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Formalized model of cellulose thermopolarization processes in natural wood in a non-uniform temperature field

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Abstract. Temperature fluctuations are the most common and significant factor in the environmental impact on the properties of plastic and biocomposite materials. Therefore, the development of a fundamental concept of the conformation mechanisms of long molecules under conditions of stable temperature gradient is one of the urgent problems of modern technologies in the field of creating materials with given properties. The purpose of the research was substantiation of basic relation for conducting a computational experiment to determine the parameters of the kinetics process for thermally stimulated cellulose polarization within the framework of classical thermodynamics. The objects of the experimental study were microsections of cylindrical birch wood with a thickness of about several hundred microns. During the measurement, the specimens were placed between two massive cylindrical measuring electrodes. Heating was carried out at a constant rate, ensuring the constancy of the temperature gradient along the cut thickness. A potential difference was formed in the wood under experimental conditions due to pyroelectric and piezoelectric effects in cellulose crystallites. The emerging electric field contributes to polarization of the side groups of macromolecules in the amorphous part of the cellulose. In this work, a basic model relation for calculating the potential difference was obtained. The difference occurs in a thin wood specimen. Model efficiency was determined by the method of estimating the dimensionless Nash-Sutcliffe criterion. The proposed model can be applied for data systematization on the thermally stimulated biocomposite polarization (with crystalline and amorphous components). Systematization is made by means of computational experiment to determine the parameters characterizing their unique features.

Keywords: microstructure, crystallites, composites, cellulose macromolecules, synthesized materials

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Формализованная модель процессов термополяризации целлюлозы в натуральной древесине в неоднородном температурном поле

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Аннотация. Флуктуации температуры являются наиболее распространенным и существенным фактором воздействия окружающей среды на свойства пластиков и биокомпозитов. Поэтому разработка фундаментальной концепции механизмов конформации длинных молекул в условиях устойчивого градиента температуры является одной из актуальных проблем современных технологий в области создания материалов со свойствами, необходимыми для решения определенных задач. Цель работы – обоснование базового соотношения для проведения вычислительного эксперимента по определению параметров процесса кинетики термостимулированной поляризации целлюлозы в природной древесине в рамках классической термодинамики. Объектами экспериментального исследования были микросрезы древесины березы цилиндрической формы толщиной порядка нескольких сотен микрон. В процессе измерения образцы помещались между двумя массивными измерительными электродами цилиндрической формы. Нагревание проводилось с постоянной скоростью, что позволило обеспечить постоянство градиента температуры вдоль толщины среза. В условиях эксперимента в древесине формируется разность потенциалов, обусловленная пироэлектрическим и пьезоэлектрическим эффектами в кристаллитах целлюлозы. Возникающее электрическое поле способствует поляризации боковых групп макромолекул аморфной части составляющих целлюлозы. В работе получено базовое модельное соотношение для расчета разности потенциалов, возникающей в тонком образце древесины. Эффективность модели определялась методом оценки безразмерного критерия Нэша-Сатклиффа. Предлагаемая модель может быть использована для систематизации данных о термостимулированной поляризованности биокомпозитов, имеющих кристаллическую и аморфную составляющие, путем вычислительного эксперимента по определению параметров, характеризующих их уникальные особенности.

Ключевые слова: микроструктура, кристаллиты, композиты, макромолекулы целлюлозы, синтезированные материалы

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Introduction

The optimum of the solutions in the field of designing materials with given properties based on natural composites largely determines understanding of the dynamics of changes in their microstructure under the influence of external factors [1]. Therefore, the characteristics of macromolecules [2–4], physical and chemical properties of cellulose [5–6], and properties of other biocomposite constituents of natural origin [7–8] have been actively studied recently. However, unique supramolecular structure of the polymer composite is mainly destructurized in the process of research [9–11], making it difficult to form ideas about the effect of biocomposite complexity on its properties. Development of methods for non-destructive testing of wood microstructure makes it possible not only to preserve the uniqueness of supramolecular structure during the research, but also to expand existing ideas about thermopolarization mechanisms in complex biocomposites. Temperature influence is the most common environmental factor. Therefore, fundamental concept development of the conformation mechanisms of long molecules under conditions of stable temperature gradient is one of the urgent problems of modern technologies in the field of creating materials with the properties necessary to solve certain tasks.

A formalized model is currently being developed based on long-term studies of polymer polarization processes [12–16]. It would become the basis for a comparative analysis and prediction of the effect of inhomogeneous temperature field on the microstructure of a complex

biocomposite (wood). The purpose of the research was to substantiate the axiomatic relation for conducting a computational experiment. The aim of the experiment is to determine the parameters of the kinetics process of thermally stimulated cellulose polarization in natural wood. The process is based on the analysis of the entropy change in the system under study.

Theoretical part

Temperature gradients induce piezoelectric and pyroelectric effects in wood cellulose crystallites. As a result, a potential difference is formed, contributing to the polarization of macromolecule side groups. It takes place in the amorphous part of cellulose, having natural heterostructure. Thus, the description of a response of a high-molecular-weight biocomposite (wood) to a constant temperature difference is a complex task. Specimen polarization $P_{i\sigma}$ is determined as the sum of four terms comparable in magnitude order [16]:

$$P_{i\sigma} = -\int_{T_0}^{T_0+\Delta T} d_{ijk} c_{kjml} \mu_{ml} \alpha_T dT + \int_{T_0}^{T_0+\Delta T} \gamma_i h dT + \Delta P_{in} + P_\sigma, \tag{1}$$

where T_0 is initial temperature, ΔT is temperature change, d_{ijk} is tensor of piezoelectric module, c_{kjml} is modulus of elastic stiffness, μ_{ml} is ratio of Young's modulus of lignin to Young's modulus of cellulose, α_T is coefficient of lignin thermal dilatation, γ_i is cellulose pyroelectric coefficient, h is microsection thickness, ΔP_{in} is change of orientational polarization in the macromolecule side polar groups of the amorphous parts of cellulose and hemicelluloses in the emerging electric field [1, 12–16], P_σ is dipole orientational polarization of water molecules in wood pores. With a stationary heat flux in a thin microsection of wood biocomposite, we can assume that d_{ijk}, c_{kjml}, μ_{ml}, α_T and γ_i coefficients practically do not depend on the temperature. Then the equation (1) takes the form:

$$P_{i\sigma} = -d_{ijk} c_{kjml} \mu_{ml} \alpha_T \Delta T + \gamma_i h \Delta T + \Delta P_{in} + P_\sigma. \tag{2}$$

The change in the orientation polarization ΔP_{in} at a constant temperature gradient along its thickness is mainly determined by the increase in ΔN number of the ordered side groups (noncrystalline part of cellulose). In the framework of classical electrodynamics, it is determined by the relation $\Delta P_{in} = p_i \Delta N$ (p_i is the average dipole moment of the side group of the cellulose macromolecule, which can be determined from its conformation) [16]. The number of side groups of macromolecules is limited in a microsection by a certain value N^*. The process of orientation of individual side polar groups is a random one. Therefore, we can write the equation for the logarithm of the thermodynamic probability change W in the orientational polarization ΔP_{in} of the side polar groups of a macrosystem of long molecules in the following form:

$$\ln W = \theta \left(\ln \frac{\Delta N}{N^*} - \ln \frac{N^* - \Delta N}{N^*} \right), \tag{3}$$

where θ is all possible orientations of side groups of cellulose macromolecules in a microsection. Transforming the equation (3) for dW/W, we obtain:

$$\frac{dW}{W} = \theta N^* \frac{d(\Delta N)}{(N^* - \Delta N)\Delta N}. \tag{4}$$

The well-known Boltzmann relation determines entropy in the considered system through the logarithm of thermodynamic probability:

$$S = k \ln W, \tag{5}$$

where k is Boltzmann's constant. In the process under study, the decrease in the entropy dS occurs due to the side group orientations. Therefore, it is largely formed by the amount of heat δQ flowing in the microsection under experimental conditions. Then, within the framework of classical thermodynamics we have a relation.

$$k \frac{dW}{W} = dS = \frac{\delta Q}{T} = \lambda \frac{\Delta T}{hT} \sigma dt, \tag{6}$$

where T is ambient temperature. The above-mentioned relation was formed taking into account that, $\delta Q = \lambda(\Delta T/h)\sigma dt$ flows (λ is thermal conductivity of wood) in the approximation of flow stationarity through the microsection area (σ) for an elementary period of time (dt). The following equation can be derived from the relations (4) and (6):

$$\frac{dW}{W} = \theta N^* \frac{d(\Delta N)}{(N^* - \Delta N)\Delta N} = \frac{\lambda\sigma\Delta T}{khT} dt. \tag{7}$$

Let us introduce the notation, meaning the ratio of the stationary heat flux power (through the microsection) to the energy of chaotic motion of all side groups in all possible states in the amorphous part of cellulose. Then (7) is transformed into the following equation:

$$\frac{d(\Delta N)}{(1-\beta\Delta N)\Delta N} = \alpha dt, \tag{8}$$

where $\beta = 1/N^*$. Taking into account the initial conditions ($t_0 = 0$, $\Delta N = \Delta N_0$), it has an analytical solution. Let us denote $P_0 = p_i\Delta N_0$. Then the equation for the change in the orientational polarization is obtained:

$$\Delta P_{in} = \frac{P_0 \exp(\alpha t)}{1 + \beta P_0(\exp(\alpha t) - 1)/p_i}. \tag{9}$$

From (2), taking into account (9), an expression follows for determining the potential difference that forms in a dry microsection of wood over time (in the approximation of a flat capacitor):

$$U_s = U_{dp\gamma} + \frac{U_0 \exp(\alpha t)}{1 + \eta(\exp(\alpha t) - 1)}, \tag{10}$$

where U_0 is initial value of potential difference, $U_{dp\gamma}$ is potential difference formed by piezoelectric pyroelectric response of the crystalline cellulose part, $\eta = P_0/(N^* p_i)$ is the proportion of oriented side groups at the initial moment of time.

Relatively recently, the influence of wood moisture on polarization processes in a non-uniform temperature field has been studied. The results showed that potential difference in a specimen with moisture content φ can be modeled by the relation [1]:

$$U = U_s\left[1 + \varphi\kappa\Big/\left(\varepsilon_i(1-\varphi)\right)\right], \tag{11}$$

where κ characterizes polarization properties of bound water in the pores of wood, and ε_i is its dielectric constant. As a result, in the computational experiment, it is expedient to use the following relation:

$$U_s = U_{dps} + \frac{U_{0s} \exp(\alpha t)}{1 + \eta(\exp(\alpha t) - 1)}, \tag{12}$$

where $U_{dps} = U_{dp\gamma}\left[1 + \phi\kappa\Big/\left(\varepsilon_i(1-\phi)\right)\right]$, $U_{0s} = U_0\left[1 + \varphi\kappa\Big/\left(\varepsilon_i(1-\varphi)\right)\right]$. Relation (12) is the base for a formalized model of a computational experiment to determine U_{dps}, U_{0s}, α and η parameters. The model is based on the data of the experiment on the formation dynamics of a potential difference in wood microsections in a non-uniform temperature field.

Experimental part

Microsections of birch wood of a cylindrical shape with a thickness of about several hundred microns were studied in this research. During the measurement, the specimens were placed between two massive cylindrical measuring electrodes, the thickness of which significantly exceeded the thickness of the microsection. The upper electrode was equipped with a heat sink, and the side surface of the wood was thermally insulated with a specially made gasket. An inhomogeneous temperature field with a gradient along its thickness was formed in the specimen [16], determined by the following relation:

$$\nabla T = \frac{2\beta_T}{\lambda_0 S}(c_e m_e + c_0 m_0), \tag{13}$$

where c_e is specific heat capacity of the electrode material, m_e is mass of the upper electrode, λ_0, c_0, m_0 are thermal conductivity, specific heat capacity, and mass of natural wood microsection, respectively, β_T is bottom electrode heating rate, and S is area of bottom electrode. Thus, in a microsection, the magnitude of the temperature gradient along its thickness was determined by the properties of wood substance and parameters of the measuring cell of flat capacitor. Heating was carried out at a practically constant rate (Fig. 1). Straight line in the figure was constructed using the least squares method, and the relative deviation of the temperature measurement data from it did not exceed 2%. As a result, the temperature gradient under the measurement conditions can be considered a constant according to the relation (13).

In the experiment, biocomposite response to the presence of a constant temperature gradient along the thickness of the microsection was realized in the formation of a potential difference, which was measured with controlled accuracy. Determination of the model parameters in the computational experiment was carried out by the method of soft computations [17]. Optimization was made on the basis of the Nash-Sutcliffe efficiency criterion (*ME*), which is traditionally used in the problems of checking the adequacy of process models in partially self-organizing systems [18]. According to general ideas, the value of the criterion is calculated by the ratio:

$$ME = 1 - \frac{\sum_k (U_k^{\exp} - U_k^{theory})^2}{\sum_k (U_k^{\exp} - U_{mean})^2}, \qquad (14)$$

where $U_k^{\exp}$ are data of the experiment on measuring the potential difference in the microsection, U_k^{theory} are results of computational experiment (according to the relation (12)), U_{mean} is mean value of $U_k^{\exp}$. The value of the *ME* criterion cannot be more than a unit. The closer it is to one, the more the model matches the ideal data description.

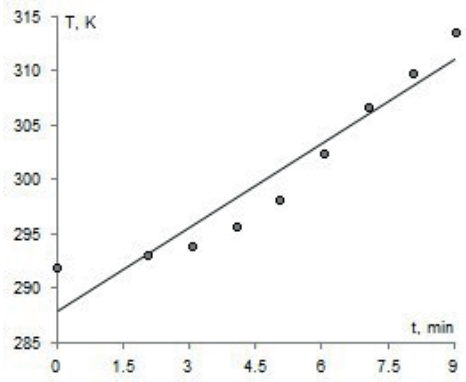

Fig. 1. Dynamics of temperature changes of the heated electrode

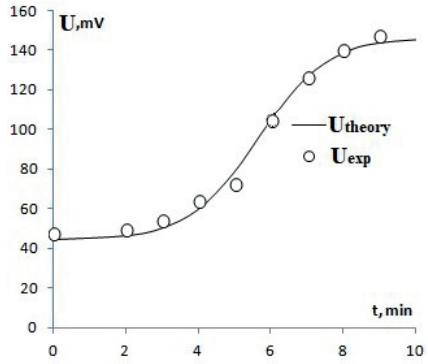

Fig. 2. Dynamics of the potential difference formed in a birch wood specimen with a moisture content of 40% when the lower electrode is heated at 1.43 K·min^{-1}

Results and Discussion

The analysis of the experimental data showed that the nature of changes in the potential difference magnitude over time is non-linear one (Fig. 2). Potential difference stabilizes from a certain time point, which indirectly indicates the formation of maximum polarization of macromolecule side groups in the microsection.

The results of the computational experiment for birch microsections with a moisture content of 40% showed that the maximum value of the Nash-Sutcliff criterion was 0.993 with the following model parameters: U_{0s} = 0.28 mV, α = 1.04 min^{-1}, U_{dps} = 44.5 mV and η = 0.98%. At the same time, the average deviation of the experimental data from the data, calculated according to the basic ratio of the proposed model (Fig. 2), did not exceed 4%.

It should be noted that the research demonstrates successful application of computational experiment to the analysis of measurement data on the wood response to the influence of

inhomogeneous temperature field. Thus, it is necessary to combine laboratory tests with the methods of physical and mathematical modeling of the studied processes to identify the kinetic parameters of complex biocomposite microstructure

Conclusion

The conducted studies proved the following:

1) The kinetics of the potential difference formation in inhomogeneous temperature field can be modeled within the framework of classical thermodynamics.

2) The measurement data of the potential difference in inhomogeneous temperature field (in combination with a computational experiment) makes it possible to determine the parameters of kinetic processes in natural heterostructures with sufficiently high accuracy.

3) The parameters of formalized model formed in the framework of thermodynamic approach have clear physical meaning. They can be used in the analysis of the states of supramolecular structure of complex semi crystalline composites.

4) The paper theoretically shows the role of various wood components in the formation of thermally stimulated potential difference in the presence of a constant potential difference in its microsections at room temperature.

5) The proposed method of formalized modeling can become the basis for the methods of comparative evaluation of natural heterostructures, if their microsections can be used in converters of thermal energy into electrical one.

Thus, in this research, a formalized model of the formation processes of potential difference in a non-uniform temperature field was proposed for the first time. Complex wood biocomposite was taken as a material under study. The model was based on the existing representation of the composition and supramolecular composite structure. The main relations were obtained in the framework of classical thermodynamics. In this case, the model can be used to systematize data on thermally stimulated polarization of biocomposites with crystalline and amorphous components.

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