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Structural transition in cellulose triacetate films

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Electron microscopy data are used to comparative analysis of the topological structure of the surface of two samples of cellulose triacetate (CTA) films. The samples were obtained from CTA solutions without use (sample № 1) and with the use of a small sodium fluoride additive that lowers the viscosity of the solution (sample №2). It is shown that in sample № 1, the nodes of the physical network of macromolecules are periodically alternating regions of local orientation order — microdomains of average size $d \sim 18$ nm. In sample № 2, due to repackaging of microdomains on the scale $R > d$, a uniformly disordered fractal cluster of the mesophase CTA is formed. The fractalization of the surface and the growth of structural anisotropy are consistent with the decrease in the viscosity of the solution and explain the change in the deformation properties of sample № 2 compared to № 1.

Keywords: polymer films, electron microscopy, microdomains, mesophase, structural transition, fractal clusters.

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1. Introduction

The samples of cellulose triacetate (CTA) with combined acetic acid percentage of $\alpha = 60.0-61.9\%$ are classified as polymers with rigid macromolecules [1], which are capable of forming anisotropic aggregates in solutions [2].

It is known that mass concentration of polymer c defines the nature of CTA macromolecules aggregation in the solution [2], at the interphase boundary between the solution and solid body [3], and at film formation [4]. The formation of particle aggregates in solutions of various CTA specimens is detected by IR-spectroscopy [2,3]: at $c > 6$ wt% the number of anisotropic clusters increases abruptly, and at $c > 10$ wt% a lyotropic liquid-crystal state is formed [5].

In [4], the microdomain structure of films produced from CTA solutions ($\alpha = 61.9\%$) is proved using the method of electron microscopy (EM). Microdomains were understood as local areas with a size not more than $d \sim 30$ nm, which should have correspondent nematic ordering of macromolecule segments [6]. It was shown that with growth of polymer concentration c in the solution the stacking density of microdomains in the film increases. In the series of film specimens formed from solutions with different concentrations a structural transition was detected in the scale of c parameter near the value of $c \sim 9$ wt%. This transition points out the emergence of a homogenous infinite cluster of CTA mesophase and is related to the spread of „density-density“ type correlations over a distance, which is considerably more than d.

Since the nature of macromolecule aggregation in a solution depends also on the nature (quality) of the solvent [2,7], there is a possibility to control the anisotropic supermolecular structure of CTA [8] in the films by introducing modifying additives into the film forming solution [9,10]. For example, intensification of specific salvation of CTA acetyl substituent carbonyl groups by molecules of proton-donor solvents with injection of small quantities (0.001−0.1 wt.% of CTA) of some inorganic salts, in particular sodium fluoride, into the solution results in noticeable decrease in dynamic viscosity [2,11]. The drop of viscosity is a sign of ordering of the cluster structure in the solution and consistent with the change in strain properties of the obtained films — the increase in tensile strain at break and decrease in thermostatic shrinkage [11]. However, in [11] there is no data of structural analysis explaining the changes in some physical and mechanical properties of the films.

This work reports on the comparative study of the topological surface structure of two CTA film specimens produced from polymer solution without and with the use of small sodium fluoride additive. To perform the structural analysis of the surface in the submicron scale range, an original EM-method of decorating with gold the electrically active replica from amorphous germanium was used [12]. Decorating gold particles distribution density idicatrices, correlation functions of „density-density“ type, and parameters of supermolecular CTA structure on the surface of the films are calculated according to the EM data. The purpose of this work is to explain the „composition–structure–properties“ interrelation on the basis of microdomain (cluster) model of CTA films morphology.

2. Research targets and methods

In this work the industrial partially hydrolyzed CTA with a combined acetic acid percentage of $\alpha = 60.1\%$ and a polymerization degree of 300 was used. X-ray amorphous [4] films with a thickness of $\sim 130\,\mu$m were formed from 10 wt.% solutions of CTA in the mixture of methylene chloride and ethanol $(9:1)$ on a mirror glass at 298 K without (specimen № 1) and with the use of sodium fluoride small additive (0.005 wt.% of CTA) (specimen № 2). The specified quantity of modifier corresponds to minimum dynamic viscosity of film forming 10 wt.% solution of polymer [11].

The concentration of $c = 10$ wt.% for the CTA specimen used in this work is slightly higher than the threshold value $c^* = 9.7$ wt.% [2], that corresponds to formation of continuous fluctuation network of macromolecules [7]. According to the results reported in [4], the selected concentration mode of film formation should result in emergence of infinite cluster of CTA metaphase in films.

Two-layer germanium-carbon replicas were formed from „air" surface of polymer films. To produce the replicas, an amorphous layer of extra-pure grade germanium with a thickness of 5 nm and a backup layer of carbon were successively deposited by vacuum thermal sputtering on the surface of the specimen. In the process of separation of the two-layer replica from the backup film the layer of germanium became positively charged, and spatial localization of the charge was correspondent to the nature of distribution of electron-donor acetyl substituents of CTA on the specimen surface [12]. Electrically active replicas were decorated by gold [13] using vacuum thermal sputtering of metal to deposit an effective layer thickness of 0.4 nm [14]. To avoid photo emission of electrons and relaxation of the electric charge, the replicas were produced and gold-decorated in conditions of darkness.

The images of gold-decorated germanium-carbon replicas recorded by transmission electron microscope display the distribution of CTA macromolecules stacking density on the surface of specimens (Fig. 1). It is important to note that in this case the most probable distance r between nanoparticles of gold is 6 nm. It improves considerably the resolution capability of the EM-method described above as compared with that used in [4,14], i.e. the method of gold-decoration of „chemical marks" of chemisorbed molecular bromine, because in the latter case the value of r is significantly higher.

The spatial correlations of „density-density" type on the surface of specimens were studied using so called „coarse-grained" radial functions $g(R)$ of decorating gold nanoparticles distribution. To obtain these functions, a computer step-scan technique was used to scan the density of particles distribution on two-dimensional images of the surface with a step of δ, corresponding to value of r [14]. Correlation length ξ was determined by the positions of singular points of function $g(R)$. Density indicatrices ρ of gold nanoparticles distribution were calculated at averaging over $2r \times \xi$ rectangulars with centers in particles and measuring angle θ of rectangulars orientation [14].

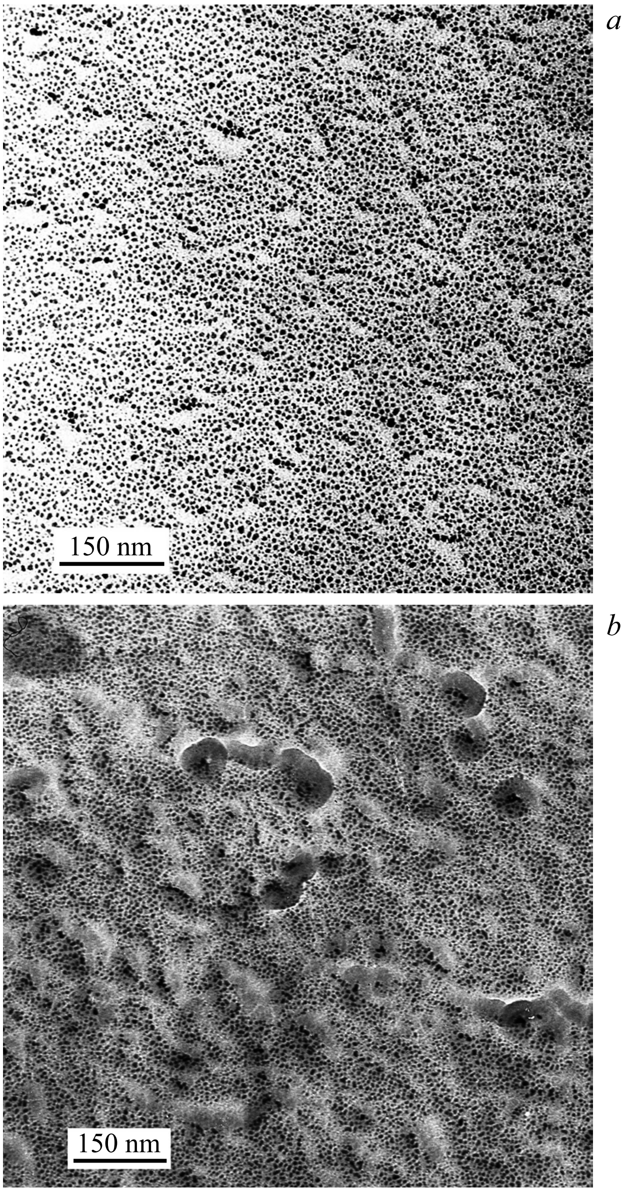

Figure 1. Electronic microphotos of gold-decorated germanium-carbon replicas from the surface of CTA films: specimen № 1 (*a*), specimen № 2 (*b*).

3. Results and discussion

In the electronic microphotos of decorated replicas from the surface of film specimens (Fig. 1) nanoparticles of gold are localized in a nonuniform manner: along with areas of quite densely located decorating particles there are areas free from gold. The continuous quasilattice of nanoparticles corresponds to the infinite cluster of densely stacked macromolecules of CTA (polymer mesophase). The degree of surface filling with the cluster Ω [15] is 0.64 and 0.54 for specimens № 1 and 2, respectively. The decrease in Ω with transition from specimen № 1 to specimen № 2 is accompanied by compaction of quasilattice, nodes which is reflected by the slight broadening of the first peak of function $g(R)$ of decorating nanoparticles radial distribution (Fig. 2). At the same time, mean coordination number of the quasilattice [15] increases from 4 to 6.

Transformation of the decorating particles quasilattice accompanies the change in nature of spatial correlations of the „density-density"type in the cluster of CTA mesophase. „Coarse-grained" radial functions $g(R)$ of decorating nanoparticles distribution (Fig. 3) demonstrate essentially different behavior with growth of scale value R.

In specimen № 1, the correlation function $g(R)$ of „density-density" type oscillates periodically with a period of $L \sim 42\,\text{nm}$ near the value of $g(R) = 1$ (Fig. 3, *a*), suggesting periodically-nonuniform topological structure of the CTA mesophase cluster. Spatial correlations spread over the distance of $\xi = 2L$, where ξ is correlation length. The form of $g(R)$ function is consistent with the microdomain model of CTA for periodically alternating particles of medium size $d \sim 18\,\text{nm}$ and fractal dimension [16] $D = 1.80 \pm 0.05$, defined at approximation of the initial section of the $g(R)$ function graph by the power law dependence of $g(R) \propto R^{D-2}$. Parameters d and D of microdomains corresponds to the data of small-angle X-ray scattering (SAXS) [4]. Computer processing of the angular dependence of the scattering intensity $I(\theta)$ in the range of $8' < 2\theta < 15'$, including that with the use of Guignet procedure, results in parameter values of $d = 24\,\text{nm}$ and $D = 1.7 \pm 0.1$ for scattering structons [4,17]. It should be noted that the SAXS diagram of specimen № 1 has no manifested the discrete reflection corresponding to the period of $L \sim 42\,\text{nm}$ of microdomains alternation due to low scattering capability of the polymer film [4,17].

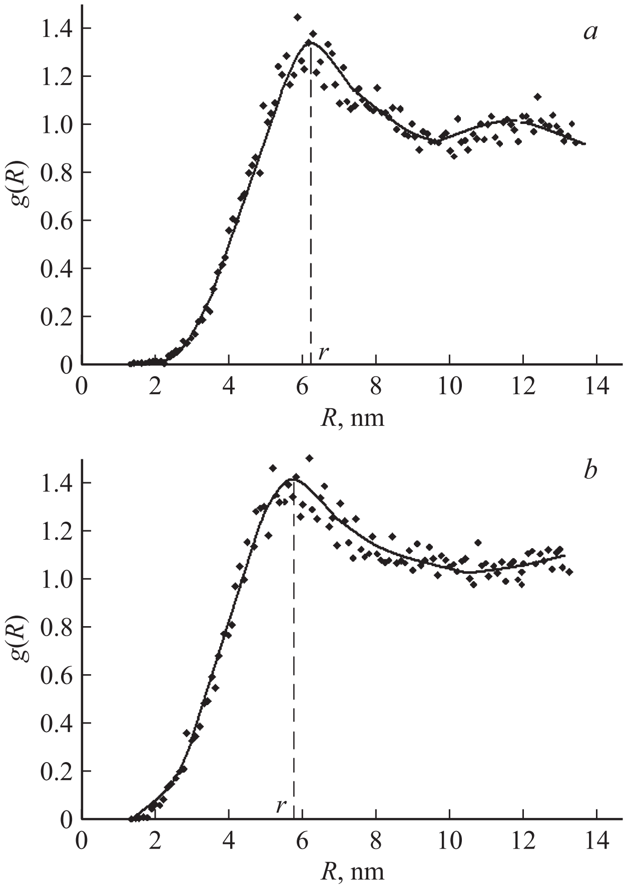

Figure 2. Radial functions $g(R)$ of gold nanoparticles distribution on the decorated replicas from the surface of CTA films: specimen № 1 (*a*), specimen № 2 (*b*). Step of surface image scanning $\delta = 1\,\text{nm}$.

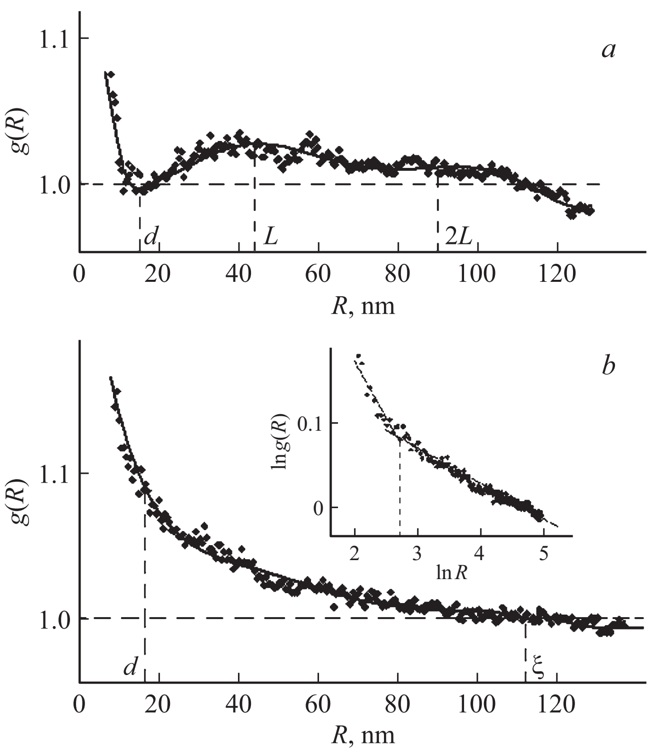

Figure 3. „Coarse-grained" radial functions $g(R)$ of gold nanoparticles distribution on the decorated replicas from the surface of CTA films (correlation functions $g(R)$ of „density-density" type): specimen № 1 (*a*), specimen № 2 (*b*). Step of surface image scanning $\delta = 6\,\text{nm}$. In the insert: $g(R)$ function in double logarithmic coordinates for specimen № 2.

In contrast to specimen № 1, in specimen № 2 the „coarse-grained" correlation function $g(R)$ drops according to power law with growth in scale value R (Fig. 3, *b*): $g(R) \propto R^{D-2}$, with value of the fractal dimension D dependent on R. The $g(R)$ function plotted in double logarithmic coordinates (Fig. 3, *b*, insert) shows that with $R < 18\,\text{nm}$ the values of $D = 1.84 \pm 0.02$ corresponds to microdomains, while with $R > 18\,\text{nm}$ the fractal dimension of $D = 1.96 \pm 0.01$ characterizes the body of the CTA mesophase cluster. It's worth noting that the average size of $d \sim 18\,\text{nm}$ of microdomains in two examined film specimens is kept unchanged (Fig. 3, *a*, *b*) and consistent with the value of thermodynamic segment for various ethers of cellulose [1].

Thus, comparing specimens № 1 and 2 in the scale of $R > d$ we can observe a structural transition related to restacking of ordered microdomains and formation of the body of uniformly unordered fractal cluster of CTA mesophase.

Figure 4 shows indicatrices of relative local density ρ of gold nanoparticle distribution over the surface of specimens. The obtained angular dependences $\rho(\theta)$ give an evidence of axial texture of the film surface. The presence of axial texture may be related to both orientational effects during films formation [12] and formation of the mesophase. With the transition from specimen № 1 to specimen № 2 the anisotropy of density increases, and the difference in the density along the texture axis and across it increases by more than two times reaching 5% for specimen № 2 (Fig. 4, *b*).

Figure 5 shows correlation functions $g_\perp(R)$ calculated across the texture axis of the specimens under examination. In specimen № 1, in the direction normal to the texture axis periodic density oscillations are observed with a period of ~ 18 nm (Fig. 5, *a*). The „density-density" correlations spread over a distance of more than 120 nm without decay within the entire studied scale interval. It is important to note that according to the SAXS data [18] for CTA films heated at 453−483 K, in the range of scattering angles of $2\theta = 18{-}24'$ there are a plateau or a bend corresponding to large periods $\sim 15{-}21$ nm. This feature of X-ray patterns is a consequence of processes of thermal destruction and crystallization of CTA [18]. Thus, a genetic relationship can be traced between the unidimensional periodicity in the structure of mesophase cluster of specimen № 1 and the large periods in heat-treated CTA films, that are detected by the SAXS method [18].

In specimen № 2, as compared with № 1, there are no periodic oscillations of density across the texture axis (Fig. 5, *b*), which gives evidence of relative disordering of the CTA cluster structure.

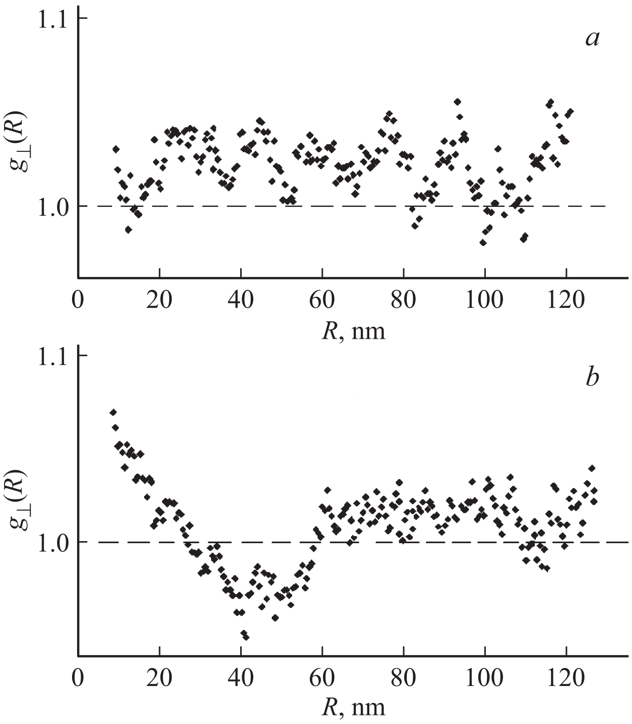

Figure 5. Radial functions of density distribution built across the axis of axial texture on the surface of CTA films: specimen № 1 (*a*), specimen № 2 (*b*). Step of surface image scanning $\delta = 1$ nm.

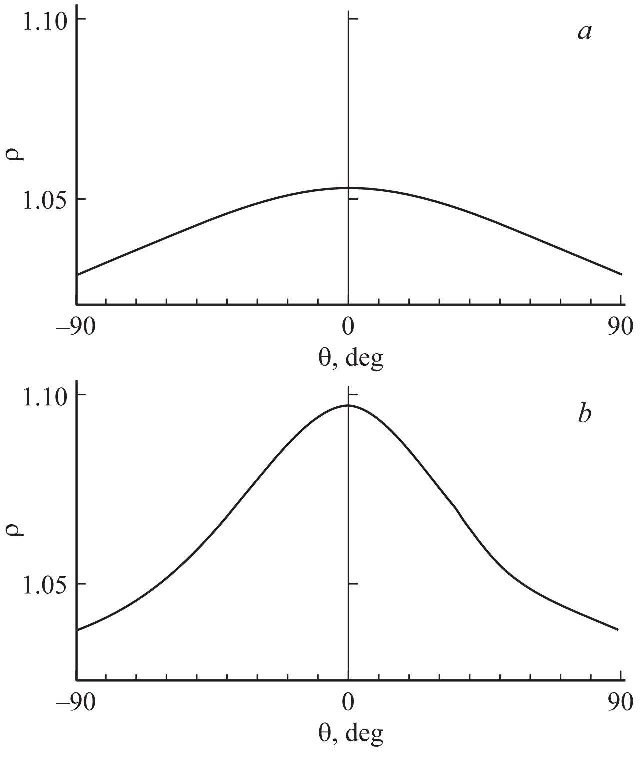

Figure 4. Indicatrices of relative (in relation to the mean value over the surface) density ρ of gold nanoparticles distribution on the decorated replicas from the surface of CTA films: specimen № 1 (*a*), specimen № 2 (*b*). Axis of the ordinates ($\theta = 0$ degrees) corresponds to the texture axis — the direction with maximum value of ρ.

4. Conclusion

The use of small quantities of modifiers decreasing viscosity of concentrated solutions of rigid-chain polymers makes it possible to change the topological structure of the mesophase cluster in the produced films. These modifiers for CTA include some inorganic salts, for example, sodium fluoride. These salts affect the salvation of functional groups of the polymer by the solvent and, thus, predefine the nature of macromolecules aggregation [2].

A structural transition of „order–disorder" type is found between two specimens of CTA films produced in the same conditions from polymer solutions without and with a small addition of sodium fluoride. This transition is related to restacking of the ordered microdomains that are the nodes of fluctuation network of macromolecules in the body of CTA mesophase cluster. In this case the periodically ununiform cluster is transformed into the uniformly unordered cluster attaining fractal properties, increasing its local density and anisotropy. This transformation explains the change in strain properties of the films: an increase by 30% of the tensile strain at break and a two times decrease in thermostatic shrinkage [11].

Conflict of interest

The author declares that he has no conflict of interest.

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