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Partially polarized fluorescence of a mechanically stressed polyurethane disc

© V.V. Kesaev, V.A. Barbashov, N.A. Putilin, S.S. Kopenkin, A.N. Lobanov, S.A. Ambrozevich

Lebedev Physical Institute, Russian Academy of Sciences, Moscow, Russia
E-mail: vladimir_kesaev@mail.ru

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This study theoretically and experimentally investigates the effect of partial polarization of fluorescence in a polyurethane disk under diametral compression. The degree of fluorescence polarization is described using a dipole approximation and a statistical bimodal Fisher distribution model that characterizes the preferential orientation of dipoles. An experimental setup with normal excitation and observation of photoluminescence is proposed, allowing visualization of the preferential orientation field of the dipoles. The degree of fluorescence polarization in the compressed polyurethane disk was experimentally studied, revealing agreement between the visualized data and the theoretically predicted directions of principal stress planes according to elasticity theory. The aim of the study is to establish the foundations of a „polarization-luminescent method" for remote and continuous monitoring of the stress-strain state.

Keywords: degree of polarization, polarized luminescence, stress-strain state, anisotropy.

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Photoluminescence is the emission of light by a substance excited by an external source (in most cases, an ultraviolet or visible light source). It is used widely to study the electronic structures and energy levels and finds application in analytical chemistry, biomedicine, optoelectronics, and other fields. Polarization studies of luminescence (polarized luminescence, PL), which include its kinetic aspects, are an important tool for the examination of molecular symmetry and anisotropic and rheological properties [1–3]. Advances in PL research are associated with the names of such Russian scientists as S.I. Vavilov, V.L Levshin, and P.P. Feofilov [4,5].

PL is sensitive to structural features of the luminescent medium, which makes it promising for the analysis of the stress-strain state of materials. The work of Forman (1972) [6], who proposed the use of ruby photoluminescence for pressure estimation, deserves a special mention among the approaches to luminescence-based stress measurement and has laid the foundation for piezospectroscopy. In recent years, an approach for measuring residual stresses (see, e.g., the work of Wang [7]) has been developed based on this method. Polarization aspects of luminescence related to the orientation of emitters in the matrix were discussed in the review by Grell and Bradley [8] that is focused on PL in polymers. A correlation between the orientation of dyes in the matrix and the change in polarization characteristics of emission has been revealed recently in [9]. Our research builds on these concepts.

The present study is focused on the specific features of polyurethane PL under complex stress-strain conditions. Photoluminescence was excited and observed normally to the sample surface in our experiment, which simplifies remote monitoring of stresses (in a similar way to photoelastic coatings). However, a luminescent layer may be significantly thinner than photoelastic coatings (on the order of several micrometers), which is achieved by introducing luminescent markers into paint coatings in minimal concentrations that do not affect their performance properties and external appearance. Thus, PL complements interferometry [10] and machine vision [11] methods, does not require any complex equipment, is easily scalable, and is suitable for analysis of large structures without putting them out of service.

A sample in the form of a diametrically compressed disk with a diameter of 29 mm and a thickness of 9 mm made of commercially available cast SKU-6 polyurethane (TU 84-404-78) was examined in the experiment (Brazilian test). Despite the lack of additives or dyes, the material exhibits weak fluorescence with a maximum in the yellow spectral region (around 580 nm). Under the influence of stresses, orientation anisotropy of polymer chains and elementary emitters bound rigidly to them is established in the material, which ultimately leads to spatial modulation of the polarization state of emitted light.

A simplified PL model may be obtained in the dipole approximation, where the absorbing and emitting elementary oscillators are examined in the form of an angular distribution on a unit sphere. We assume in this model that the axes of the absorbing and emitting dipoles are fixed and matching. With zero mechanical stresses, the disk material is isotropic, and the dipoles are distributed with equal probabilities for all directions; however, as stresses and the associated strain intensify, a preferential orientation will emerge at each point in the disk. The „intensity" and direction of this orientation depend on the magnitude of strain at the point in question. The symmetric bimodal Fisher distribution [12] may be used to characterize the

preferential orientation of dipole axes **d**:

$$W_{\kappa,\boldsymbol{\rho}}(\mathbf{d}) = \frac{\kappa}{8\pi \sinh \kappa}(e^{\kappa \boldsymbol{\rho}^{\intercal}\mathbf{d}} + e^{-\kappa \boldsymbol{\rho}^{\intercal}\mathbf{d}}), \qquad (1)$$

where

$$\mathbf{d}, \boldsymbol{\rho} = \big(\sin(\theta_{d,\rho})\cos(\varphi_{d,\rho}), \sin(\theta_{d,\rho})\sin(\varphi_{d,\rho}), \cos(\theta_{d,\rho})\big)^{\intercal}$$

are unit radius vectors specifying the dipole direction and the preferential orientation direction (Fig. 1, *b*) and κ is the concentration parameter that plays the role of inverse variance (by analogy with the normal Gaussian distribution). As the value of κ increases, the dipole axes become increasingly concentrated along the $\boldsymbol{\rho}$ direction. The distribution is bimodal, except for the $\kappa = 0$ case where it becomes uniform. This distribution satisfies the condition of axial dipole symmetry: $W(\kappa, \boldsymbol{\rho}) = W(\kappa, -\boldsymbol{\rho})$. Note that concentration quenching and the interaction (resonance) between oscillators are neglected here. This approach is valid in the case of low emitter concentrations found in coatings, but is only an approximation of the conditions in the polyurethane disk examined in the experiment and should be used with caution.

Figure 1, *a* shows the diagram of the experiment. Linearly polarized light from continuous-wave laser *Lr* with a wavelength of 532 nm was used to excite photoluminescence. The beam passed through half-wave plate HWP, was diverged by low-power lens L_1, and illuminated the surface of sample *S* at an angle less than 10° to the normal. The polarization state of laser radiation was controlled by azimuthal rotation of HWP. The resulting fluorescence was recorded along the normal to the sample by camera *C* with long-focus lens L_2 (with a field of view less than 6°). The polarization state was analyzed using polarizer *Pl* positioned at the required azimuth in front of the lens. A spectral filter with a passband of 540−700 nm was mounted in front of the lens to cut off laser radiation. The approximate distance from the camera to the sample was 0.6 m. Owing to the small angle of fluorescence excitation, excitation and observation could be considered to be performed along the normal. The right-hand coordinate system and spherical angles shown in Fig. 1, *b* are convenient for derivation of expressions for the intensity of polarization components of luminescence. Plane *zy* coincides with the studied disk surface; therefore, illumination and observation are performed along axis *x*.

The fluorescence intensity of a single dipole is proportional to product $W_e^2 W_r^2 W_a^2$, where $W_e = \mathbf{p} \cdot \mathbf{d}$, $W_r = \mathbf{e}_x \times \mathbf{d}$, and $W_a = \cos(\angle \mathbf{a}, \mathbf{d}_{yz})$. Here, $\mathbf{p} = (0, \sin\theta_P, \cos\theta_P)$ is the unit vector of exciting polarization in plane *zy*, $\mathbf{e}_x$ is the unit vector in the direction of axis *x*, and $\angle \mathbf{a}, \mathbf{d}_{yz}$ is the angle between unit vector of analyzer direction **a** and projection $\mathbf{d}_{yz}$ of the dipole axis onto plane *yz*. Thus, the intensity is proportional to dipole excitation (absorption) probability W_e, probability of emission W_r in the direction of axis *x*, and projection W_a of dipole polarization $\mathbf{d}_{yz}$ (collinear to the dipole axis) onto axis **a** of polarizer *Pl*. The intensity

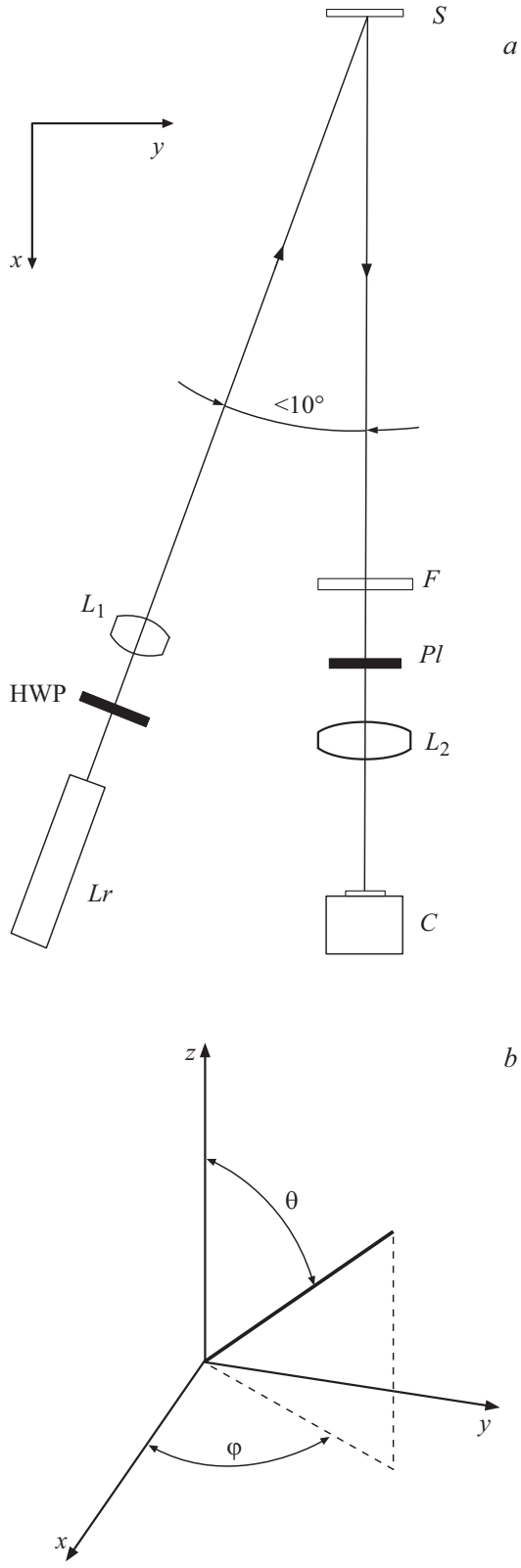

Figure 1. *a* — Experimental setup for polarized luminescence measurements. *Lr* — laser ($\lambda = 532$ nm) emitting linearly polarized light, HWP — half-wave plate, $L_{1,2}$ — lenses, *S* — sample, *F* — spectral filter, *Pl* — polarizer, and *C* — camera. *b* — coordinate system for dipole orientation used to calculate luminescence intensities I_{ij}.

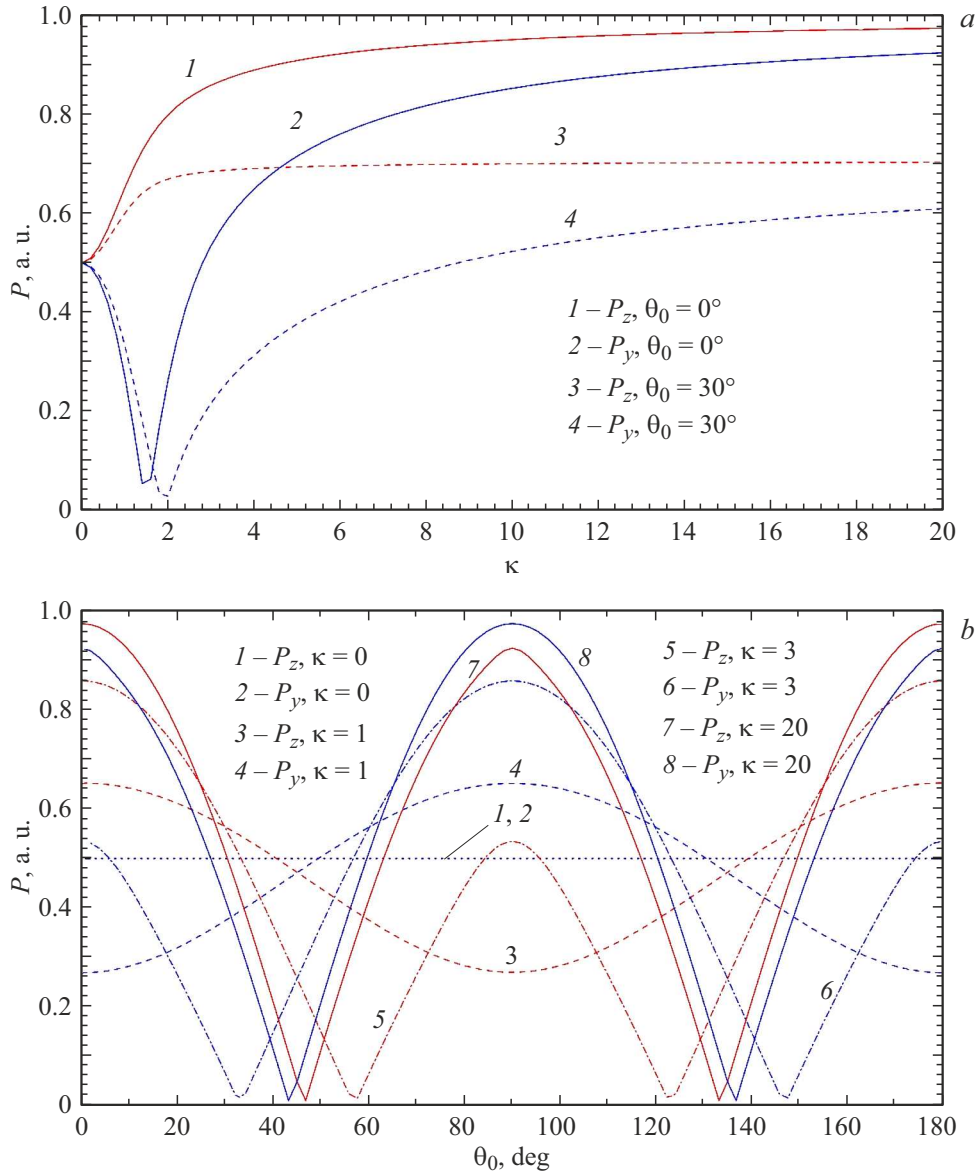

Figure 2. *a* — Polarization degree P_i upon excitation by linearly polarized light along axes $i = z, y$ as a function of concentration parameter κ for parallel preferential orientation $\theta_0 = 0°$ and for $\theta_0 = 30°$; angle $\varphi_0 = \pi/2$. *b* — Dependences of the polarization degree on preferential orientation direction θ_0 ($\varphi_0 = \pi/2$) for certain values of κ.

expression for the entire dipole distribution is proportional to the integral with factor $W^2_{\kappa,\boldsymbol{\rho}}$:

$$I \propto I_e \int W^2_{\kappa,\boldsymbol{\rho}} W_e^2 W_r^2 W_a^2 d\Omega. \qquad (2)$$

Here, I_e is the laser intensity, and integration is performed over solid angle $d\Omega = \sin\theta d\theta d\varphi$ ($0 \leqslant \theta \leqslant \pi$, $0 \leqslant \varphi \leqslant 2\pi$). Assuming for convenience that the direction of polarization of exciting light coincides with axis z, we immediately obtain the following known expressions for the intensities for parallel and perpendicular excitation polarization [13] corresponding to an equally probable distribution ($\kappa = 0$, $W_{\kappa,\boldsymbol{\rho}} = 1/4\pi = \text{const}$): $I_{zz} \propto \frac{4\pi}{15} I_e$, $I_{zy} \propto \frac{4\pi}{5} I_e$ and limit polarization degree $P = |I_{zz} - I_{zy}|/(I_{zz} + I_{zy}) = 1/2$. The first subscript here corresponds to the direction of excitation polarization, while the second one represents the recorded polarized component of luminescence. Note that the direction of axes in the proposed experimental arrangement is conditional. The intensity expressions for excitation along the y axis are similar: $I_{yz} \propto \frac{4\pi}{15} I_e$, $I_{yy} \propto \frac{4\pi}{5} I_e$, (the latter follows also from the symmetry of the experimental arrangement). Combining these results, one obtains easily luminescence intensities for nonpolarized excitation $I_{uz} = I_{zz} + I_{zy} = I_{yz} + I_{yy}$ with resulting polarization degree $P = 0$.

The patterns changes if preferential direction $\boldsymbol{\rho}$ is present; the indicated expressions for intensities and polarization degrees are no longer valid in this case. Specifically,

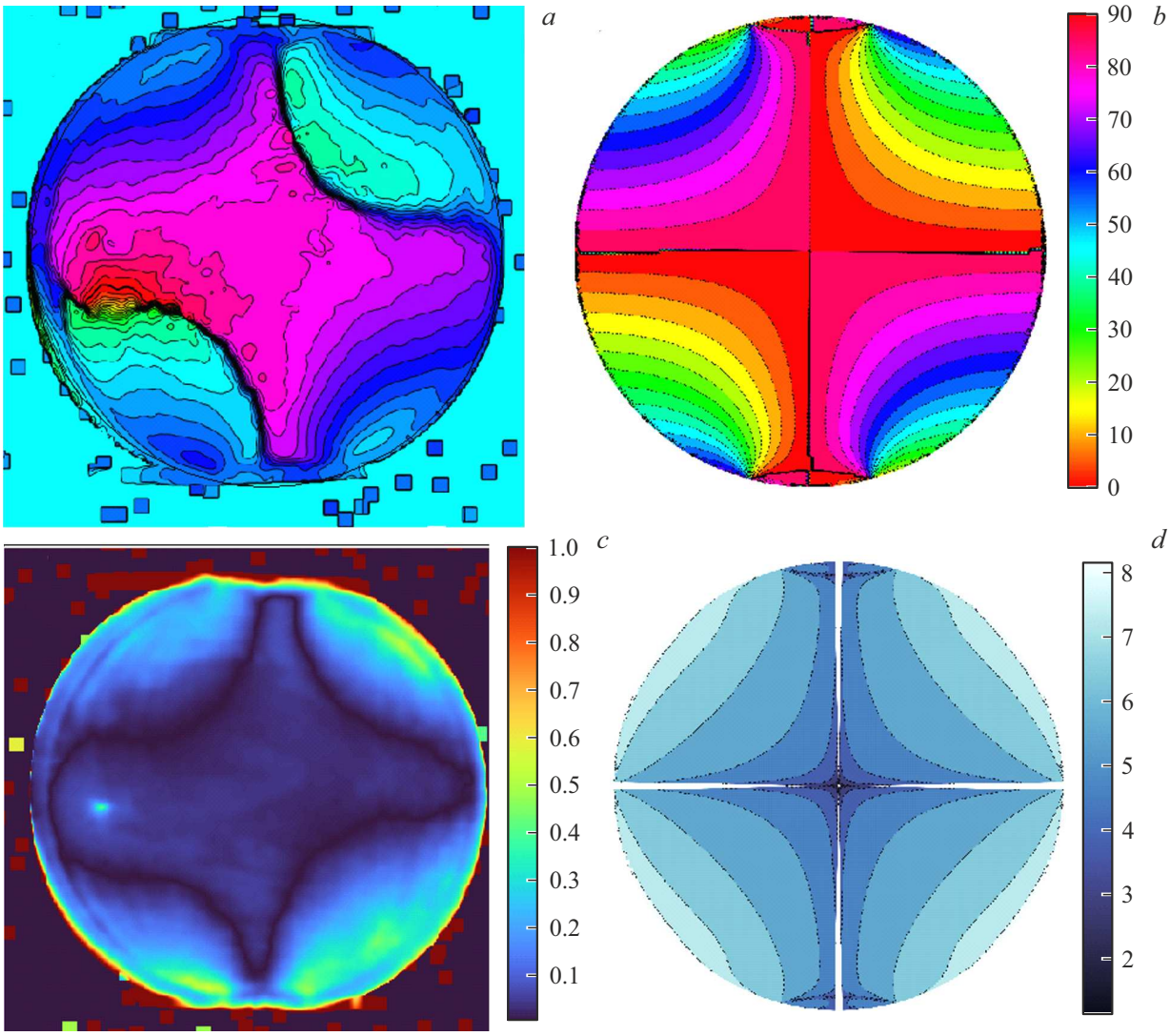

Figure 3. *a* — Experimentally obtained field of preferential orientation θ_0; *b* — isocline field calculated theoretically with the use of formulae from [14]; *c* — experimentally obtained field for polarization degree $0 < P < 1$; and *d* — directional strain tensor component $\lg \bar{D}_{\varepsilon_{yz}}$. The disk was compressed diametrically in the vertical direction (axis z) by radial pressure distributed over a sector of 20°. A color version of the figure is provided in the online version of the paper.

when the concentration parameter tends to infinity, the limit polarization degree is equal to unity, $P(\kappa \to \infty) = 1$, even in the case of nonpolarized excitation. A strict orientation of dipoles will indeed be observed at $\kappa \to \infty$; only constants will remain in the integrand in (2), and integration will not produce any averaging effect. Figure 2, *a* shows the dependences of polarization degree P on parameter κ at fixed azimuth θ_0 (the preferential orientation of dipoles; in this case, $\varphi_0 = \pi/2$). The curves were obtained by numerical integration of (2) in the cases of linear polarization of exciting light directed along axes z and y. Note that the measured polarization degree actually depends on azimuths θ_0 and θ_P and is maximized when they match. In this scenario (and at a small difference in azimuths $\theta_P - \theta_0 < \pi/8$), the polarization degree increases monotonically with increasing κ. In the contrary case with $\theta_P - \theta_0 > \pi/8$, P passes through the minimum before starting to increase. An explanation for this is provided by Fig. 2, *b*, which shows the curves for P determined as a function of angle θ_0 at certain fixed values of κ.

It is easy to extract information on field $\theta_0(yz)$ from the experimentally obtained I_{ij} combinations. Let us use the statistical independence of radiation of a large ensemble of dipoles for this purpose. Owing to this independence, radiation lacks chiral component s_3 of the Stokes vector. The azimuth is then

$$\theta_0 = \tan^{-1}\left(\frac{I_{i45} - I_{i-45}}{I_{\parallel} - I_{\perp}}\right),$$

where $I_{i45,-45}$ are the luminescence intensities measured with the azimuth of polarizer Pl mounted at an angle of $+45$ and $-45°$ to azimuth (i) of exciting light polarization

(Fig. 1, *a*). The result of such a calculation is presented in Fig. 3, *a*. It was obtained by processing four photographic images of the polyurethane disk taken through polarizer *Pl*. The adopted direction of coordinate axes is preserved in this figure. Specifically, the *z* axis (along which the disk is compressed) is directed vertically. The reconstructed field is consistent with the isocline field presented in [14], which is shown in Fig. 3, *b* for ease of comparison.

The key issue is the relation between parameter κ and the strain and stress field. Since parameter κ is a scalar quantity, it cannot characterize fully the strain magnitude (except for the simple uniaxial stress state). However, it follows from general considerations that κ characterizes the intensity of the stress state; evidently, a contribution to concentration κ will be produced by a combination of components of directional strain tensor $\bar{D}_\varepsilon$. Figure 3, *c* shows the experimentally measured field for polarization degree $0 < P < 1$. Its symmetry and structure (Fig. 3, *d*) match the theoretically calculated directional angular strains $\bar{D}_{\varepsilon_{yz}} = \bar{D}_{\varepsilon_{zy}} = \frac{\gamma_{yz}}{\gamma_i} = \frac{\gamma_{zy}}{\gamma_i}$. Here, $\gamma_{yz} = \gamma_{zy}$ is the angular strain and γ_i is the shear strain intensity [15]. Both patterns were calculated with account for a finite area of application of the compressive force [16].

The obtained data confirm that the polarization anisotropy of luminescence is driven by the orientation deformation of polymer chains and allows one to probe experimentally the stress-strain state of the studied sample. The study demonstrates the feasibility of application of PL in stress-strain state analysis, which opens up prospects for continuous monitoring of technical objects.

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Conflict of interest

The authors declare that they have no conflict of interest.

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