\mathrm{PE}}}{\varepsilon_{33}}\left((C_1 - C_2 z)\Delta h - \frac{2\alpha_{T,\mathrm{PE}}\theta_0}{\gamma_{\mathrm{PE}}} \times \right.$$

$$\times \left(1 - \frac{p}{2d_{31}\tilde{E}_{\mathrm{PE}}\alpha_{T,\mathrm{PE}}} \right) \exp(-\gamma_{\mathrm{PE}}(z - h_1)) \times$$

$$\left. \times \mathrm{sh}\!\left(\gamma_{\mathrm{PE}}\frac{\Delta h}{2} \right) \right), \tag{6}$$

$$\theta_0 = \frac{\alpha^2 P_0}{2\chi\gamma s(\alpha^2 - \gamma^2)}, \quad s = \mathrm{sh}(\gamma h_1) + \frac{\gamma_{\mathrm{PE}}\chi_{\mathrm{PE}}}{\gamma\chi}\,\mathrm{ch}(\gamma h_1),$$

$$\gamma = \sqrt{\frac{\omega}{2D_T}}(1 + i), \quad \gamma_{\mathrm{PE}} = \sqrt{\frac{\omega}{2D_{T,\mathrm{PE}}}}(1 + i),$$

where χ, D_T, χ_{PE}, and $D_{T,\mathrm{PE}}$ are the coefficients of heat conductivity and thermal diffusion (temperature conductivity) of the sample and the piezoelectric, respectively; α is the absorption coefficient of light by the sample; $\alpha_{T,\mathrm{PE}}$ and $\tilde{E}_{\mathrm{PE}}$ are the coefficient of heat expansion and the reduced Young modulus, respectively. The coefficients C_1 and C_2 depend on thermal, elastic, and geometric parameters of the structure.

An analysis of expression (6) in the general case is rather complex. Below we consider the particular case when the surface layer of the sample absorbs the light. Let the modulation frequencies of the light flux be low enough, let the sample width be larger than the typical length of thermal diffusion, and $\alpha \gg \gamma$. Under these conditions, the expression of $\hat{U}$ is essentially simplified and takes the form

$$\hat{U} = U_m \frac{(Z - Z_s)\Delta h}{(\gamma h)^2}\left(1 - \frac{2n}{\gamma h} \right), \tag{7}$$

$$U_m = \frac{d_{31}\alpha_T h\tilde{E}P_0}{\chi\varepsilon_{33}(1 + (\eta - 1)H_1)(Z_b - Z_s)},$$

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$$Z_s = \frac{2}{3} \cdot \frac{1 + (\eta - 1)H_1^3}{1 + (\eta - 1)H_1^2}, \quad Z_b = \frac{1}{2} \cdot \frac{1 + (\eta - 1)H_1^2}{1 + (\eta - 1)H_1},$$

$$n = \frac{Z - Z_b}{2Z_b(Z - Z_s)}, \quad H_1 = \frac{h_1}{h}, \quad Z = \frac{z}{h}, \quad \eta = \frac{\tilde{E}}{\tilde{E}_{\mathrm{PE}}}. \quad (8)$$

Now we clarify the physical meaning of the parameters Z_s and Z_b. The plate performs vibrations that are a combination of tension and compression. At the upper part of the plate, where the sample heats, the tension acts. At the lower part, the sample is compressed. A coordinate of the neutral plane may be found from Eq. (2) by using the condition $T = 0$. Let us consider the pure surface tension of the plate. The coordinate of the neutral plane z_s in this case is equal to

$$z_s = \frac{C_1}{C_2}. \quad (9)$$

The ratio C_1/C_2 could be found from the condition that the resultant moment equals zero:

$$\int\limits_0^h Tz\,dz = \tilde{E}\int\limits_0^{h_1}(C_1 - C_2 z)z\,dz +$$

$$+\tilde{E}_{\mathrm{PE}}\int\limits_{h_1}^h(C_1 - C_2 z)z\,dz = 0. \quad (10)$$

From (10), we get

$$z_s = \frac{2}{3} \cdot \frac{1 + (\eta - 1)H_1^3}{1 + (\eta - 1)H_1^2}h. \quad (11)$$

Then $Z_s = \frac{z_s}{h}$ is a relative coordinate of the neutral plane of the plate under pure surface tension.

Acting in the same manner, we may show that Z_b is the relative coordinate of the neutral surface of the plate under the pure bending. The ratio C_1/C_2 in this case may be obtained from the condition that the resultant force is zero.

An interesting dependence of a sign of the voltage picked up from the piezogage on the structure parameters follows from (7). It could be explained in the following way. The structure performs bending vibrations under the action of thermal elastic stresses. Depending on a relation between thickness and elastic parameters of the sample and the piezogage, the coordinate of the neutral plane changes. That is why the elastic stresses of different signs (tension, compression) may act in different parts of the piezogage. Depending on their relation, the electric voltage on the piezogage may have different signs and even be zero.

Now we analyze this problem in more detail. Let us consider relatively high modulation frequencies of the light flux modulation, when $\gamma h \gg 2n$. In this case, a sign of $(Z - Z_s)$, as seen from (7), defines a sign of the informative signal. At relatively high frequencies, we deal practically with pure surface tension. Fig. 2 presents the dependences of $(Z - Z_s)$ on the relative thickness of the sample H_1 for different reduced Young moduli of the sample and the piezogage. From Fig.2, one could see that the informative signal changes a sign (from conditionally negative) with increase in the sample thickness only for the substances with $\tilde{E}$ larger or of the same order in comparison with $\tilde{E}_{\mathrm{PE}}$ (curves 1—5). The relative thickness H_1 of the substance film under investigation (when the informative signal changes a sign) increases with decrease in $\tilde{E}/\tilde{E}_{\mathrm{PE}}$. For $\tilde{E} \ll \tilde{E}_{\mathrm{PE}}$, the quantity $|Z - Z_s|$ decreases monotonically with increase in H_1 and tends to zero (curve 7), at $H_1 \to 1$ (the signal does not change the sign).

A point of inversion of the signal sign allows us to find the quantity $\eta = \tilde{E}/\tilde{E}_{\mathrm{PE}}$. In fact, we could experimentally define the sample thickness corresponding to the change of a sign of the electric voltage and find Z_s. After this, we define η from (8). However, this situation cannot be always realized, as is seen from the previous.

In [6], in studying the properties of solids in a similar structure, a layered piezogage was used. Consider a two-layer piezogage with identical layers of equal thickness $h_2/2$. The ratio of voltages that are taken from these layers could be written as

$$\frac{\hat{U}_1}{\hat{U}_2} = \frac{(Z_1 - Z_s)(2n_1/\gamma h - 1)}{(Z_2 - Z_s)(2n_2/\gamma h - 1)}, \quad (12)$$

where $\hat{U}_1$, $\hat{U}_2$, Z_1, Z_2, n_1, and n_2 are parameters of the first from the sample (index 1) and the second from the sample (index 2) of the piezogage layers.

A comparative analysis of the parameter Z_s with the coordinates Z_1 and Z_2 of piezogage layers as a function of the relative sample thickness H_1 shows that Z_s may be larger or smaller than Z_1. But it could not be larger than Z_2. It follows from (12) that the ratio $\hat{U}_1/\hat{U}_2$ could change a sign with varying H_1 as in the case of the one-layer piezogage. However, the sign changing point of the ratio $\hat{U}_1/\hat{U}_2$ depends only on the voltage that is taken from the piezogage of the first layer (relation $Z_1 = Z_s$). Fig. 1 shows the dependence of $\frac{Z_1 - Z_s}{Z_2 - Z_s}$ on the relative thickness of the sample H_1 for two values of the ratio $\tilde{E}/\tilde{E}_{\mathrm{PE}}$.
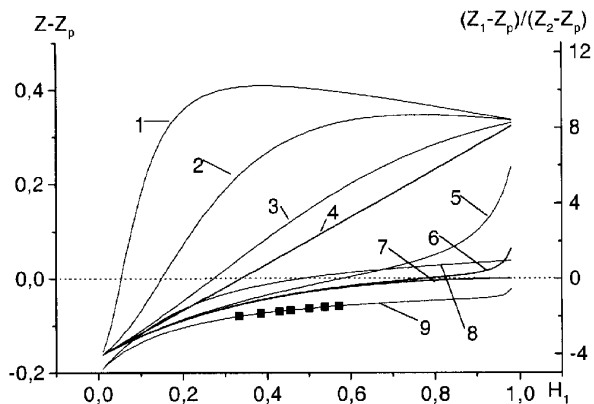
Fig.2. The dependences $(Z - Z_s)$ (1 — 7) and $\frac{Z_1 - Z_s}{Z_2 - Z_s}$ (8 — 9) on the relative thickness of pattern H_1 for different ratios of the reduced Young modules of the sample and piezogage: 1 — 100; 2 — 10; 3 — 2; 4 — 1; 5 — 0.1; 6 — 0.01; 7 — 0.0002; 8 — 2; 9 — 0.0002. The curves present the theory; dots correspond to the experiment

An analysis of (12) shows that the ratio of the signal amplitudes (U_1/U_2) that are taken from individual layers of the piezogage, and the tangent of the phase difference between them $(\text{tg}(\Delta\varphi))$ transform with increase in the frequency to approximately linear dependences on the square root of the frequency:

$$\frac{U_1}{U_2} = \frac{Z_1 - Z_s}{Z_2 - Z_s}\left\{1 - (n_1 - n_2)\frac{1}{\sqrt{F}}\right\}, \qquad (13)$$

$$\text{tg}(\Delta\varphi) = \frac{n_1 - n_2}{\sqrt{F}}, \qquad (14)$$

where $F = \frac{\pi h^2}{D_T}f$, $f = \frac{\omega}{2\pi}$.

This evaluation shows that, for the substances with $\tilde{E} \sim \tilde{E}_{\text{PE}}$ and the thermal diffusion coefficient of about 10^{-6} m²/s, the frequencies that satisfy dependences (13) and (14) are of the order of 10^2 Hz. This could be easily reached experimentally.

These peculiarities of the amplitude-frequency $\frac{U_1}{U_2}(f^{-1/2})$ and the phase-frequency $\text{tg}(\Delta\varphi)(f^{-1/2})$ dependences of the PTA signals at relatively high frequencies of the light modulation could be used to define the elastic and heat parameters of the polymer materials and, in particular, the reduced Young modulus $\tilde{E}$ and the heat diffusion coefficient D_T. Indeed, extrapolating the experimental dependence $\frac{U_1}{U_2}(f^{-1/2})$ to the point $(f^{-1/2}) = 0$, we could obtain Z_s from (13). Then exploiting the known magnitude of the reduced Young modulus of the piezogage, it is possible to find $\tilde{E}$ of the sample. Knowing Z_s and calculating n_1 and n_2 from the experimental dependences $\frac{U_1}{U_2}(f^{-1/2})$ or
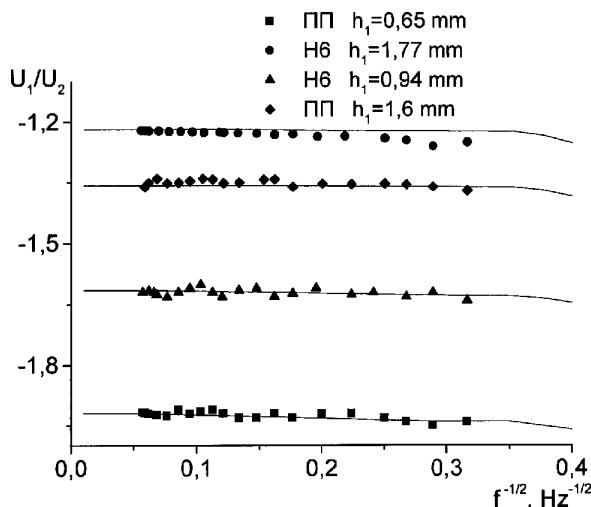

Fig.3. The ratio of signal amplitudes U_1/U_2 that taken from individual layers of piezogage versus the inverse square root of the frequency $f^{-1/2}$ for polypropylene and nylon. Curves present the theory; dots correspond to the experiment
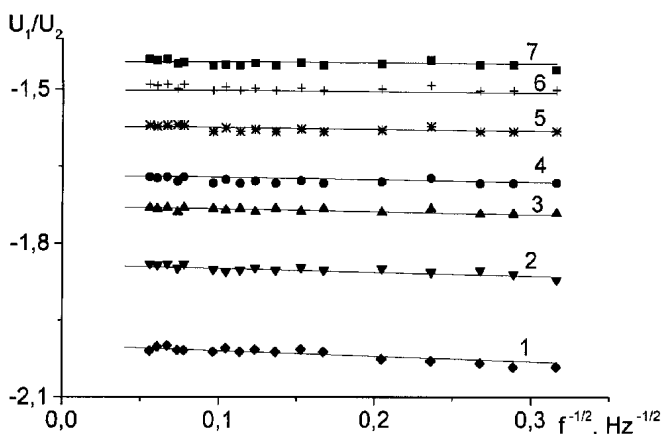

Fig.4. The ratio of signal amplitudes U_1/U_2 that are taken from individual layers of piezogage versus the inverse square root of the frequency $f^{-1/2}$ for polyurethane samples of different thickness: 1 — 0.6 mm; 2 — 0.75; 3 — 0.9; 4 — 1; 5 — 1.2; 6 — 1.4; 7 — 1.6

$\text{tg}(\Delta\varphi)(f^{-1/2})$ by using expression (13) or (14), we define D_T.

The experiment was performed with the samples of polyurethane, polypropylene, and nylon. The piezogage contained two identical layers of piezoceramic TsTS-19 0.6 mm in thickness. The samples and piezogage were made in the form of gaskets 15 mm in diameter. Thicknesses of the samples were in a range 0.6—1.8 mm. The modulated light of a laser LG-38 ($\lambda = 632$ nm) uniformly illuminated the samples. We studied the amplitude-frequency and phase-frequency dependences
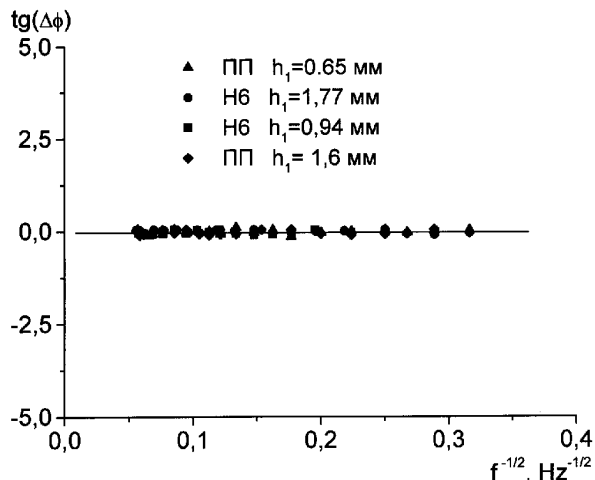
Fig.5. The tangent of phase difference between the signals from individual layers of the piezogage $\mathrm{tg}(\Delta\varphi)$ versus $f^{-1/2}$ for polypropylene and nylon. Curves present the theory; dots correspond to the experiment

of signals that were taken from individual layers of the piezogages in a frequency range 10—500 Hz. The polyurethane samples had different thicknesses.

The results of experimental study are given in Figs.2—6. A minus sign of U_1/U_2 means that the signals from different layers of the piezogage have different signs. An analysis of the phase-frequency dependence shows that, for all samples, the tangent of the phase difference of the signals from individual layers of the piezogage is approximately equal to zero. As an example, Fig.5 shows curves $\mathrm{tg}(\Delta\varphi)$ versus $f^{-1/2}$ for polypropylene and nylon. Data of Figs. 3—5 show that the frequency dependences of U_1/U_2 and $\mathrm{tg}(\Delta\varphi)$ on $f^{-1/2}$ are practically linear in the frequency range under study. This means that one could use formulas (13) and (14) for the theoretical calculations and determination of $\tilde{E}$ and D_T. We have found the reduced Young modulus and the thermal diffusion coefficient from the experimental dependences given in Figs.3—5 with the help of the method described above for all the polymers under investigation. The elastic constants of TsTS-19 ($E = 6 \cdot 10^{10}$ N/m^2, $\sigma = 0.42$) were taken from [6]. The experimental values of $\tilde{E}$ and D_T of the polymers are given in the table.

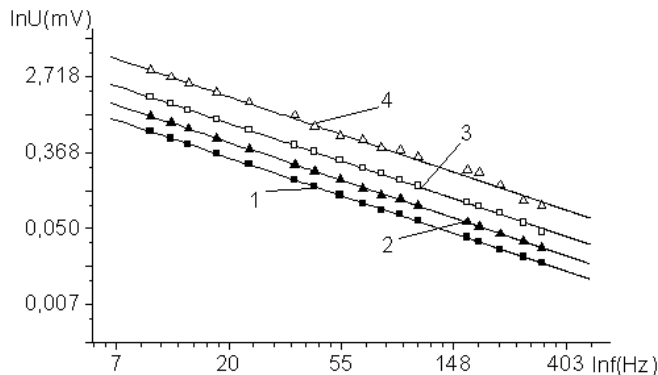| Substance	$\hat{E}$, N/m^2	D_T, m^2/s
Nylon	$3.3 \cdot 10^9$	$7 \cdot 10^{-8}$
Polypropylene	$1.7 \cdot 10^9$	$6 \cdot 10^{-8}$
Polyurethane	$2 \cdot 10^9$	$9 \cdot 10^{-8}$

Fig.6. The amplitude-frequency dependences of photothermoacoustic signals from individual layers of piezogage: U_2 (1, 3) and U_1 (2, 4) on the double logarithmic scale for two samples of polyurethane of different thickness: $h_1 = 1.6$ mm (1, 2) and $h_1 = 0.6$ mm (3, 4)

The experimentally defined ratio $\frac{Z_1-Z_s}{Z_2-Z_s}$, according to the data of Fig.4, for different samples of polyurethane is illustrated by Fig.2 (curve 9).

By using the experimentally defined $\tilde{E}$ and D_T that are collected in the table, we calculated U_1/U_2 and $\mathrm{tg}(\Delta\varphi)$ according to (13) and (14). The results of these calculations are presented in Figs. 2—5 by continuous lines.

The experimental and theoretical dependences of the amplitudes of signals that were taken from different layers of the piezogage on the light modulation frequency are shown in Fig.6 on the double logarithmic scale in relative units for two samples of polyurethane. The theoretical calculations have been carried out according to (7). To relate the experimental dependences to the theoretical ones, we used $U_1(f)$ at a point $f = 10$ Hz of the sample with $h_1 = 1.6$ mm. As one could see from the results of the study presented in the paper, the experiment and the theory are in good agreement.

In conclusion, we would like to underline that the photothermoacoustic effect in a layered structure in the form of a thin plate with the piezoelectric registration of the informative signal at low frequencies of the light flux modulation could be used for a study of polymer films and the determination of the reduced Young modulus and the thermal diffusion coefficient.

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ФОТОТЕРМОАКУСТИЧНИЙ
ЕФЕКТ В ШАРУВАТИХ СТРУКТУРАХ
ПОЛІМЕРНІ ПЛІВКИ—П'ЄЗОЕЛЕКТРИК

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Р е з ю м е

Теоретично та експериментально досліджено фототермоакустичний ефект у полімерних плівках з п'єзоелектричною реєстрацією інформативного сигналу. Досліджено полімери: поліуретан, поліпропілен і нейлон. Показано, що фототермоакустичний ефект в шаруватій структурі полімер—п'єзоелектрик у вигляді тонкої пластини при низьких частотах модуляції світлового потоку можна використовувати для визначення деяких пружних і теплових параметрів. Експериментально визначені зведений модуль Юнга та коефіцієнт теплової дифузії досліджуваних полімерів.