

The study of the mechanical properties of thin films using piezoceramic acoustic resonators

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Abstract. The paper describes a method for determining the properties of thin films: elastic constants, viscosity and density. The method is based on the analysis of changing the characteristics of the acoustic resonator, on the surface of which the film under study is deposited, in comparison with a free resonator. Using the described method, the properties of two organic films based on the mycelium of basidiomycete *Hericium erinaceus* (Bull.) Persoon were determined.

1 Introduction

One of the possible applications of the acoustic piezoresonators is the determination of the mechanical characteristics of films. The method for determining these characteristics is based on a simple idea: the investigated film is deposited on the surface of the resonator and changes its resonant frequencies. To determine the characteristics of the film under study, one can measure the electrical impedance of a free resonator without a film in a sufficiently wide frequency range. The material constants of the resonator material can be determined using the equivalent Mason scheme [1, 2] or by solving the “inverse problem” [3]. The latter method is called one of broadband acoustic spectroscopy. After that, the investigated film is applied to the resonator, and the impedance measurement in the indicated frequency range is repeated. The solution of the inverse problem for a resonator with a film, using the adjusted values of the material constants of the piezoresonator, allow to determine the acoustic properties of the film. To effectively solve the inverse problem, one must be able to quickly calculate the values of the electrical impedance of the resonator at various frequencies, for example, using the finite element analysis. A resonator in the form of a circular disk, which is excited by thin metal electrodes located at the faces of the disk, is well suited for this purpose. The test film is applied to one of the faces, directly to the electrode. A thin metal electrode does not affect the mechanical connection of the film with the resonator; however, it completely shields the effect of electric fields on the film

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that arises in the piezoelectric material of the resonator. Therefore, it is impossible to determine the dielectric permittivity and electrical conductivity of the film with this arrangement.

The possibility of using films from the mycelium of basidiomycetes to create chemical gas sensors was previously shown [2, 4]. To simulate such devices, information is needed on the physical characteristics of such films. In this regard, the previously developed method was used to determine the elastic constants, viscosity and density of the studied organic films based on the mycelium of *Hericium erinaceus* (Bull.) Persoon.

2 Preparation of organic films from homogenized mycelium and mycelium extracts

At the first step, the selection of a nutrient medium that provides a high mycelial growth rate and does not contain insoluble particles was carried out. This is because the water-insoluble ingredients can lead to uncontrolled penetration of compounds of nonfungal origin into the film. Thus, glucose, yeast extract and mineral salts were chosen as components of a nutrient medium for the cultivation of basidiomycetes.

Nine strains of basidiomycetes (*Agrocybe aegerita* (V. Brig.) Singer, *Armillaria mellea* (Vahl) P. Kumm., *Flammulina velutipes* (Curtis) Singer, *Ganoderma lucidum* (Curtis) P. Karst, *Hericium erinaceus* (Bull.) Persoon, *Hypsizygus ulmarius* (Bull.) Redhead, *Lyophyllum shimeji* (Kawam.) Hongo, *Lentinus edodes* (Berk.) Singer, *Trametes versicolor* (Berk.) Singer) were evaluated for their growth and biomass production on the selected culture medium. Basidiomycetes were obtained from the stock collection of GINA Laboratory of biosynthesis of bioactive compounds. Stock cultures of basidiomycetes were maintained at 2 °C on potato-dextrose agar (PDA).

Fungal mycelium was grown under submerged culture conditions for 6 days. Submerged cultivation of basidiomycetes was carried out at 26 °C on a rotary shaker at 230 rpm in 750 mL Erlenmeyer flasks with 100 mL of nutrient medium inoculated with 10 mL of liquid seed culture. Nutrient medium contained (g/l of tap water): anhydrous glucose - 20,0; yeast extract - 10,0; potassium hydrophosphate - 2,0 and magnesium sulfate - 0,2. The seed culture was grown in a 750 ml Erlenmeyer flasks containing 100 ml 4° Balling unhopped barley wort at 26 °C for 6-7 days (depending on the growth rate of the strain). The seed medium was inoculated by mycelial agar plugs (3 mm diam.) containing ten-day-old PDA cultures of basidiomycetes.

The submerged cultivation of *H. erinaceus* provided the highest yield of air-dry mycelium – 12g/l. This strain was selected for further experiments.

Further, the selection of solvent for preparation of organic films was carried out. Solvents such as water, acetone, ethanol, ethyl acetate, water-ethanol mixture (1:4) were tested. The mycelium of *H. erinaceus* was filtered and washed with distilled water before homogenization. The solvent in a ratio of 1:12 was added to the wet biomass and homogenized for 5 minutes using an IKA T 18 Digital Ultra-TURRAX dispersant. The homogenized mycelium of *H. erinaceus* in a solvent was dropped to glass slides, dried and studied with Olympus CX42 light microscope. The selection criterion was the uniform distribution of the homogenized mycelium in the liquid phase. The uniformity of distribution was increased in the series: ethyl acetate <acetone <ethanol <water-ethanol mixture (1:4) <water. Taking into account the obtained results, water was chosen as the solvent for the preparation of organic films.

The suspension of homogenized mycelium in distilled water was divided into two equal parts. One part was used to create films containing biomass. The second part was centrifuged at 4000 rpm for 10 minutes, and the supernatant was used to create films from an aqueous extract of mycelium.

To obtain films with a thickness 50, 100 and 150 μm , 500, 1000 and 1500 μl of an aqueous extract of mycelium and 250, 500 and 750 μl of homogenized mycelium respectively were placed on the surface of two of the resonators with diameter 22 mm. The application was carried out several times, gradually drying the resulting films until the full use of the required sample volume. Then, the resonators were kept in the air in a laminar chamber in order to avoid dust on the samples during the day before the final evaporation of moisture.

3 Determination of the physical properties of mycelium films

To determine and study the properties of the films, 6 acoustic resonators made of the ZTBS-3 piezoceramics were used. The resonators were disk-shaped with a diameter d of about 22 mm and a thickness h^d of about 2 mm. Acoustic oscillations were excited using thin silver electrodes deposited on opposite faces of the disk. The electric field vector induced by these electrodes was parallel to the axis of the disk and the polar axis Z of the piezoceramics (Fig. 1). During the measurements, the disk is placed on a low-impedance foam support, which does not affect its resonance properties. A viscoelastic film with a known thickness h^f but unknown mechanical properties that must be determined can be located on the top disk surface.

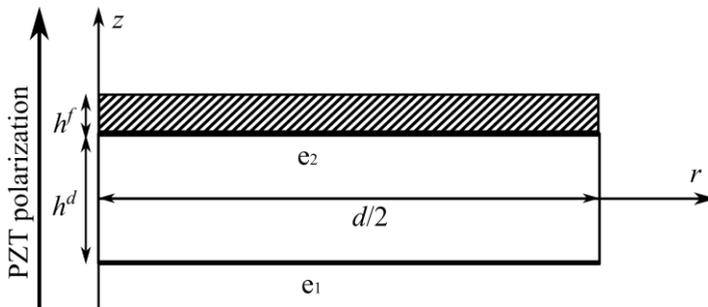


Fig. 1. The geometry of the problem. A piezoceramic disk of thickness h^d is obtained by rotating the shown figure around the Z axis. An exciting electric field is created by electrodes e_1 and e_2 . Viscoelastic film with a thickness of h^f may be absent.

Consider the problem of forced vibrations of a circular piezoceramic disk. A disk with a diameter d and thickness h^d is made of piezoceramics belonging to the crystallographic class 6mm. The polarization direction of the ceramics is parallel to the axis of the disk (z -axis on fig.1). Metallic electrodes e_1 and e_2 are located on the lower and upper sides of the disk. It is necessary to find the distribution of acoustic and electric fields inside the disk. In this formulation, the problem is axisymmetric and becomes two-dimensional (in the coordinates r and z). The desired solution can be written as:

$$\left. \begin{aligned} u_r &= u_r(r, z) \exp(I\omega t) \\ u_z &= u_z(r, z) \exp(I\omega t) \\ \varphi &= \varphi(r, z) \exp(I\omega t) \end{aligned} \right\}, \quad (1)$$

where u_r , u_z is the radial and axial components of mechanical displacement, φ is the electrical potential, I is the imaginary unit, ω is the angular frequency, t is the time. The torsion component of the mechanical displacement u_θ can not be excited with this arrangement of electrodes, therefore, it can be omitted from solution. Thus, in the problem one can take into account only four components of the deformation tensor S :

$$\{S\} = \begin{Bmatrix} S_{rr} \\ S_{\theta\theta} \\ S_{zz} \\ 2S_{rz} \end{Bmatrix} = \begin{bmatrix} \frac{\partial}{\partial r} & 0 \\ \frac{1}{r} & 0 \\ 0 & \frac{\partial}{\partial z} \\ \frac{\partial}{\partial z} & \frac{\partial}{\partial r} \end{bmatrix} \begin{Bmatrix} u_r \\ u_z \end{Bmatrix} = [L_u] \{u\}, \quad (2)$$

and two components of electric field E :

$$\{E\} = \begin{Bmatrix} E_r \\ E_z \end{Bmatrix} = - \begin{bmatrix} \frac{\partial}{\partial r} \\ \frac{\partial}{\partial z} \end{bmatrix} \varphi = - [L_\varphi] \varphi. \quad (3)$$

In the two-dimensional axisymmetric case under consideration, some rows and columns can be removed from the matrices of material constants, and the corresponding matrices can be written as:

$$[c] = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 \\ c_{12} & c_{11} & c_{13} & 0 \\ c_{13} & c_{13} & c_{33} & 0 \\ 0 & 0 & 0 & c_{44} \end{bmatrix} (1 + I\omega\eta), \quad [e] = \begin{bmatrix} 0 & 0 & 0 & e_{15} \\ e_{31} & e_{31} & e_{33} & 0 \end{bmatrix}, \quad [\varepsilon] = \begin{bmatrix} \varepsilon_{11} & 0 \\ 0 & \varepsilon_{33} \end{bmatrix}.$$

Thus, the resonator material is characterized by five elastic constants c_{11} , c_{12} , c_{13} , c_{33} , c_{44} , three piezoelectric constants e_{15} , e_{31} , e_{33} , two dielectric permittivity constants ε_{11} , ε_{33} , density ρ and scalar viscosity factor η . The problem is described by a system of equations:

$$\left. \begin{aligned} -\omega^2 \int_V \rho \{u\}^T \{u\} dV + \int_V ([L_u] \{u\})^T [c] [L_u] \{u\} dV + \int_V ([L_u] \{u\})^T [e] [L_\varphi] \varphi dV = 0 \\ \int_V ([L_\varphi] \varphi)^T [e] [L_u] \{u\} dV - \int_V ([L_\varphi] \varphi)^T [\varepsilon] [L_\varphi] \varphi dV = 0 \end{aligned} \right\}, \quad (4)$$

with the following boundary conditions. The mechanical boundary condition is set on the axis of the disk: $u_r = 0|_{r=0}$, the remaining surface is mechanically free. The value of the amplitude of the electric potential is explicitly set on the electrodes: $\varphi = V_1|_{z=-h^d/2}$, $\varphi = V_2|_{z=+h^d/2}$, the remaining surface is electrically free. The solution of this problem using the finite element method allows us to calculate the electrical impedance of the disk for a given frequency and known material constants of piezoceramics.

At the first stage of the work, the geometric dimensions and mass of each resonator were carefully measured. In addition, the frequency dependences of the real and imaginary parts of the electrical impedance in the frequency range 50 kHz – 1450 kHz with a step of 100 Hz were measured for each resonator. The measurements were carried out with a KEYSIGHT E4990A impedance analyzer at a constant temperature of 25 °C. The obtained dependences contained a number of maxima of the electrical impedance, which corresponded to different modes of acoustic disk oscillations (Fig. 2a). The values of these maxima and the corresponding resonant frequencies for each of the 6 resonators slightly differed from each other, due to both small differences in the dimensions of the resonators

and the spread of their material constants. Then, a mathematical model described above was created for each resonator. It exactly corresponded to the geometry of a particular resonator and allowed to calculate the value of its impedance depending on the frequency of the exciting field (direct task).

The solution of the inverse problem made it possible to refine the material constants of piezoceramics from which a specific disk sample was made. The initial values of the material constants of piezoceramics were taken from the literature [5]. The density was determined by weighing each sample. The viscosity factor was determined from the shape of the resonance curves according to the formula:

$$\eta = \frac{\Delta\omega}{\omega_{\max}^2}, \quad (5)$$

where ω_{\max} is the resonance frequency and $\Delta\omega$ is the width of the resonance peak. The refined values of material constants were determined using the Nelder-Mead algorithm [3]. The objective function, which was minimized by the algorithm, was written as:

$$F = \sqrt{\sum_{i=1}^n (\log|Z_i^e| - \log|Z_i^l|)^2}. \quad (6)$$

Here $|Z_i^e|$ and $|Z_i^l|$ are the measured and calculated absolute values of electric impedance at the frequency f_i , respectively, n is the number of measurement points. The advantage of the chosen algorithm is that it does not require the calculation of derivatives of the minimized function. It was found that the refined values differed from the initial values by no more than 5%. As a result, the theoretically calculated using the refined values of the material constants and the experimentally measured values of the frequencies of the resonant peaks differed by no more than 100 Hz for each resonator sample.

At the second stage of the work, the studied film was deposited on one face of each resonator. The films from homogenized mycelium of *H. erinaceus* with a thickness of 50, 100, and 150 μm were deposited on 3 resonators. The films from an aqueous extract of mycelium with a thickness of 50, 100 and 150 μm were also deposited on the other 3 resonators. The presence of the film at the face of the resonator disk changed the properties of this oscillatory system. To take this into account, an isotropic viscoelastic layer of thickness h^f was added to the theoretical model. This layer was conjugated with piezoceramics using the mechanical boundary condition of continuity in the region of the electrode e_2 : $u_i - u_i^f = 0, (T_{ij} - T_{ij}^f)n_j = 0|_{z=h^f/2}$, where the values with index f refer to the film, n_j is the normal to disk surface.

The model parameters included both material constants and ceramic density, as well as elastic constants c_{11}^f, c_{44}^f , viscosity η^f , and density ρ^f of the film material. In this case, the effective elastic constants of the film in the calculations had the form $c_{ij}^f = c_{ij}^f (1 + I\omega\eta^f)$. Upon repeated measurement of the frequency dependence of the real and imaginary parts of the electric impedance, the resonant frequencies decreased by 0.1 – 0.4% (Fig. 2b). All measurements were carried out at a constant temperature and its fluctuations did not exceed 1 °C. The humidity in the room during the measurement did not exceed 20%. For each resonator with a film, an appropriate finite element model has been created taking into account the thickness of the film, under the assumption that this thickness is constant on the entire surface of the film. Ceramic parameters corresponded to the refined parameters for this sample, and the film parameters were varied and subjected to refinement. The density of the films was preliminarily estimated by weighing the resonators before and after the deposition of the films.

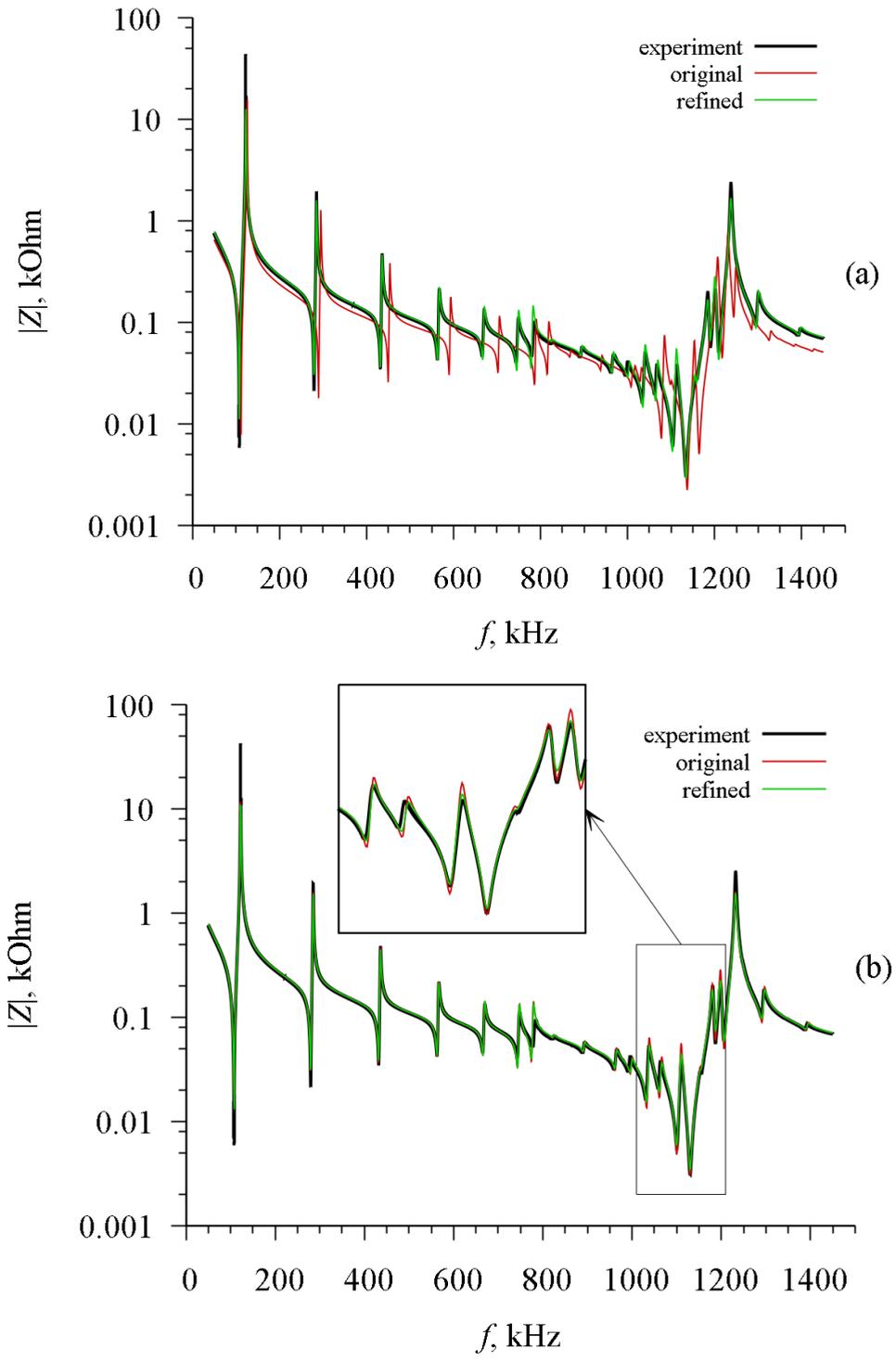


Fig. 2. Frequency dependences of the electrical impedance for a free resonator (a) and a resonator with a film (b). Comparison of the experiment and the result of the refinement procedure for sample No. 1.

4 Results and conclusions

The calculation results of the material constants of the studied films are shown in Table 1. The analysis has shown that the films from homogenized mycelium of *H. erinaceus* are characterized by large values of the elastic constants and density in comparison with the films from the extract. Apparently, this is due to the greater uniformity of the film and its less friability in comparison with the films from the extract. It has been also found that with increasing thickness of the films, both homogenized and those obtained from the extract, their elastic constants and viscosity decrease, and the density increases. The relative change in density is 17%. A change in density can be caused by different concentrations of water molecules remaining in the films of different thicknesses upon drying. At that, the inhomogeneity of real films in thickness may also influence the calculation results. The relative change in the elastic constants with increasing film thickness is about 30%. A decrease in the elastic constants of the films with increasing thickness can be associated with an increase in the number of boundaries between the layers with a sequential increase in the film thickness.

Table 1. The physical characteristics of the films based on *H. erinaceus* mycelium

Sample	$c_{11}, \times 10^9 \text{ Pa}$	$c_{44}, \times 10^9 \text{ Pa}$	$\eta, \times 10^{-9} \text{ s/rad}$	$\rho, \text{ kg/m}^3$
homogenizate 50 μm	10.103	6.246	3.700	371.2
homogenizate 100 μm	9.314	5.958	3.894	434.0
homogenizate 150 μm	7.167	4.495	2.909	446.0
extract 100 μm	5.427	3.980	2.430	211.0
extract 150 μm	5.148	3.206	2.233	225.7

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References

1. I.E. Kuznetsova, B.D. Zaitsev, A.M. Shikhabudinov, IEEE Trans. on Ultras., Ferroel. and Freq. Contr., **57**, 2099-2102 (2010)
2. I.E. Kuznetsova, B.D. Zaitsev, A.M. Shikhabudinov, O.M. Tsivileva, A.N. Pankratov, E. Verona, Sens. and Act. B, **243**, 525-531 (2017)
3. A. A. Teplykh, B. D. Zaitsev, A. M. Shikhabudinov, I. A. Borodina, Radiotech. **7**, 64-69 (2017)
4. Y.E. Silina, T.A. Kuchmenko, Y.I. Korenman, O.M. Tsivileva, V.E. Nikitina, J. Analyt. Chem., **60**, 678-683 (2005)
5. S. Ibrahim, R. Ramadan, and A. Mohamed, Piezoelectric Ceramic Materials, Lap Lambert Academic Publishing GmbH & Company KG (2011)