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Influence of mechanical stresses on the coefficient of thermal expansion of polymerized steel-filled epoxy resin

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It has been experimentally shown that the standard theory of thermoelasticity cannot describe the dependence of laser-excited acoustic vibrations on stress in an epoxy composite with a conductive filler. To explain the data obtained, a theoretical model of thermoelasticity was used, which takes into account the thermal perturbation of non-stationary defect states with relaxation. The proposed model also takes into account the change in electron gas pressure due to the excitation of defects in metals. It is shown that the dynamic coefficient of thermal expansion in this material is determined primarily by the conductive component.

Keywords: thermoelasticity, ultrasound, epoxy composites, mechanical stress.

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Laser ultrasound (LU) methods are successfully used for diagnostics of materials with heterogeneous microstructure, including composite and additive materials [1–3]. The choice of laser photoacoustic methods makes it possible to analyze various optical, thermal and elastic properties of materials. The analysis is based on the knowledge of the processes for transformation of various forms of energy in the radiated specimen and generation of the corresponding LU signal. However, the theoretical models of photoacoustic processes, despite being well-matched with the results of measurements for ideal solid bodies, often are unable to explain the behavior of the signal from the specimens with heterogeneous nano- and microstructure. For example, the discrepancy between the results of theoretical analysis within the classical thermodynamics and experimental data manifests in the study of the laser generation of ultrasound in the specimens with mechanical stresses [4]. At the same time it was found that the main effect at the LU signal was provided by the deformations due to the dependence of the thermoelastic bond on stresses [5]. In the disordered materials it is often necessary to take into account the relaxation processes in their defective subsystems [6–8].

In this paper we studied the interconnection between the LU signals and the mechanical stress in the polymer composite material, using an example of the model problem with the known stress distribution. The objects of the study were parallelepipeds made of steel-filled epoxide compound Loctite® 3473 with the size of $5.0 \times 5.7 \times 6.7$ mm and a hole in the center with diameter of 0.9 mm and depth of 0.4 mm. The hardened composition, according to the specification, has the following properties: Young's modulus $E = 5.0$ GPa, compressive strength 60 MPa, temperature conductivity 0.003 cm^2/s, thermal expansion ratio (TER) $120 \cdot 10^{-6}\,\mathrm{K}^{-1}$ at temperature above 24°C. LU images were obtained when scanned by a focused (diameter of $\sim 20\mu$m) modulated laser beam on the sample surface with the simultaneous compression of the specimen parallel to the surface. The average power of radiation with wavelength 532 nm on the object surface was 10 mW. The signal was recorded by a piezoelectric sensor on the rear side of the specimen at modulation frequency of 101 KHz. The resolution in the experiment was determined by the diameter of the laser spot on the surface, since the thermal wave length was equal to 1 μm and was much smaller.

Stress distribution near the hole under uniaxial load is known, and in the polar coordinates it is determined by the solution of the Kirsch's problem [9]

$$\sigma = P - P\frac{2a^2}{r^2}\cos 2\varphi, \tag{1}$$

where P is the applied load, r is the distance from the center of the hole, polar angle φ is counted from the direction of the load application, and a is the hole radius.

Images of the regions in the studied specimens around the holes under the external uniaxial load produced by the method of laser ultrasonic scanning microscopy are presented in Figure 1. The signal has two components which may be presented in the form of amplitude and phase. The amplitude of the signal, contrary to the phase, depends on the surface absorption of the laser radiation, therefore, the amplitude image contains multiple fine inclusions. The phase of the signal depends more on the volume properties of the specimen. As a result of low heat conductivity, the thickness of the near-surface layer that determines the behavior of the signal was around $1-2\,\mu$m. Both amplitude and phase images demonstrate the signal change under load, which is specific for the Kirsch's problem solution (equation (1)). Since thermal generation of acoustic waves

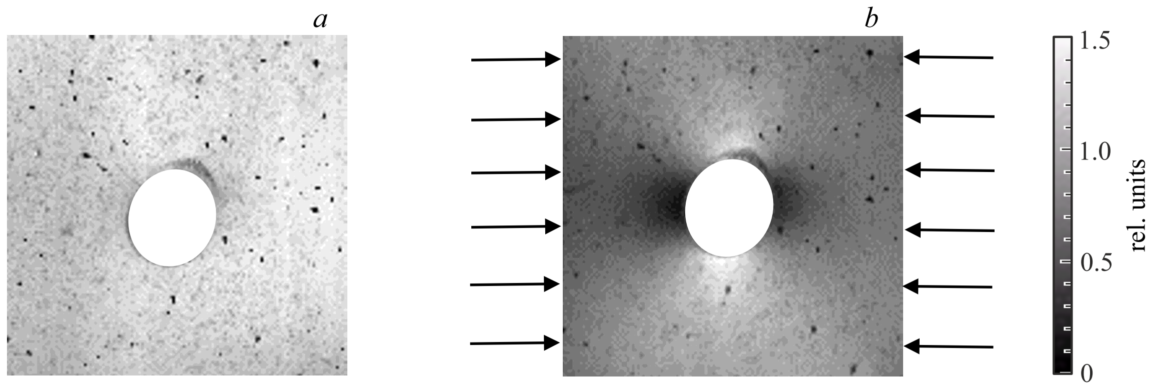

Figure 1. LU image for free specimen (a) and specimen under pressure 10 MPa (b). Image size 2.6×2.6 mm.

in the solid body is determined by the thermoelastic coefficient, the LU signal is generally proportional to CTE of material α, and with low dependence of CTE on stress the signal may be written in linear approximation as follows

$$S(r,\varphi) = \frac{\alpha(\sigma)}{\alpha_0} S_0 = \big(1 + b\sigma(r,\varphi)\big) S_0, \qquad (2)$$

where S_0 is the signal in the absence of stresses, b is the coefficient of linear dependence, α_0 is the CTE in the absence of stress.

Figure 2 shows the behavior of the signal amplitude along the circumference at $r = 0.56$ mm for the free specimen and under load and along the radius at $\varphi = 0^\circ$ and $\varphi = 90^\circ$ under load of 10 MPa. Distribution of the signal for the uniaxially loaded specimen around the hole is close to theoretical distribution, therefore from the distribution of the experimental signal $S(r,\varphi)$ one can find coefficient b. In this case $b = -32 \pm 5\,\mathrm{GPa}^{-1}$. The minus sign means that the signal increases with compression and decreases with tension.

According to the thermodynamic theory, the dependence of CTE on stress is [10]

$$\alpha(\sigma) = \alpha_0 - \frac{1}{E^2}\frac{\partial E}{\partial T}\,\sigma, \qquad (3)$$

where E is the Young's modulus for non-deformed material, T is the specimen temperature. Comparing to equation (2), we get $b = -E^{-2}\alpha_0^{-1}\partial E/\partial T$. Substituting the above data for the studied composite with account of the estimate $\partial E/\partial T \sim -0.05$ GPa/K [11], we will get $b \sim +15\,\mathrm{GPa}^{-1}$. The positivity of the coefficient b does not comply with the data of our experiment at all.

Previously the abnormal behavior of CTE in the LU experiments was found by us for metals and ceramics [12,13]. In both cases the value of the coefficient b was several orders higher than the one calculated according to Eq. (3), and for metals b turned out to be negative. To explain these effects, a theory of thermoelastic generation of acoustic oscillations in real solid bodies with the presence of the sufficient number of defects was proposed [14]. The proposed approach is based on the concepts of slow dynamics. It is known that the presence of meso-scale irregularities of the structure in the materials with complex structure results in substantial effect at their elastic properties [15,16], which may not be explained within the ordinary theory of elasticity. Relaxation processes of various types [17–19] need to be taken into account in order to characterize these effects. To determine deformations arising in the conducting materials during relaxation, it is necessary to take into account the variation of the electron subsystem state. Oscillations in the defective subsystem of the conductor may cause change of the electron pressure [20]. In general, coefficient b is determined by relaxation dynamics of defects in dielectric and conducting components. We demonstrated that in case of excitation with alternating laser radiation, coefficient b for the dielectric component is determined by expression

$$b_d = -\frac{1}{\alpha_0 E^2}\frac{\partial E}{\partial T} + \frac{n_d \tau_d}{\tau_{d0}}\frac{\Omega_d^2}{k_b T}\frac{1}{1 + i\omega\tau_d}, \qquad (4)$$

where T is the temperature, n_d is the concentration of defects and Ω_d is the dilatative parameter of dielectric component, τ_d is the relaxation time, τ_{d0} is the time of the order of the period of atom oscillations in a lattice, k_B is the Boltzmann constant, ω is the cyclic frequency of radiation modulation and accordingly the signal frequency.

For conducting materials, a term is added which corresponds to the excitation of electrons of the defects of the conducting component

$$b_c = -\frac{1}{\alpha_0 E^2}\frac{\partial E}{\partial T} + \frac{n_c \tau_c}{\tau_{c0}}\frac{1}{1 + i\omega\tau_c}\left(\Omega_c - N_d N_V \frac{E_F}{K}\right), \qquad (5)$$

where K is the module of uniform compression, E_F is the Fermi energy, N_d is number of atoms per defect, N_V is the valence, n_c, Ω_c, τ_c and τ_{c0} are parameters similar to parameters in Eq. 4, but for the conducting component,

CTE and the LU signal for dielectric materials increase as the tension stress increases, while for metals they may decrease at $N_d N_V E_F/K > \Omega$. For composite materials with metal components, the dependence of the LU signal on stress must be described by average value b, which includes both b_c and b_d. However, the negative experimental value b

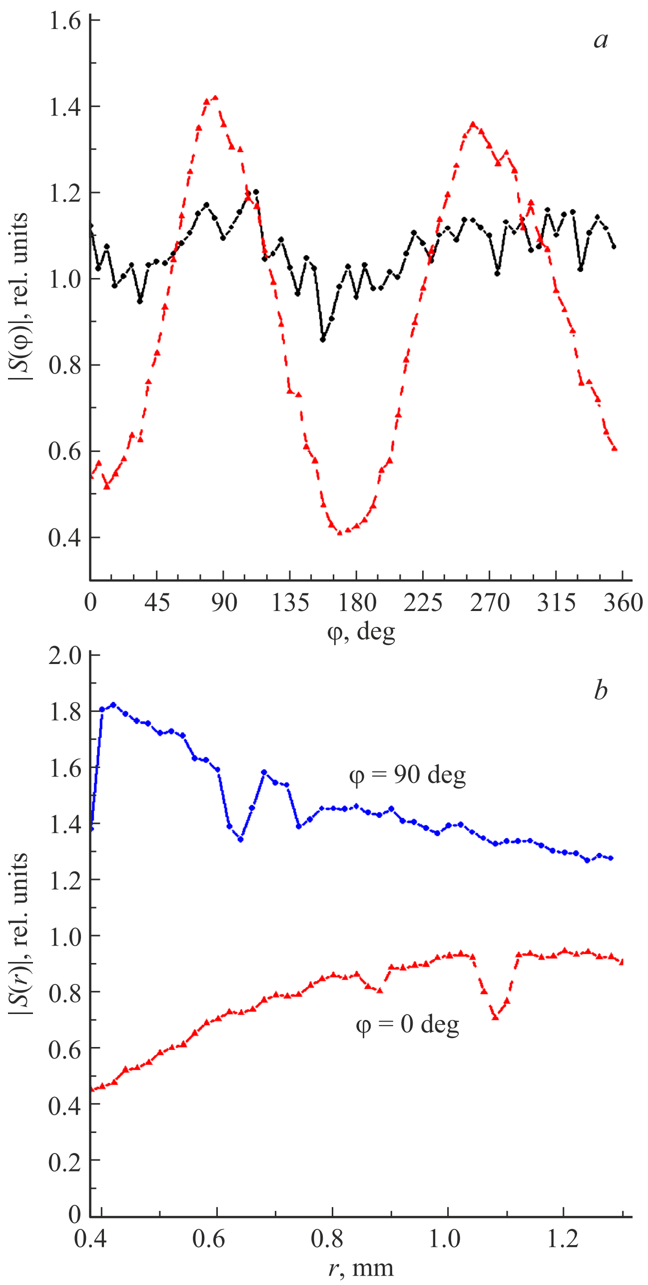

Figure 2. Distribution of the LU signal amplitude near the hole. (*a*) Distribution along the circumference with radius of 0.56 mm. Solid black line corresponds to the specimen without external load, red dotted curve corresponds to the specimen under pressure of 10 MPa. (*b*) Distribution along radius at angles 0° and 90°.

shows that the main contribution is made by the member corresponding to the excitation of electrons of defects of the conducting component [15].

To conclude, the paper studied the behavior of the LU signals near the hole in the stressed composite materials. Theoretical analysis shows that the thermodynamic approach to the thermoelasticity is not adequate to explain the experimental data on the dependence of the thermoelastically generated ultrasound on stress. The possible cause for abnormal behavior of the LU signals is excitation and relaxation of non-stationary defect states, mostly in the conducting component. Besides, the conducting component in the steel-filled epoxide composite makes the main contribution to this dependence by variation of the pressure of electron gas during excitation of quasi-bound electrons.

The laser method for generation of ultrasound oscillations in combination with hole drilling may be used to assess mechanical stresses in the composite materials with the complex structure.

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Conflict of interest

The authors declare that they have no conflict of interest.

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