Control of the Anisotropic Structure of Cellulose Hydrate Films by Variations of Coagulation Variables

O. A. Khanchich[a]; A. T. Serkov[a]; N. V. Morozov[a]; D. V. Loshadkin[a]; E. G. Rozantsev[a]

[a] High-Molecular Compounds, Moscow State University of Applied Biotechnology, Moscow, Russia

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O. A. KHANCHICH*, A. T. SERKOV, N. V. MOROZOV, D. V. LOSHADKIN and E. G. ROZANTSEV

High-Molecular Compounds, Moscow State University of Applied Biotechnology, Moscow 109316, Russia

The evolution of the structures, that developed in cellulose hydrate films from a rayon after coagulation in the precipitating bath from organic solvent, water and sulfuric acid in presence of inorganic salt has been investigated. The specific features of structure formation at coagulation and cellulose hydrate film extension have been found. It was shown that there is a high diversity of supermolecular structures, whose morphology depends on the precipitation conditions and preliminary orientation. The films structure characteristics correspond to its strength properties. An increase in salt concentration resulted in a films with a more homogeneous, tensile strength structures and small sizes of spherulites. The films of high resistance is formed, in a precipitation bath of organic solvent, because of the realization of the liquid crystalline phase in the coagulation process.

Keywords: Cellulose hydrate; Crystallization; Anisotropy; Coagulation variables; Model of coagulation

INTRODUCTION

The study of the structure formation mechanism during chemical fiber and film production is a necessary first step to choose technology parameters which would allow to obtain materials with optimal physical properties [1]. For the cellulose systems, the investigation of

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*Corresponding author.

structure formation processes at coagulation and orientation is complicated because under usual conditions the cellulose crystallization does not lead to the formation of anisotropic structures such as spherulites which can be monitored by fast-acting optical methods. That is why the interest in studying the optically anisotropic super-molecular structures formation from rayon is justified by the expectation of using the results in the industrial applications. Knowing the regularities of structure formation and the relationship between the morphology features and physical properties of films will allow to predict certain properties of rayon films [2]. Until now, there is no structural concept relating formation conditions, super-molecular structure and physical properties of cellulose hydrate films. This work is devoted to clarifying this relationship.

EXPERIMENTAL PART

Cellulose Hydrate Film Preparation

The cellulose hydrate film were prepared from rayon containing 8,4% α-cellulose, 6,28%-NaOH, with a state of etherification – 45. The solution was placed on a glass plate with a layer thickness of 0,3 mm, then it was immersed in the precipitating bath containing N,N-dimethylformamide (DMFA) with addition of 20 mass% of water containing 20 wt/vol% conc. sulfuric acid. Some sets of samples were obtained by precipitation in the same bath but in the presence of zinc sulfate (0 – 12 g/l). To prevent a masking effect of low molecular compound's crystallization, the films were thoroughly washed in distilled water. To prevent the polarization-optical distortions caused by the stress anisotropy around the surface asperities, the homogeneity of samples was controlled in the non-polarized light.

Preparation of Ethylcellulose Film Samples

The ethylcellulose film samples were obtained by spreading a drop of ethylcellulose 10% solution in CH_3COOH over a water surface.

Test Methods

The structure formation processes were studied by using polarized microscope and polarization-optical devices which register the light transition change in crossed polaroids, and also the light dissipation at small angles. The structure of dry films was additionally investigated by X-ray diffraction methods.

RESULTS AND DISCUSSION

The microscopic investigations showed that during the cellulose hydrate precipitation from solution the coagulation processes and structure formation are separate in time. The solution coagulation is accompanied by formation of optically isotropic gel (see Fig. 1a) consisting, predominantly of cellulose xanthate, which is confirmed by the solubility of gel-type film in water or aqueous alkali. From the beginning of the film formation moment (depending on the water and precipitating mixture content), an increase is seen of centrosymmetrical radial structures (Fig. 1B). Consecutive light and dark film portions with clearly defined dividing borders appear (Fig. 1B). The points of dividing border's crossover are the spherulites centers or their fragments.

The obtained pictures have mostly the polarization-optical character, and in the natural light the film seem to be homogeneous. The next step is the material ordering inside of space between the radial structures: the angle sizes of sectors and their amount increase and the inner spherulites packing are perfected, leading to the formation of perfect spherulites of high density (Fig. 1Γ). It should be noted that spherulite's fragment are formed inside the borders which are determined by the size of the initial anisotropic sections. At this point, the rate of the radial structure's increase is unusually high for processes taking place in very viscous gels and at low water content in the precipitator and can reach tens of μm/s.

It is obvious that during precipitation, two processes occur simultaneously: increase of the polymer solid phase according to the laws of primary structure formation from the nucleus centers, and
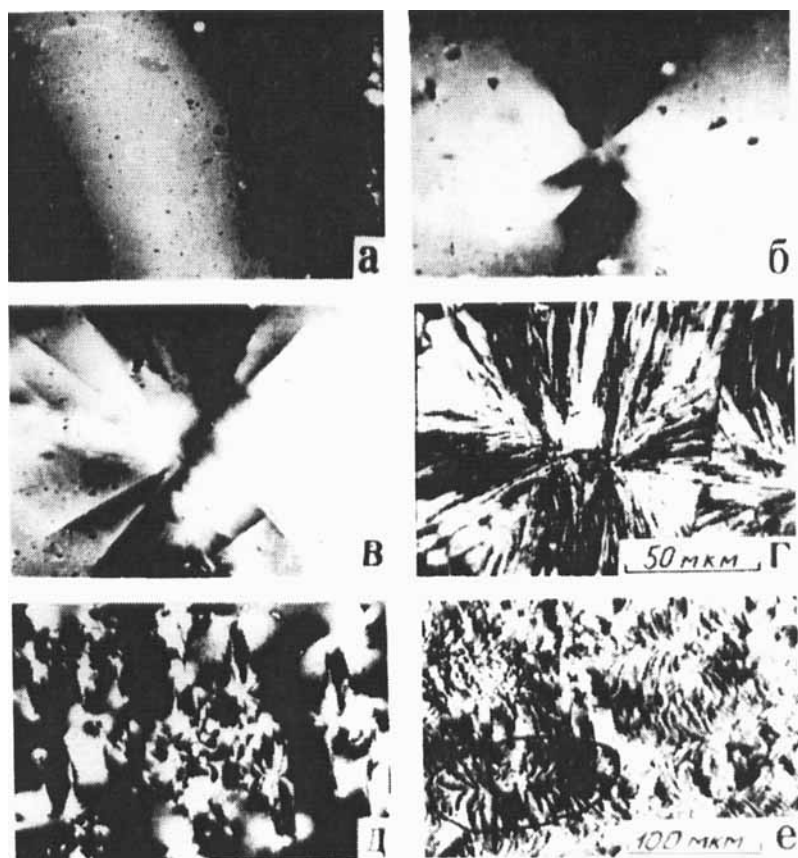
FIGURE 1　Microphotographs (×400) showing formation of spherulites in cellulose hydrate gel at orientation absence(a-Γ) and at preliminary orientation (д, e). a – optically isotropic gel; 6, д B – increase of centro-symmetric structures; д – increase of fibrillar elements perpendicular to stretching direction; Γ, e – formed spherulites. Time from the moment of coagulation: a – 0; 6 – 30 sec; B – 45 s; Γ – 90 s; д – 35 s; e – 90 s.

formation of ordered macromolecules sectors – the initial structure elements – through the whole volume of the solid phase.

Comparative study of physical properties of ordinary and spherulite containing cellulose hydrate films showed that such samples have approximately the same strength but different values of elongation's at break. This is typical for spherulite containing polymers elongation mechanisms: rotation and mutual movement of fibrils made of spherulites, without change of their fine molecular structure [2].

By transition from wholly isotropic films to ones containing perfect spherulites, there are intermediate shapes of spherulite organization which are characterized by similar sizes yet different states of inner ordering. Physical tests of a set of samples showed that the film strength in all samples was approximately the same, but the elongation at break gradually increased proportion to the perfection of the spherulite structure.

At elongation of the isotropic film (Fig. 1a) of 40–50%, a formation of radial structures and spherulites (Fig. 1, д, e) was found which are characterized by growth of perpendicularly oriented fibrillar elements. Such phenomenon is usually peculiar to structure formation under conditions of preliminary orientation. However, in deviation from what is commonly described in literature, the large axes of the spherulites were directed along the applied elongating force. The regularities of structure formation at coagulation and orientational elongation of cellulose hydrate into fiber and films have certain similarity with the crystallization mechanism of synthetic polymers from solutions and melts [3] but they also have some unique features. The unusual two-step character of spherulite structure formation, location of spherulites in preliminary oriented films along the orientation direction, and similarity of tensile strength of samples having rather different super-molecular structure, cannot be satisfactorily interpreted based on the traditional models of structure formation during phase decomposition of polymer solutions and spherulite growth due to auto-epitaxy, doubling and branching [4].

The spherulite organization perfection can be explained by the influence of DMFA in the precipitating bath which acts as crystallization suppressor [5] and, possibly, as a plasticizer operating according to the structure plasticization mechanism. On the other hand, in the framework of the 'doubled' structure formation model, the effect of sulfuric acid cannot be ignored. The acid accelerates the coagulation and helps the partial crystallization. Because of this, to compensate the mutual influence of the basic coagulation variable, the following series of tests was conducted in a precipitation bath with DMFA and sulfuric acid in the presence of zinc sulfate.

Upon changing the concentration of zinc sulfate in the bath from 0 to 12 g/l, the spherulites size reduced by an order of magnitude (Fig. 2).
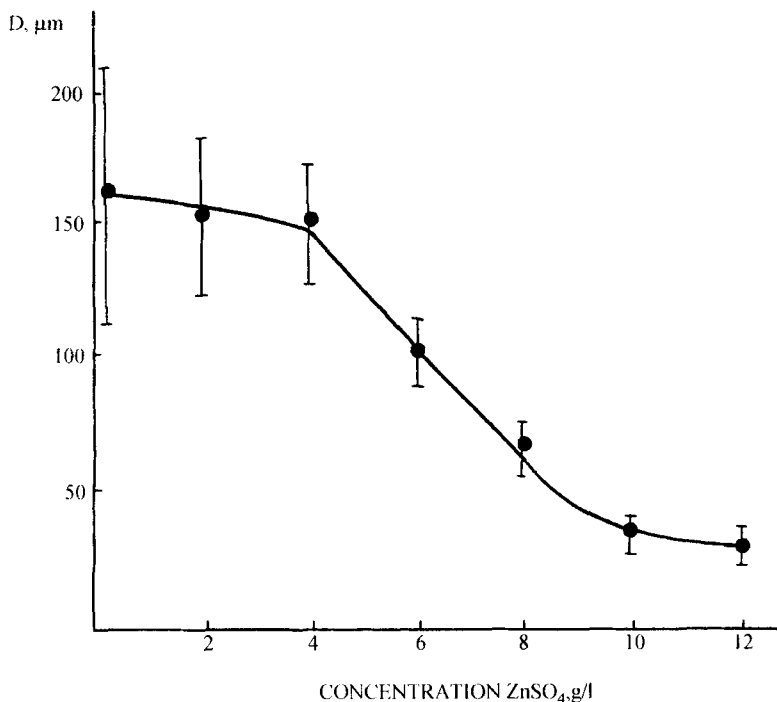
FIGURE 2   Dependence of spherulites size on zinc sulfate concentration in the precipitating bath.

Based on the data, in the range of zinc sulfate concentration from 0 to 4 g/l, the spherulites diameter practically did not change. The data scatter has a trend to be reduced with $ZnSO_4$ concentration increase, and the inner structure of the spherulites change. The latter was determined by small-angle light dispersion and X-ray analysis. The essence of the transformations is probably related to the transition from meso-phase cellulose (Fig. 3, curve 1) to cellulose II (Fig. 3, curve 2). The X-ray patterns of films containing spherulites had the shape characteristic of the patterns of cellulose II (Fig. 3, curve 2) having certain degree of crystallinity. The character of molecular conformational ordering evaluated by spectroscopy is practically unchanged and is characteristic of mesomorphic cellulose. As the zinc sulfate concentration in the precipitating bath increases further, the parameters of spherulite structure, inner ordering do not change noticeably.
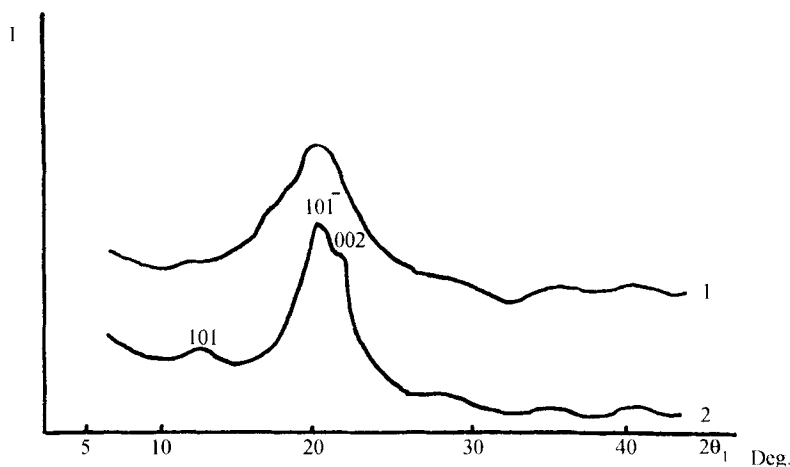
FIGURE 3 X-ray irradiation dissipation intensity curves for cellulose hydrate films obtained at zinc sulfate concentration in precipitator based on DMFA: 1 – 0.1 g/l: 2 – more than 2.0 g/l.

TABLE I Effect of zinc sulfate concentration on physical properties of hydrocellulose (orientational extension 80%)

Concentration of ZnSO₄, g/l	Tensile strength, MPa	Elongation at break,%	Strength loss in wet state,%
0	19,1	6,3	56,4
2	17,9	7,4	50,1
4	19,8	6,1	43,4
6	21,0	6,8	40,9
8	25,4	8,2	38,6
12	30,4	14,5	34,7

Thus, changes spherulite size and their inner structure occur separately (based on the zinc sulfate concentration scale) which gives the opportunity to evaluate the input of each of these factors into the physical properties of the samples [2]. The test results are given in Table I.

It is clearly seen that the tensile strength and elongation at break of cellulose hydrate films and fibers formed in a DMFA medium increase only in the range of zinc sulfate concentrations exceeding 6–8 g/l, corresponding to a significant decrease in spherulites size (Fig. 2). Hence, at forming in the zinc-containing baths, not only the cellulose xanthate decomposition is retarded, but the obtained films and fibers with a small-spherulite structure have improved tensile and strain

properties [6, 7]. From data in Table I, it also follows that addition of a small amount of zinc sulfate to the precipitating bath leads to a significant increase of tensile properties in the wet state but does not change the tensile and strain properties in the dry state. This is very important, for example in packing of food products.

It was very difficult to directly observe the existence of amorphous super-molecular pseudo-spherulite structures by physical methods available to us. Nevertheless, the investigation, for example, of structure of the ethylcellulose films obtained by spreading of a drop of 10% solution in CH_3COOH over a water surface, showed that on the film surface there is a relief in a shape of central-radial structures (Fig. 4). Such formations were found only during investigation in natural light rays, which indicates the amorphous character of the investigated samples.

In the polarized light it is possible to find that the centers of structure formation are mostly undissolved polymer fibers. Such effects can be easily explained by the growth of amorphous polymer concentration in the polymer phase near the nucleus centers which are sections with super-critical concentration.

It is possible that the phase decomposition occurs according to the mechanism of predominant growth of nuclei of a concentrated
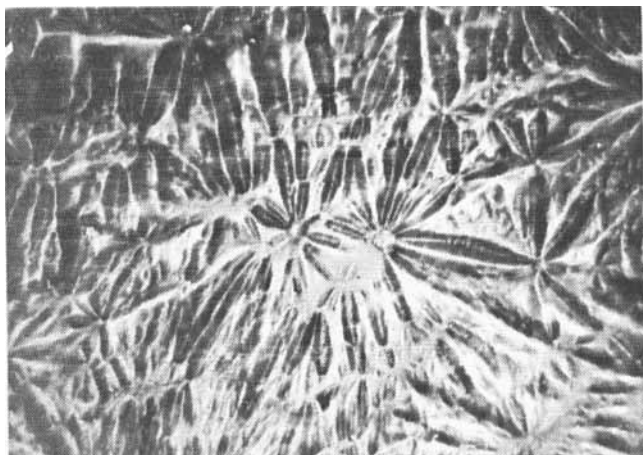

FIGURE 4 The centro-symmetrical structure in films ethylcellulose. (Microphotographs × 200 in non-polarized light.)

polymer phase. There are reasons for such an assumption:

1. The rate of solvent molecules diffusion is two – three orders of magnitude higher than the rate of macromolecules. The size of a molecular chain is several times larger than the size of molecules of low molecular compound in the coagulating mixture. The low growth rate of the phase formed by large particles corresponds to the fast growth of the phase formed from the small particles.
2. The molecular chains are interpenetrated in the concentrated solution. Because of this, it is necessary to take into account not only diffusion [8] but also the possible movement of macromolecules or their segments caused by chain interaction while analyzing the structure transformation during phase transitions. The process started in one nucleus center can quickly propagate to other ones.

Thus, it is possible to use an approach based on the predominant growth of nuclei of a concentrated polymer phase along with the known models of gel formation. As it is analogous to the fractal propagating process from one point in isotropic media, the growth of polymer phase fragments must have a centro-symmetrical character. The continuity of transition form one fragment to another one is provided by mutual interpenetration of molecular chains. Such model is close to the classical views on the structure of amorphous polymers described in [9]. However there is an exclusion in that in this case existence of any intermolecular or intersegmental interaction is not assumed. We discuss only the general regularities of isotropic process propagation in an isotropic medium. However, the modified model of phase decomposition suggested by us can conveniently explain the phenomena associated with growth of 'correct' structures in polymeric gels after decomposition of amorphous phases.

By applying the model to the case of rayon-precipitator system, it is easy to explain the fast growth of anisotropic structures in the highly viscous gel – as the result of intermolecular ordering of supermolecular pseudo-spherulite forms on the 'traces' of the amorphous phase decomposition. The spherulites arrangement in the oriented gel along the stretching direction seems to be the only possible case because the pseudo-spherulite structures must transform exactly so at orientation. The imposed sizes of spherulites (see Fig. 1) can provide a small increase of fibers and films strength at extension.

According to the data in Table I, the character of physical properties of cellulose hydrate fibers and films change practically follows the regularities known for ordinary rayon films [10]. The difference between isotropic and spherulite containing samples appears only in the character of consecutive ordering based 'on trace' of the initial structure formation. The conditions of precipitation in aqueous medium are less favorable for the 'proper' ordering because the water activity helps the crystallization of cellulose crystallites. On the contrary, the organic solvents retard the cellulose crystallization, and the ordering occurs due to transition into mesomorphic state.

The description of a suggested mechanism is possible by using the synergetic approach to the structure formation process analysis taking into account the collective effects and self-ordering of spherulites' structures. In this experimental investigation we found that the scale-hierarchy of ordered structural elements growing in cellulose hydrate films may serve as the basis for the determination of the relationship between micro- and macro-parameters of spherulite growth by using fractal theory to describe the self-similar ordering elements, and the fractal dimension as the characteristic of the dynamic object structure.

If we consider the crystal phase growth as a non-equilibrium phase transition in the points of nuclei formation, then it is necessary to determine the fractal dimension of the structures which control the free spherulite growth. The structures around the nuclei are the dynamic multitude possessing properties of universality and invariability and also an ability of self-similar growth. The fractal structures possess the same abilities. Because of this, we tried to use the concept of fractals for quantitative description of spherulite structures. This is the basis for determination of universal relationship between parameters of dynamic structure and physical properties.

According to Mandelbrot [11], the self-similarity means that there is a function which copies the universality on itself with the help of a scalar Z which is a self consistent ratio. For nonstandard self-similar shapes, the whole can be divided to M parts obtained through the ratio Z and connected with the fractal dimension by the expression:

$$Z^D = 1/M \tag{1}$$

at $0 < D < 3$.

To use the expression in analysis of self-organizing structures, it is necessary to determine the physical meaning of M. It arises from the equation of single spherulite growth kinetics which is described by self-similar growth.

$$r^{i-1}/r^i = \Delta^{1/M} \tag{2}$$

where r^{i-1} and r^i are previous and next spherulite size in the direction of crystal growth, correspondingly. The M is number which changes according the law of geometric progression and corresponds to the cycles' periodicity in the self-organizing systems. The number determines the upper boundary of the intermediate asymptotic block at $M \rightarrow \infty$ and the lower border at $M = 1$. The function $\Delta^{1/M}$ is just the function of self-similarity which is self replicating and determines the periodicity of repetition of an intermediate asymptotic block at self-similar spherule growth. The function gives a compressed information on different scale levels. The possibility of information compression is determined by the scale invariance of the system. Because of this, the self-similar spherulite growth can be represented as blocks of intermediate asymptotics in which the consequence of spherulite sizes thresholds takes place. At the consequence, in each exit from the block of intermediate asymptotics, the spherulite size increases on value Δ^{-N}, where N is the number of iterations. This allows to use the function $\Delta^{1/M}$ at $M \rightarrow \infty$ as a self- similar function Z in (1) expressing it as follows:

$$Z^D = \Delta^D = 1/i_r^c \tag{3}$$

where i_r^c – scale coefficient taking into account the ratio of maximal scale to minimal scale of observation, characterizing the spherulite critical parameters.

To provide the quantitative description of spherulite structures growth, it is necessary to give numbers to the nuclei centers image, for example by replacing it with a lattice of n points (usually n is about 10^{16}) [12]. The generalized dimension can be then calculated by several independent methods: the 'sand box' methods, the density – density correlation function method, the radius of gyration method [12]. In this work, we used the radius of gyration method. The results show that the dimension is $1,8 \div 1,9$.

CONCLUSIONS

The detailed investigation of coagulation process allowed to developed a model of gel formation at cellulose hydrate precipitation. In the model the destruction of polymer solution occurs predominantly according to the mechanism of nuclei growth in a concentrated polymer phase. Determination of a fractal dimension of the investigated system allows to use computerized methods of data treatment in the future to consider the genesis of super-molecular structures at cellulose hydrate coagulation in film formation.

The discussed approach provides an opportunity to quickly determine the quality of film material in commercial production conditions based on the relationship between super-molecular structures and physical properties by combining the results of fast optical methods with consecutive conclusions obtained from fractal dimension. It is obvious that the fractal dimension describes not only the process of its formation but provides significantly more precise data about material properties.

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