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Temporal dependence of fracture of biopolymer films under tension

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The temporal dependence of the effects of irreversible deformation and fracture of biopolymer films made of chitosan in the range of tensile strain rates of $1.6 \cdot 10^{-3} - 440$ 1/s is investigated. It is shown that the temporal effect appears in a significant change in the fracture time, fracture deformation and material toughness with a change in the strain rate. Temporal effect is insignificant for the yield strength and elastic modulus: they are changed little with a change in the strain rate. The temporal dependence of the material toughness and fracture time on the loading rate is described using the structural-temporal approach

Keywords: strength, fracture, temporal effects, chitosan films.

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Introduction

Currently, the development and study of new generation materials with defined properties is one of the main fields of new technologies. In the field of medicine, there is a need for materials designed for long-term contact with the tissues of a living organism. Chitosan-based materials are widely used in medicine, tissue engineering, and pharmacology due to its biocompatibility, biodegradability, and ability to enhance regenerative processes in the repair of damaged tissues. Due to these properties, chitosan-based materials are well suited for use in wound healing and the manufacture of artificial leather [1,2]. For instance, clinical studies of human wound healing is presented in Ref. [3]. It has been shown that the use of chitosan dressing is more effective in comparison with a standard medical dressing. Histopathological studies have shown that under a chitosan bandage, the restoration of skin cell layers and tissue architecture is stimulated. Clinical results of the use of soluble hydrogel dressings made of pure chitosan in rats are presented in Ref. [4]. Studies have shown significantly better wound healing and less scar tissue formation when using hydrogel bandages compared to gauze bandages.

During the inflammatory phase of wound healing, mechanical stress is one of the main triggers of increased disorganized collagen deposition. The constant tension of a thickening scar can cause abnormal reconstruction of the extracellular matrix, leading to the formation of a hypertrophic scar. Therapeutic approaches, such as the use of bioactive wound coverings, taping tapes, and biomedical devices, can prevent or reduce hypertrophy of scar tissue, therefore bioactive polymers and composites can be an ideal experimental platform for the development of matrices that transmit changing spatiotemporal signals to cells.

Development of new materials requires studying their physico-mechanical properties, such as the change in the modulus of elasticity depending on the composite component [5]. It is important to study the effect of the manufacturing method on the strength, modulus of elasticity, and fracture performance of high-strength chitosan films [6]. It is known that materials are sensitive to the temporal characteristics of exposure, in particular, to the strain rate, which can be expressed in various effects. Some materials are characterized by an increase in yield strength with an increase in the strain rate [7]. For others, the yield strength and strength of the material may be insensitive to the loading rate, but the fracture strain may decrease significantly with increasing loading rate and decreasing exposure time [8]. The temporal sensitivity of the yield strength of bulk samples from a chitosan-based composite under uniaxial compression at strain rates from 0.1 to 800 1/s is considered in Ref [9]. It is shown that for the materials under study, the yield strength increases with an increase in the strain rate to its critical value. The dependence of the yield strength on the strain rate becomes more pronounced with an increase in the degree of hydration of the material. The dependence of the modulus of elasticity, strength, and fracture energy of a hydrogel on the strain rate in the range from 10^{-4} to 10 1/s is analyzed in Ref. [10].

The mechanical characteristics of the fracture of a film made of pure chitosan in the range of strain rates from $1.6 \cdot 10^{-3}$ to 440 1/s are experimentally and analyti-

cally studied in this paper. The analysis of the effect of the strain rate on the amount of strain, time and energy of destruction of the material is carried out. The structural-temporal approach [11] is used to predict the limiting characteristics of the destruction of the studied material from an external temporary impact. This study is important for confirming the applicability of the proposed approach to a class of materials -biopolymers. The time dependence of mechanical characteristics is important for understanding the rheology of a material and is necessary for subsequent modeling of bioengineered structures. The study of a biopolymer film made of pure chitosan is also valuable for subsequent assessments of the effect of composite additives on the mechanical characteristics of chitosan-based materials.

1. Material

The films were obtained from a 4 % chitosan solution in 2 % acetic acid. Chitosan from BiologHeppe GmbH, Germany, with a molecular weight of $M_m = (1.64-2.1) \cdot 10^5$ and a degree of deacetylation of DD = 92 % was used. The chitosan solution was stirred in water for 30 min until chitosan swelled and partially dissolved. Then acetic acid was introduced into the resulting solution, its concentration in the solution was 2 %. The solution was mixed for 180 min, then filtered and deaerated in vacuum chamber for 24 h at pressure of 10 kPa. The films were poured by means of the solution extrusion through a slit die onto a glass substrate, dried at temperature of 50 °C for 1 h. Then, the films on the glass substrate were deaerated in the vacuum chamber for 24 h at pressure of 10 kPa and then dried in air at room temperature for 24 h. The films were converted from the salt to the basic form by keeping them in a mixture of 10 % aqueous solution of NaOH and C_2H_5OH with a component ratio of 1 : 1 for 10 min, washing with distilled water and drying in the air. The thickness of the films was $(40 \pm 5)\,\mu$m.

2. Sample preparation and test conditions

The geometric parameters of the samples comply with the recommendations for tensile testing of polymer films: sample length — 40 mm, length of the working part of the sample — 10 mm, sample width — 5 mm. For each sample, the thickness was measured at three points of the working part and the average value was calculated. Before testing, the samples were kept in a desiccator at a relative humidity of 60% and a temperature of 23 °C of at least 24 h. Tensile tests were performed at strain rates of 0.016, 0.16, 300 and 440 1/s. At least five samples were prepared for each strain rate. The tests were carried out using the testing machine Shimadzu AG-50kNXD at strain rates of $d\varepsilon/dt = 0.016$ and 0.16 1/s, as well as the drop tower Instron Ceast 9350 at strain rates of $d\varepsilon/dt = 300$ and 440 1/s at humidity of 60 % and temperature of 23 °C.

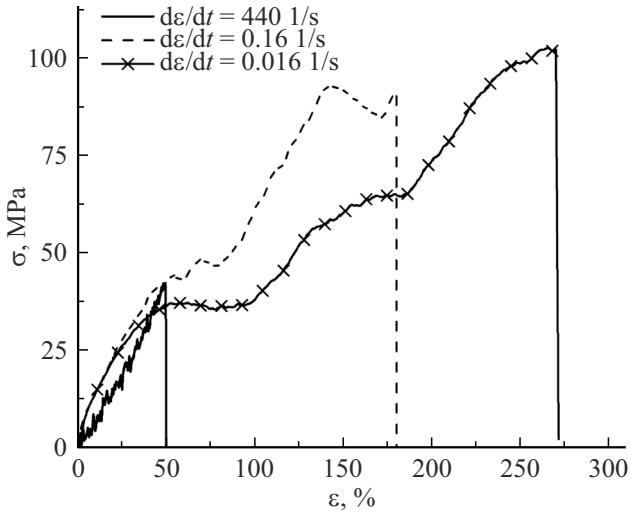

Figure 1. Stress versus strain dependence for strain rates 0.16, 0 and 016 and 440 1/s.

The strain curves of the experimental data at different strain rates are shown in Fig. 1. The formation of a neck was observed in the samples for all the strain rates studied and this neck spread along the entire length without localization, which is typical for polymer materials and is the cause of significant plastic strain [12].

3. Data analysis

A time dependence of the material characteristics is observed for experimental data (Fig. 1). The value of the yield strength and modulus of elasticity increases slightly with increasing strain rate. For strain rates of 0.16 and 0.016 1/s, a strain curve with several stages of a yield plateau and hardening is observed, i.e., deformation processes consistently develop in the material. Similar strain dependences are observed in the study of polymer materials at different loading rates [13,14]. Based on the relaxation theory and the representation of the polymer as a system of interacting chains, it is possible to assume the sequential development of strain processes in the material with different activation energies. When a certain energy level is reached, highly elastic strain develops, the corresponding polymer chains straighten out, and the polymer structure becomes more oriented. The orientation of the material's structure affects its strength properties: stress begins to increase with increasing strain until the next activation energy is reached. Constant stress pads are not observed at strain rates of 300 and 440 1/s. Presumably, the fracture processes prevail over strain processes at strain rates of 300 and 440 1/s.

A striking manifestation of the temporal sensitivity of the material under study is that the fracture strain are significantly reduced from 300 % up to 50 % with an

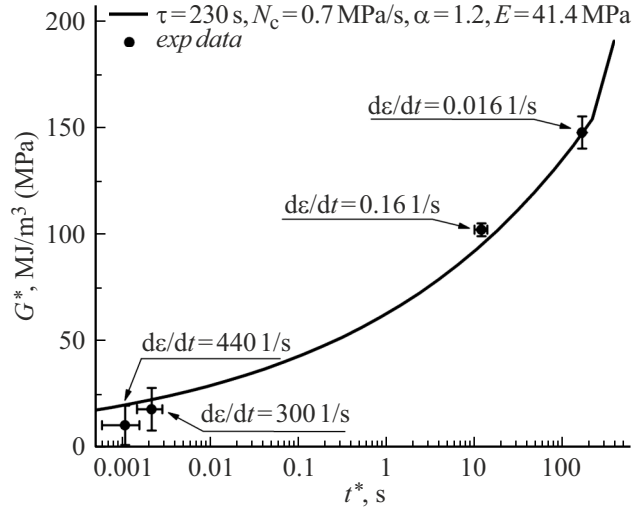

Figure 2. Dependence of the strain energy density (1) from the time of destruction: points correspond to experimental data with the specified measurement error, line corresponds to theoretical curve of the criterion (2).

increase in the strain rate from 0.016 to 440 1/s. A structural-temporal approach based on the introduction of the incubation time parameter is widely used to describe time dependencies [11]. Incubation time is a characteristic parameter of the process preceding the development of macrostructural changes in the material. This approach is used to describe the properties of a material depending on the rate of impact: deflection fracture caused by shock waves [15], dynamic hardening in metals [16] and plastics [17], detonation in gases [18], brittle-viscous transition during the destruction of solids [19].

3.1. Destruction criterion

The strain energy per unit volume that a material can absorb before breaking is a significant characteristic of the fracture process.

$$G^* = \int_0^{\varepsilon^*} \sigma(\varepsilon) d\varepsilon, \qquad (1)$$

where $\sigma(\varepsilon)$ is the stress dependence on strain, ε^* is the fracture strain. Fig. 2 shows experimental data on the dependence of the critical value of the strain energy density G^* on the strain rate. The time sensitivity of the material under study is also manifested in a decrease in the required energy and fracture time with an increase in the strain rate.

Biopolymers are characterized by the self-organization of polymer chains into an ordered structure due to hydrogen bonds between neighboring chitosan chains under tension [20]. As a result, a durable material with an oriented mesh is formed. Based on experimental data (Fig. 2) and the properties of polymers, it can be assumed that with an increase in the rate of stretching, polymer chains do not have time to create an ordered structure, and less energy is required for destruction. Accordingly, it is assumed that the rate of energy input is essential for the biopolymer film under consideration. It is proposed to consider a structural-temporal approach in the form of a power-type energy criterion to model the dependence of the energy used for destruction on the strain rate of polymer films:

$$\frac{1}{\tau} \int_{t-\tau}^{t} \left(\frac{N(s)}{N_c} \right)^{\alpha} ds \le 1, \qquad (2)$$

where $N(t) = \frac{\partial G}{\partial t}$ is the power per unit volume (energy input rate), τ is the incubation time of destruction, N_c is the power, α is the material parameter.

To simulate fracture with significant plastic strain, the stress-strain dependence is chosen in the approximate form $\sigma(t) = E\varepsilon(t)$, where E is the effective modulus. The time dependence of the strain is defined as $\varepsilon(t) = (d\varepsilon/dt)tH(t)$, since the experimental data were obtained at a constant strain rate $d\varepsilon/dt$ from time $t = 0$, $H(t)$ is the Heaviside function. The result of applying criterion (2) is shown in Fig. 2. The parameters were selected using the least squares method [21]. The regression remainder for the parameters $\alpha = 1.2$, $N_c = 0.7$ MPa, $\tau = 230$ s, $E = 41.4$ MPa is 0.1. A structural-temporal approach in the form (2) describes quite well the rate dependence of a chitosan biopolymer film in the considered range of loading rates.

When polymer materials are stretched at high impact rates, the mobility of the segments is „frozen“, and the supplied energy is used only for intermolecular strain. The mobility of the segments increases at a lower impact rate, and the external impact also affects intermolecular friction. Thus, with a decrease in the impact rate or an increase in the exposure time, more energy will be required for deformation. This is consistent with criterion (2) and is demonstrated in Fig. 2. A similar approach was used to describe the detonation conditions in gas mixtures, where, as in our case, the role is played not by the level of the force field, but by the rate of energy injection into the medium [18]. As is known, the heating of a polymer at the neck front is similar to the heating of a gas at the flame front, and both processes can be described by self-similar wave equations [22]. Interestingly, not only the previous processes are similar, but also subsequent critical events, since they are described by one condition (2).

Conclusion

The time dependence of the effects of irreversible strain and destruction of biopolymer chitosan films has been investigated. Strain curves, energy values, and fracture strain values for different loading modes are obtained. Experimental data demonstrate a significant time dependence for the ultimate strain and fracture energy. A strong time dependence of the yield strength and modulus of elasticity is not observed in the considered range of tensile strain rates. Based on the structural-temporal approach, criterion (2) is

proposed, which uniformly describes the destruction of the material at both low and high impact rates. It is shown that the applied approach makes it possible to qualitatively and quantitatively describe the strain, energy and fracture time of the material in the considered range of strain rates.

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Conflict of interest

The authors declare no conflict of interest.

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