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NONLINEAR ACOUSTICS

A Study of the Elastic Properties of the Polymer PLA by Static and Ultrasonic Methods

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Abstract—The article presents the results of experimental studies of the elastic properties of the polymer polylactide (PLA), which is widely used in 3D printing technology. The dependences of the mechanical stress on the static deformation magnitude are measured, and the dependence of the hysteresis is found. The values of the Young's modulus in the linear sections of loading and unloading of the sample are estimated. It is established that the periodic loading and unloading of the sample lead to its strengthening in the region of elastic deformations. An equation that relates the change in the velocity of acoustic waves in a thin rod with the value of its static deformation is obtained, which is suitable for describing the PLA sample under study. A linear dependence of the relative change in the elastic wave velocity in the sample on the magnitude of its static deformation is found. Based on the measurement results, the third-order elastic coefficients are determined and the nonlinear acoustic parameter in the PLA polymer is calculated.

Keywords: ultrasonic wave velocity, PLA polymer, third-order elasticity coefficient, nonlinear elastic parameter

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INTRODUCTION

The 3D printing of various objects, widely used in many fields of science and technology, has become increasingly popular in the last decade. 3D printing makes it possible to create composite samples both from polymer materials [1–5] and various metal alloys [6–8]. 3D printing is a potentially cutting-edge technology in a number of industries, including aerospace, biomedical, and automotive industries. A 3D printer is a machine with computer numerical control, in which a layer-by-layer printing method is used for rapid prototyping of models and objects. The gradual buildup of components allows one to create parts with complex geometry and fine tune the final product.

Polymer materials, such as thermoplastics capable of reversibly transforming into an elastic state when heated, are often used as printing material. The choice of materials varies depending on both the required melting point and the strength characteristics of the final product. Polylactic acid (PLA) is among the promising materials for 3D printing. It is a biodegradable and biocompatible polymer that can be produced from plant materials. PLA is a linear aliphatic polyester, the monomer of which is lactic acid (2-hydroxypropionic acid), which can exist in the form of optically active D or L enantiomers [9]. PLA decomposes via hydrolysis followed by bacterial biodegradation [10]. Currently, PLA is already being used in production for the food industry, as well as for biomedical purposes. A review of the effects of the chemical composition, production methods, and material modification on the physical (including mechanical) properties of the family of PLA-based polymers is given in [11]. In the last decade, PLA has been also considered as a basis for a number of biocomposite materials in line with replacing synthetic materials with natural ones [12].

The mechanical properties of PLA and materials based on it were previously investigated mainly by static methods. In [13], tensile and fatigue life tests on pure and modified PLA samples were performed. It has been found that PLA has a sufficiently high stiffness and high strength compared to many synthetic polymers, while modification can improve its mechanical properties. In [14], the mechanical properties of thin PLA films made by hot pressing with stretching were studied. The effect of strain rate on the mechanical properties of PLA was also investigated. In [15], the effect of shock loading on the elastic properties of PLA polymer samples was investigated. An increase in the shear strength with an increase in the impact stress was observed. Acoustic methods were previously used to study the glass transition of PLA and polylactic-co-glycolic acid (PLGA) polymers in the temperature range of 0–70°C [16] and to monitor the process of degradation of three biodegradable polymers based on PLA [17]. In [18], the effect of combined physical and thermochemical treatment (addition of a modifying impurity, low-temperature aging after quenching, and ultraviolet irradiation in various combinations) during bending deformation of the modified PLA samples on the value of the third-order nonlinear acoustic parameter measured by the harmonic generation method was studied. It is noted that the largest increase in the third-order nonlinear parameter occurs either with the introduction of a modifying impurity or with the combined application of all the applied processing methods.

This paper presents the results of an experimental study of the elastic properties (both linear and nonlinear) of a PLA sample by ultrasonic and static methods with continuous variation of its internal structure caused by periodic cycles of its mechanical loading–unloading. The elastic properties were studied by the pulsed method by analyzing the propagation of elastic longitudinal waves in the sample with the simultaneous application of a mechanical tensile load.

In this study, the modified Thurston–Bragger method or quasi-static method—which measures the parameters of elastic wave propagation in a solid when exposed to constant external forces—was used to analyze the nonlinear elastic properties of solids. The authors of [19] analyzed the propagation of low-amplitude acoustic waves in solids subjected to uniaxial compression and obtained a system of linear equations making it possible to determine all third-order independent components of the elastic coefficients tensor by measuring the dependence of the elastic wave velocity in a solid on the external static compressive pressure applied to it. This is one of the most widely used methods for studying the nonlinear elastic properties of solids. In [20], samples of the B95 aluminum alloy and B95/nanodiamond composite with a diamond nanoparticle impurity were studied experimentally. In these materials, the second- and third-order elastic constants were determined using a pulsed ultrasonic method and the quasi-static Thurston–Bragger method, respectively. A significant difference was revealed in the third-order elastic coefficients in the B95 alloy and B95/nanodiamond composite samples, while the second-order elastic coefficients practically coincide. This indicates a high sensitivity of the nonlinear acoustic properties of the studied alloys to the chemical composition and structure of the material. In [21], an aluminum alloy of the AMg6 brand was investigated and the third-order elastic coefficients were determined by the Thurston–Bragger method from the results of experimental measurements of the dependence of the velocity of shear and longitudinal elastic waves on the magnitude of compression. In [22], the effect of loading–unloading processes on the mechanical, linear, and nonlinear properties of the AMg6 aluminum alloy was studied experimentally. Nonlinear elastic properties in different parts of the load curve were also studied by the Thurston–Bragger method.

In this study, the Thurston–Bragger method is used for the first time to evaluate the linear and nonlinear elastic properties of a PLA sample of the eSun brand under stretching up to deformations of 0.004.

EXPERIMENTAL

A sample of the eSun PLA polymer (used in 3D printing) in the form of a thin cylindrical thread with a length of $L = 118$ mm and a diameter of $D = 1.8$ mm was used in the study. No additional thermal or other treatment of the sample was performed. The rod velocity of sound in the material of the sample in the undeformed state was measured, which was $V = 1630 \pm 20$ m/s; in addition, the density was $\rho = 1.40 \pm 0.05$ g/cm^3. The Young's modulus calculated from these data was $E = 3.3 \pm 0.1$ GPa, which agrees well with the data obtained by other researchers [15, 23].

The PLA sample was rigidly fixed in the grooves of two movable platforms, to which a force was applied by means of a screw jack capable of creating a tensile deformation in the sample. The sample was fixed in a special device that made it possible to convert the compressive force generated by the jack into tensile force. To generate and receive elastic longitudinal waves in the test sample, piezoceramic transducers with a resonance frequency of 300 kHz were used, which were attached with a spring-loaded clamp to the ends of the sample. To eliminate parasitic high-frequency components, the probe signal was passed through a low-frequency filter. A similar experimental technique that was previously used to study the mechanical and elastic properties of the n-AMg6/C_{60} nanostructured composite [24], as well as to study the peculiarities of propagation of elastic longitudinal and torsional waves in polycrystalline copper in the range of elastic and plastic deformations [25], showed itself as an effective and reliable method to obtain information on the elastic properties of the materials under study.

To experimentally study the elastic properties of the PLA polymer, an automated ultrasonic unit developed on the basis of the Ritec RAM-5000 automated ultrasonic system was used. The block diagram of the experimental setup is shown in Fig. 1. The pulse measurement method was implemented in the ultrasonic system.

An acoustic longitudinal wave was excited by upper piezoelectric transducer *1*, passed through sample *2*, and reached lower piezoelectric transducer *3* and generated in it an electrical signal proportional to the amplitude of the acoustic wave, which was subsequently amplified, entered ultrasonic acoustic complex *4*, processed by quadrature processing, and recorded in personal computer *5*. A four-channel digital oscilloscope (not shown in the figure) was used to observe signals in real time. Information about the change in the length of the sample and the force applied to it was recorded using analog sensors *6* and *7*. The measurement results from the sensors were digitized with an analog-to-digital converter (ADC) and supplied to a PC for storage and further analysis. During the experiment, the sample was subjected to several periodic cycles of mechanical loading–unloading.

A specially developed software package with a graphics interface was used to control the course of the experiment from a personal computer and to process the obtained data. The interface made it possible to simultaneously carry out static and ultrasonic measurements with their further archiving and processing in a personal computer.

The developed measuring unit made it possible to study the mechanical and elastic properties of the PLA sample by a quasi-static method, as follows:

1. The static method was used to measure the mechanical stress σ–deformation ε load curve under conditions of applying several loading–unloading cycles to the test specimen.

2. The modified quasi-static Thurston–Bragger method was used to determine the elasticity coefficients of the third order. The method is based on measuring the dependence of the elastic wave velocity in a solid on the magnitude of the applied mechanical tensile stress.

Propagation of longitudinal elastic waves in solid isotropic cylinders (rods) in accordance with formula

$$U = U_0 \sin(\omega t - kx) \tag{1}$$

is described by the following equations of motion and state:

$$\rho_0 \frac{\partial^2 U}{\partial t^2} = \frac{\partial \sigma}{\partial x}, \tag{2}$$

$$\sigma = E\varepsilon + \frac{1}{2} E_N \varepsilon^2, \tag{3}$$

where U is the displacement vector, σ is the mechanical stress, ω is the frequency of the elastic wave, $k = \omega/V$ is the wave vector, $\varepsilon = \left(\frac{\partial U}{\partial x}\right)_{\varepsilon_{st}=0}$ is the strain created by the acoustic wave in the investigated cylindrical specimen, $E_N = \left(\frac{\partial^2 \sigma}{\partial \varepsilon^2}\right)_{\varepsilon_{st}=0}$ is the third-order elasticity coefficient that can be interpreted as the third-order Young's modulus in the case of an elastic rod, and $E = \left(\frac{\partial \sigma}{\partial \varepsilon}\right)_{\varepsilon_{st}=0}$ is the Young's modulus. The expression below follows from Eqs. (1)–(3):

$$\left(\frac{\Delta V}{V}\right)_{\varepsilon_{st}=0} = \frac{E_N}{2E} \Delta\varepsilon_{st}. \tag{4}$$

Expression (4) is an analog of the Thurston–Bragger formula used to determine the elastic coefficients in three-dimensional solids and allows one to determine third-order elastic coefficient E_N from the results of measuring the dependence of rod velocity V in a one-dimensional solid rod on static tensile strain ε_{st} of the rod.

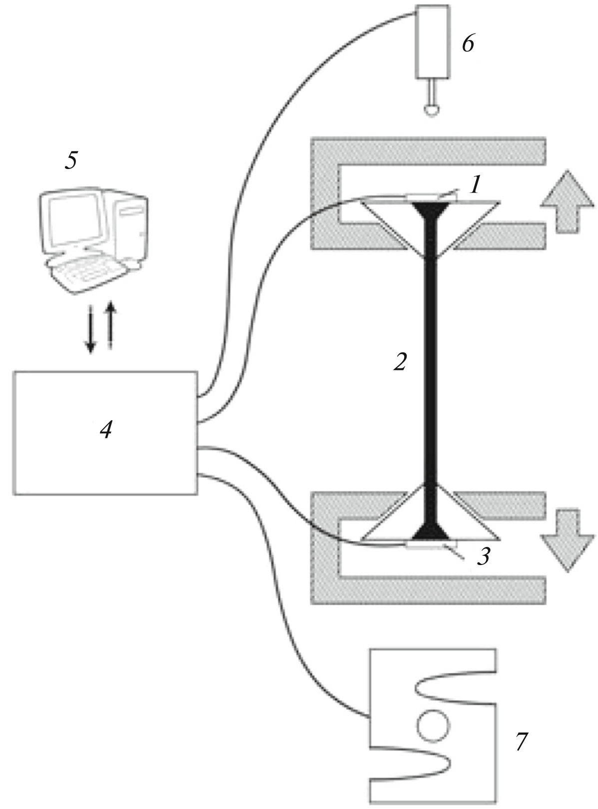

Fig. 1. Schematic diagram of experimental setup: *1*, emitting piezoelectric transducer; *2* sample; *3*, receiving piezoelectric transducer; *4*, Ritec RAM-5000 automated ultrasonic system; *5*, PC; *6*, sample elongation sensor; *7*, force sensor.

To characterize the nonlinear elastic properties of a thin cylindrical specimen, this study proposes to use—by analogy with three-dimensional solids—the following dimensionless acoustic nonlinear parameter:

$$N = \frac{E_N}{E}. \tag{5}$$

RESULTS AND DISCUSSION

In a series of experiments, information about the linear and nonlinear elastic properties of the studied specimen made of PLA of the eSun brand and about the effect of periodic processes of mechanical loading–unloading cycles on them was obtained.

Figure 2 a shows the results of measuring the stress–strain dependence σ = σ(ε) in the sample for four cycles of periodic variation of the mechanical stress applied to it. The cyclic application of force to the PLA specimen in the loading–unloading mode

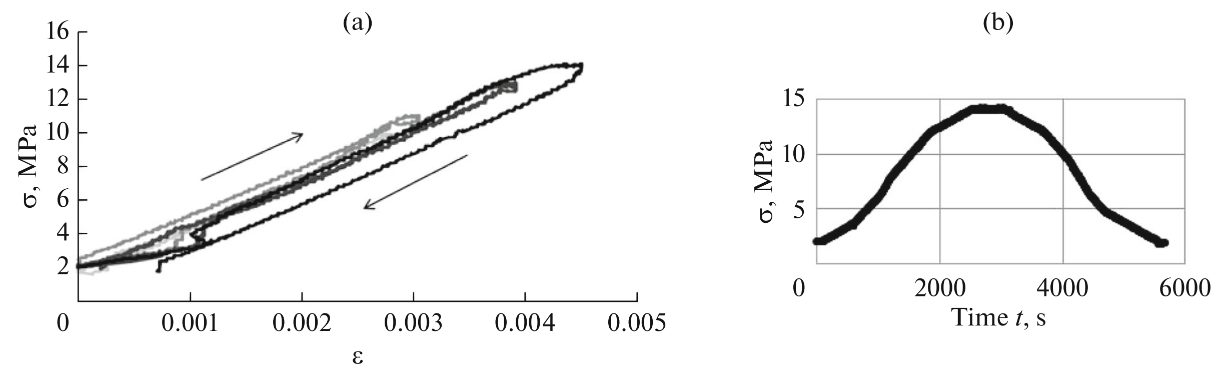

Fig. 2. (a) Load curve σ(ε); (b) example of time dependence of applied static stress for fourth cycle.

performed by scheme (0–9.9–0–11–0–12.9–0–14–0) MPa. For each loading–unloading cycle, an insignificant hysteresis of the dependence $\sigma = \sigma(\varepsilon)$ was observed. After the fourth cycle, residual strains of $\varepsilon \approx 0.0008$ were found. As can be seen from the time dependence of the voltage applied to the sample (Fig. 2b), the experiment was carried out rather slowly to minimize the influence of relaxation processes in the sample, so the process was close to a quasi-static process.

Experimental measurements of the stress–strain dependences made it possible to estimate the values of the Young's modulus in the PLA sample under study in the linear sections of loading and unloading of the sample according to the method described in [21]. An example of the approximation of the linear part of the loading–unloading cycle by the least squares method is shown in Fig. 3. Table 1 gives the values of the Young's modulus calculated from the experimental data. As Table 1 shows, a cyclic change in the loading and unloading of the sample leads to an insignificant increase in the Young's modulus E; i.e., hardening of the PLA sample under study occurs.

During the experiment, the dependences of the relative change in longitudinal wave velocity ($\Delta V/V$) in the sample on the value of its static deformation ε_{st} under periodic loading and unloading were measured simultaneously with the σ(ε) load curve. The resulting dependences are shown in Fig. 4.

A change in the elastic wave velocity in the sample on the magnitude of its deformation was found, which was approximated by a straight line (Fig. 5). Deviation from the linear dependence of the rate change at deformations of $\varepsilon < 0.0005$ is associated with the peculiarities of fixing the specimen.

To determine the third-order Young's modulus with formula (4), the $[\Delta V(\varepsilon_{st})/V]$ dependences under conditions of periodic loading and unloading were analyzed by the least squares method. The values of third-order elastic coefficients ε_{st} are given in Table 2.

Using the obtained values of the second- and third-order Young's moduli, acoustic nonlinear parameter N was determined by formula (5), the values of which are given in Table 2. It was found that cyclic loading of the sample leads first to an increase in the nonlinear acoustic parameter N and then to its decrease. We have found no published data on the absolute value of the nonlinear elastic parameter of PLA. The nonlinear

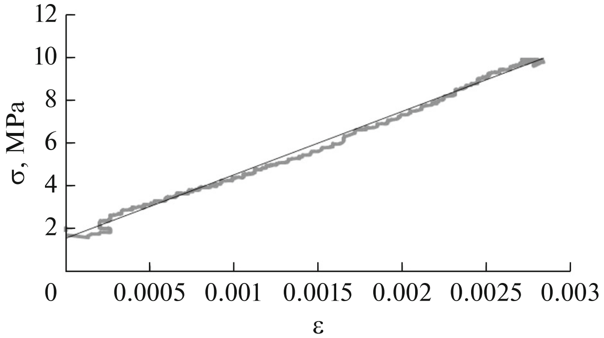

Fig. 3. Linear approximation of load curve in unloading region by least squares method for determining Young's modulus.

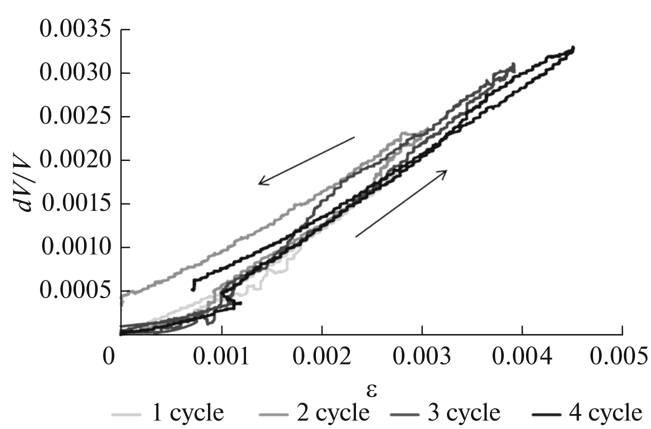

Fig. 4. Change in longitudinal wave velocity in PLA sample as function of its static deformation for four mechanical loading–unloading cycles.

Table 1. Young's modulus values of investigated PLA sample in linear sections of loading and unloading of the sample

	E, GPa, Cycle 1	E, GPa, Cycle 2	E, GPa, Cycle 3	E, GPa, Cycle 4
Loading region	2.91 ± 0.01	3.36 ± 0.01	3.09 ± 0.01	3.16 ± 0.01
Unloading region	2.71 ± 0.01	2.83 ± 0.01	2.82 ± 0.01	2.98 ± 0.01

Table 2. Values of third-order elasticity coefficient E_N and acoustic nonlinear parameter N in investigated PLA sample

	Cycle 1	Cycle 2	Cycle 3	Cycle 4
E_N, GPa	3.97 ± 0.03	5.11 ± 0.03	5.12 ± 0.02	4.71 ± 0.02
N	1.41 ± 0.02	1.65 ± 0.02	1.73 ± 0.02	1.53 ± 0.02

second-order parameter of a number of widely used polymers was measured by the focused ultrasound method [26]. Typical B/A values for polymers, such as polystyrene, acrylic polymer, polyethylene terephthalate, polyvinyl chloride, and polycarbonate, are about 9–11. In [27], second-order nonlinear parameter $\beta_2 = -\frac{\partial V(\varepsilon)}{\partial \varepsilon} \Big/ V$ was measured by the second harmonic generation method for pure and glass-fiber-reinforced polypropylene under stretching. At the initial stage of deformation, the value of this parameter for pure polypropylene varies from 5 to 10.

CONCLUSIONS

Techniques for studying the elastic properties of threads made from a sample of polymer PLA of the eSun brand using a Ritec RAM-5000 ultrasonic system with the static and ultrasonic methods have been created and developed.

The dependences of mechanical stress σ on the value of static deformation ε in a PLA polymer sample during its cyclic loading and unloading up to the deformation region of 0.004 are investigated. A hysteresis σ(ε) dependence was found.

Using the measurement results of the σ(ε) dependence by the least squares method, the values of the

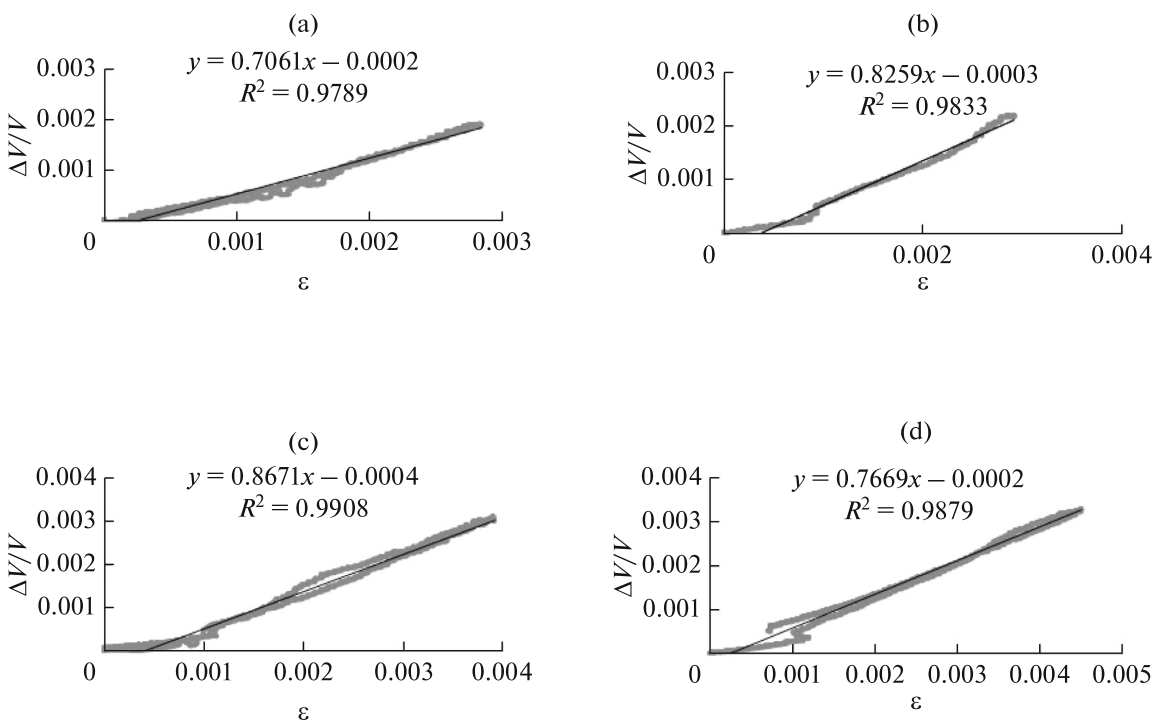

Fig. 5. Linear approximation of dependence of relative change in longitudinal wave velocity in PLA sample on value of its static deformation for (a) first, (b) second, (c) third, and (d) fourth loading–unloading cycles.

Young's modulus E were estimated in the linear sections of loading and unloading of the sample. It is found that periodic loading and unloading of the sample lead to its hardening in the region of elastic deformations and, as a result, to an increase in the value of the Young's modulus E.

Acoustic waves propagation in a thin rod subjected to static tensile deformation is analyzed. An equation that relates the relative change in the velocity of acoustic waves in the sample with the value of its static tensile deformation is obtained. This equation is an analogue of the Thurston–Bragger formula and makes it possible to determine third-order elasticity coefficient E_N in thin rods and thread-like samples.

Together with the measurement of load curve $\sigma = \sigma(\varepsilon)$, the relative change in the velocity of longitudinal waves in the deformable PLA polymer sample from the value of its static tensile deformation is measured. Linear change dependence $V(\varepsilon_{st})$ of the elastic wave velocity in the sample on the value of its static deformation was found. From the results of these measurements, third-order elastic coefficients E_N in the PLA polymer are determined.

Nonlinear acoustic parameter $N = (E_N)/E$ is calculated in PLA for different tensile load values.

The results provide information about the mechanical, linear, and nonlinear elastic properties of PLA and can be used to create composite samples using 3D printing technology.

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REFERENCES

1. C. Schumacher, B. Bickel, J. Rys, S. Marschner, C. Daraio, and M. Gross, ACM Trans. Graph. **34**, 136 (2015).
2. J. Cantrell, S. Rohde, D. Damiani, R. Gurnani, L. DiSandro, J. Anton, A. Young, A. Jerez, D. Steinbach, C. Kroese, ad P. Ifju, Adv. Opt. Methods Exp. Mech. **3**, 89 (2017).
3. Y. Kao, Y. Zhang, J. Wang, and B. L. Tai, J. Manuf. Sci. Eng. **139** (4), 041006 (2016).
4. R. Zou, Y. Xia, S. Liu, P. Hu, W. Hou, Q. Hu, and C. Shan, Compos. Part B: Eng. **99**, 506 (2016)
5. V. A. Boshnyak and A. V. Yazykov, Nauka Obraz. MGTU im. N. E. Baumana, No. **12**, 311 (2016).
6. J. H. Martin, B. D. Yahata, J. M. Hundley, J. A. Mayer, T. A. Schaedler, and T. M. Pollock, Nature **549**, 365 (2017).
7. C. Ma, Y. Dong, and C. Ye, Procedia CIRP **45**, 319 (2016).
8. C. Schulze, M. Weinmann, C. Schweigel, O. Keßler, and R. Bader, Materials (Basel) **11**, 13 (2018).
9. L. T. Lim, R. Auras, and M. Rubino, Prog. Polym. Sci. **33**, 820 (2008).
10. T. Nakatsuka, Fujikura Tech. Rep. (2011), p. 39.
11. S. Farah, D. G. Anderson, and R. Langer, Adv. Drug Delivery **107**, 367 (2016).
12. F. L. La Mantia and M. Morreale, Appl. Sci. Manuf. **42** (6), 579 (2011).
13. R. D. Averett, M. L. Realff, K. Jacob, M. Cakmak, and B. Yalcin, J. Compos. Mater. **45** (26), 2717 (2011).
14. S. M. Mirkhalaf and M. Fagerström, Mech. Time-Depend Mater. (2019). https://doi.org/10.1007/s11043-019-09429-w
15. H. O. Agu, A. Hameed, G. J. Appleby-Thomas, and D. C. Wood, J. Dyn. Behav. Mater. **5**, 377 (2019).
16. N. Parker, M. L. Mather, S. P. Morgan, and M. J. Povey, Biomed. Mater. **5**, 055004 (2010).
17. H.-C. Wua, F.-W. Shenb, X. Honga, W. V. Changa, and H. Winet, Biomaterials **24**, 3871 (2003).
18. G. Zhao, F. P. C. Gomes, H. Marway, M. R. Thompson, and Zh. Zhu, Macromol. Chem. Phys. **221**, 1900475 (2020).
19. K. Brugger and R. N. Thurston, Phys. Rev. **133** (6A), A1604 (1964).
20. A. I. Korobov and V. M. Prokhorov, Acoust. Phys. **62** (6), 681 (2016).
21. A. D. Volkov, A. I. Kokshaiskii, A. I. Korobov, and V. M. Prokhorov, Acoust. Phys. **61** (6), 651 (2015).
22. A. I. Korobov, N. V. Shirgina, A. I. Kokshaiskii, and V. M. Prokhorov, Acoust. Phys. **64** (4), 415 (2018).
23. A. Hassan, H. Balakrishnan, and A. Akbari, *Polylactic Acid Based Blends, Composites and Nanocomposites, Advances. Natural Polymers* (Springer, Heidelberg, Berlin, 2013), p. 361.
24. A. I. Korobov, N. V. Shirgina, A. I. Kokshaiskii, and V. M. Prokhorov, Acoust. Phys. **65** (2), 151 (2019).
25. A. I. Korobov, Yu. A. Brazhkin, and Wang Ning, Acoust. Phys. **51** (5), 571 (2005).
26. S. Saito, AIP Conf. Proc. **1022**, 561 (2008).
27. I. Solodov, K. Pfleiderer, H. Gerhard, and G. Busse, Ultrasonics **42**, 1011 (2004).

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