THE WOOD IN THE INHOMOGENEOUS TEMPERATURE FIELD: ESTIMATION OF CELLULOSE STRUCTURE PARAMETER FLUCTUATIONS

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In the paper, the cellulose as a fiber-forming component of wood (natural composite) has been studied. The authors put forward a technique for estimating fluctuations of cellulose microstructure in the wood through monitoring the potential difference of the thermal polarization that arises in the samples placed into an inhomogeneous temperature field with a constant temperature gradient. Formalized simulation was used for an analysis of experimental results. The proposed technique made it possible to establish that the percent of the large-sized cellulose crystallites in the wood grew with increasing smoothly temperature gradient. Similar dynamics is not typical of linear crystalline polymers whose polarization decreases with growing temperature. The obtained effect can be assigned to the fact that natural wood exhibits heterogeneous structure.

Key words: microstructure, crystallite, composite, cellulose macromolecule, synthesized material

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Introduction

Creating synthesized bioplastics with highly resistant physical properties such as strength, surface hardness and permissible hydrophobicity is one of the most urgent tasks in technology [1 – 8]. The arboform exemplifies these materials; it can be obtained through the synthesis from natural cellulose and "sulphate soap" released during the paper production process. The physical characteristics of these synthesized materials are determined by the orderliness of their fiber-forming component microstructure, as cellulose microstructure in our case. In this regard, the development of nondestructive methods for estimating microstructure fluctuations in the fiber-forming component of composite materials always attracts attention of the scientific community.

It is well known that wood is naturally occurring composite material, and its main components are partially crystalline cellulose and lignin. Cellulose is a stereoregular syndiotactic polymer [9 – 12]. The macromolecules of the fiber-forming wood component (cellulose) are schematically arranged in the form of a coiled tape with a cross-section of 0.39 × 0.83 nm. Molecular chains of cellulose are packed in a mean length of 15 – 17 nm with a «loosening» section of 2.5 – 3.0 nm in length following. In addition, hollows of 0.5 – 1.0 nm are always located inside amorphous regions [13]. Thus, the packaging process of cellulose macromolecules is characterized by the alternation of crystalline and amorphous phases and the presence of pores in microfibrils in the wood. The peculiarities of this structure allow us to assume that the response of biocomposite such as the wood substance to the change in external factors

depends on the concentration of crystallites in the fiber-forming cellulose and their physical properties.

In the present work, a formalized model is proposed for estimating the fluctuations in the microstructure of cellulose in the wood on exposure to external nonuniform temperature fields. For this purpose, the concentration of cellulose crystallites has been chosen as the fluctuation parameter.

Experimental results

The temperature-scanning method was used for experimental investigation as described in detail in Refs. [14, 15]. In this method, an inhomogeneous temperature field providing a constant temperature gradient ∇T was applied to a thin-layer composite sample, and a thermal-origin electric field evolving as a result. The origin of this electric field in the wood can be bound up with the structural difference between cellulose and lignin and with pyroelectric and piezoelectric properties of fiber-cellulose crystallites as well [15]. The potential difference (PD) across this field depends on the degree of crystallinity of cellulose and is measured with controlled accuracy using electrical measuring instruments.

To determine the response of cellulose in the wood to the applied inhomogeneous temperature field, studies in fluctuations of the PD in the samples were carried out. The samples were prepared from birch wood containing up to 40 % moisture. The sample thickness l_0 was about 100 μm. A special measuring cell was used to change the temperature gradient in the wood layer as given in Ref. [15]. Thin sections of the wood were placed between massive brass rodes with the lower one heated. Therefore, the temperature gradient in the wood layer was controlled by the heating rate of the heated lower electrode. The PD was initially removed from the electrodes.

Fig. 1 shows the dynamics of the temperature gradient in a thin layer of wood during the tests. Fig. 2 shows the experimental data for the measurement of the corresponding PD presented in the form of circles. Comparing the two figures, we can affirm that the PD correlates with the changes in the temperature gradient in the layer as established in various studies [14 – 16]. Thus, the temperature-scanning method makes it possible to control the value of the temperature gradient in the layer using electrical measuring instruments. In this regard, we propose to estimate the average size of cellulose crystallites by analyzing the obtained data on the basis of a formalized model [17–20].

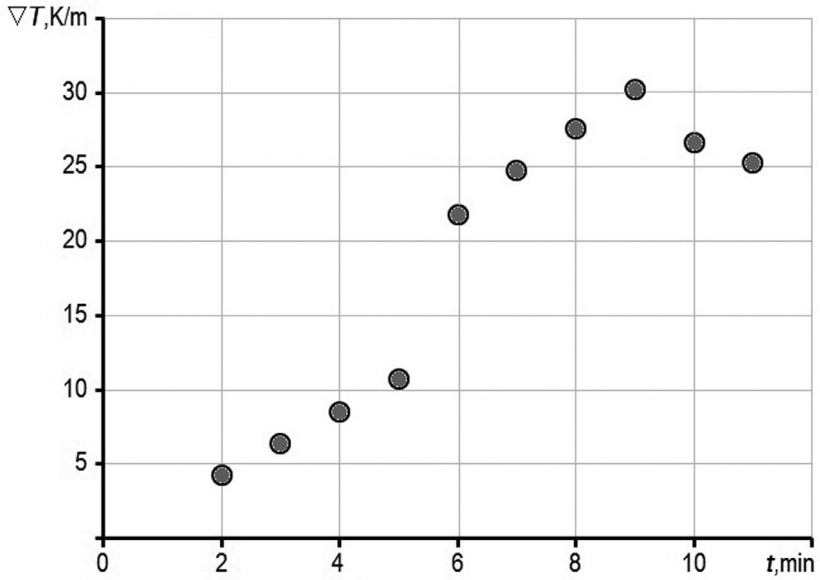

Fig. 1. The thermal-gradient dynamics for a wood thin layer during the test process

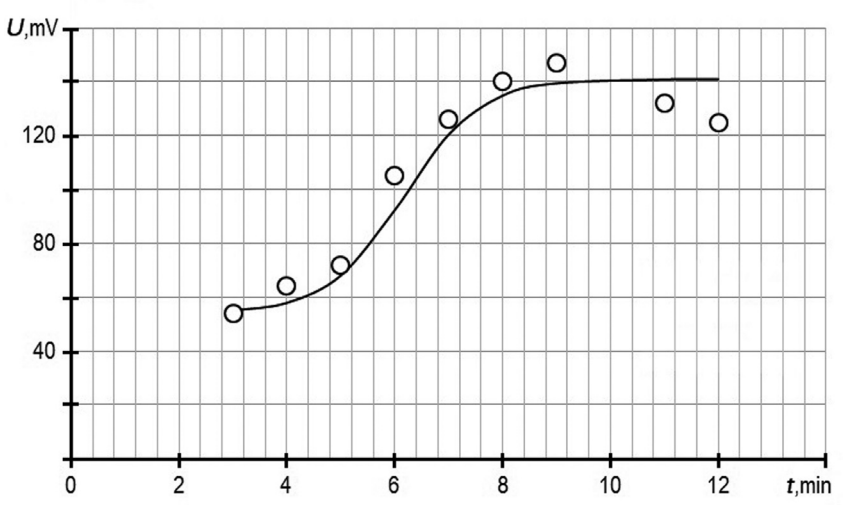

Fig. 2. The experimental (curcles) and simulated (the solid line) PD-time relation for a wood thin layer

Justification of the formalized model

It is known that the relative change in the concentration n of cellulose crystallites depends on the relative rate of a crystal growth under smoothly changing external conditions and characterized by the rate G [16]:

$$\frac{dn}{n} = Gdt. \qquad (1)$$

However, the crystal growth causes the diffusion of non-crystallizing fragments. This process is characterized by the coefficient k_D [16]:

$$\frac{dn}{dt} = -k_D \frac{dn}{dx}. \qquad (2)$$

These two processes (1) and (2) balance each other in a stationary state. Therefore, the equations can be transformed to the form:

$$\frac{dn}{dx} = (-G/k_D)n. \qquad (3)$$

The exponential function

$$n = n_0 \exp(-\Delta x/x_k)$$

is a solution of Eq. (3), where n_0 is the concentration of crystallites near crystallization centers, $x_k = k_D/G$ is the average size of the fiber-forming component crystallite.

This average size is determined when the concentration of crystallites located at a distance equal to crystallite size decreases by e times as compared to n_0.

It should be noted that these concepts of crystallites growth do not take into account the peculiarity of experimental conditions. The constant temperature gradient creates inhomogeneous growth conditions along the thickness of a sample. According to the obtained experimental results we can assume that the average size of the cellulose crystallite x_k depends on the increment of the crystallite concentration as follows:

$$x_k(n) = x_{k0}(1 + \chi\Delta n), \qquad (4)$$

where χ is a coefficient that characterizes the crystallinity degree of the cellulose in a sample, x_{k0} is the initial value of x_k.

The solution of differential Eq. (3) taking Eq. (4) into account is transformed to the following form:

$$\frac{\Delta n}{n_0} = \frac{\exp(-\Delta x/x_k)}{(1 + \chi \exp(-\Delta x/x_k))n_0}, \qquad (5)$$

where $\Delta x = \alpha l_0^2 \nabla T(t)$ is the value of the total compression of cellulose crystallites in a sample with the thickness l_0 during the expansion of lignin, α is the coefficient of thermal expansion of lignin.

According to Ref. [21] the ratio $\Delta n / n_0$ equals the relative change of crystallinity degree of cellulose in the wood. As reported in

Ref. [22], the PD appeared in the wood on exposure to an inhomogeneous temperature field is directly proportional to crystallinity degree of cellulose. Thus, the relative change in PD in the sample within the framework of this approach is simulated by the following relationship:

$$\frac{U - U_0}{U_0} = k_U \frac{\Delta n}{n_0} = \frac{k_U \exp(-\Delta x/x_k)}{(1 + \chi \exp(-\Delta x/x_k))n_0}, \quad (6)$$

where k_U is a parameter that depends on the percolation features of thermal polarization processes occurred in the composite, U_0 is the PD initial value.

Finally, we obtain the relation for estimating the PD:

$$U = U_0 \left\{ 1 + \frac{k_U \exp(-\alpha l_0^2 \nabla T/x_k)}{[1 + \chi \exp(-\alpha l_0^2 \nabla T/x_k)]n_0} \right\}. \quad (7)$$

Eq. (7) connects the PD in the sample on exposure to an inhomogeneous temperature field with the fluctuations in external conditions such as the changes in $\nabla T(t)$ and the features of fiber-forming microstructure (x_k, χ) and filler (α).

Furthermore, Eq. (7) is the basic axiom of the formalized model for the method of estimating the response of natural component-containing microstructure to fluctuations of external conditions in general and temperature in particular. The model experiment was implemented by the linear regression method using Excel spreadsheets. The results are presented by the solid line in Fig. 2. Comparing the results of the real and simulated experiments (see Fig. 2) we can conclude that it is possible to estimate the values of χ, x_k and k_U parameters from the results of physical and simulated experiments with controlled accuracy.

Summary

Thus, it has been shown that the temperature-scanning method using elements of formalized simulation makes it possible to estimate the fluctuations of supramolecular structure of the fiber-forming component in a composite when changing the external conditions. Consequently, it can also be used to study the microstructure of arboforms and synthesized plastics.

Furthermore, analysis of the PD dynamics with a smoothly increasing temperature gradient suggests that the fraction of cellulose crystallites with a large size in the wood grows with increasing the temperature gradient value. It should be noted that similar dynamics do not characterize linear crystallizing polymers, in which polarization decreases with increasing temperature. Perhaps, the considered effect is due to interaction between wood components and the cellulose characterized by the complexity of supramolecular structure.

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