

## PROCESSING OF CELLULOSE VIA HIGHLY CONCENTRATED "SOLID SOLUTIONS"

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*The examined method of processing cellulose can be used to conduct solid-phase EDA-complexation of cellulose with high-melting MMO hydrates in conditions of the effect of shear strains and pressure. The method allows: expanding the concentration range of the solubility of cellulose in MMO to 50% and obtaining highly concentrated spinning solutions with a concentration of up to 30%; decreasing the duration of dissolution to 5-10 min; regulating the process of thermal degradation of MMO and cellulose; fabricating "Orcel<sup>®</sup>" fibre with a high degree of orientation and high strength and modulus of elasticity. The solid-phase amine oxide method of processing cellulose was developed by the contract group at the All-Russian Scientific-Research Institute of Polymer Fibres (VNIIPV): Candidate L. K. Golova (director), candidate N. V. Vasil'eva, Candidate L. K. Kuznetsova, Candidate T. A. Lyubova, Research Associate O. E. Borodina, and Research Associate T. B. Krylova with the participation of leading specialists at the Institute's BI Center (director of the Center, Candidate I. Z. Eifer). The studies of the properties and structure of Orcel<sup>®</sup> fibre were conducted by leading specialists at the Institute's BIFIM Complex (Professor M. M. Iovleva, Director), Candidates V. N. Smirnova, S. I. Banduryan, T. A. Belousova, L. P. Mil'kova, I. N. Andreeva, L. P. Konovalova, V. G. Brusentsova, Dr. A. T. Kalashnik, Research Associate G. Ya. Rudinskaya, and Dr. A. Sh. Goikhman.*

Of the problems related to processing of a polymer constantly reproduced in nature — cellulose — into fibres and films, one of the most important and key problems is still the process of converting cellulose into solution. The fundamental existing viscose method of fabricating fibres and films based on wood cellulose is characterized by elevated ecological hazardousness, so that the question of environmental protection is most acute in conditions of maintaining a stable volume of world cellulose fibre production.

The search for a new, ecologically clean solvent for cellulose intensely conducted by many institutes and companies in the US, Great Britain, France, Austria, Germany, and Russia in the last two decades has allowed determining the basic direction for solving the problem of dissolving and processing cellulose. As a result of studying a relatively large number of dissolving systems, direct dissolution of cellulose in an organic solvent, N-methylmorpholine N-oxide (MMO) — the MMO process — was finally formulated as a totally realistic alternative to viscose production [1-9].

In addition to solving the ecological aspect, the MMO process is also characterized by the novelty of the technical solutions and attainment of cotton-like properties of the fibres, which distinguishes them from traditional viscose fibres. These fibres have been named "Lyocell."

Despite the fact that processing of cellulose from solutions in MMO is not yet optimum either for the technological or for the economic parameters and requires further improvement like any new process, it is already beginning to claim its position among existing cellulose fibre and yarn plants. This is indicated by the production volume of the new cellulose fibre, assimilated and planned by leading firms — the developers of this process. This primarily concerns Courtaulds (Great Britain), which created production of the new fibre Tencel in 1992 in the US (Alabama) with an output of 20,000 tons/year and is planning a subsequent increase in production to 100,000 tons/year. Lenzing (Austria) has conducted relatively broad studies of all stages of the process and according to the latest communications, is creating production of Lyocell fibre in the amount of 20,000 tons/year [10].

TABLE 1. Physical and Textile Parameters of the New Fibres [5]

Fibre	Linear density, dtex	Properties in standard state		Properties in wet state		Moisture content, %	Moisture absorption, %
		$\sigma$ , cN/tex	$\epsilon$ , %	$\sigma$ , cN/tex	$\epsilon$ , %		
Tencel	1.5	33-42	11-16	13-18	16-18	270	11.5
Lycocell	1.63	40	11.4				
Newcell	1.4-2.2	31-40	9-12	22-27	8-11		11-13
ALCERU	0.15, tex	47	14	4	46	260	
Ordinary viscose	1.7	22-26	20-25	13-17	27-30	50	13.0
Modal viscose	1.7	1-36	13-15	16-21	13-15	110	12.5

**Notation:**  $\sigma$ ) strength;  $\epsilon$ ) elongation at break;  $E$ ) modulus of elasticity.

TABLE 2. Solubility of Cellulose as a Function of Its Concentration in the Mixture and the mp of the MMO Used

Concentration of cellulose in mixture, %	mp of MMO, °C	mp of activated cellulose-MMO system, °C	State of system
20	170	135	Solution
30		130	-
40		130	-
50		130	-
55		130	Incomplete dissolution
20	150	110	Solution
30		130	-
40		130	Incomplete dissolution
20	76	110	Solution
25		120	Incomplete dissolution

TABLE 3. Heat of Reaction of the Cellulose-MMO System (mp 170°C) with Water

Concentration of cellulose, %	$- \Delta H_1$ , J/g	$- \Delta H_2$ , J/g	$\Delta H_1 - \Delta H_2$
3	5391	5175	219
5	3811	3620	224
10	1878	1656	222
20	902	682	220
25	704	482	222

**Notation:**  $\Delta H_1$ ,  $\Delta H_2$ ) heat of dissolution of mechanical and activated mixture, respectively.

A new fibre, ALCERU, has been developed with new technology at the Turing Institute of Textiles and Plastics (Rudolstadt) [11].

Akzo (Germany) occupies a special position in the creation of the new process. The studies it initiated in 1976 were protected by fundamental patents in 1979-1980 both on the technology of the process and on the final product — Newcell fibres and yarns [12, 13]. Akzo's patents were so complete that all existing processes and experimental and industrial plants are based on these patents, distinguished by engineering solutions of the separate stages of the process almost alone or their modifications as a function of the type of final product — fibre, yarn, film, sponge, ultrathin fibre, etc.

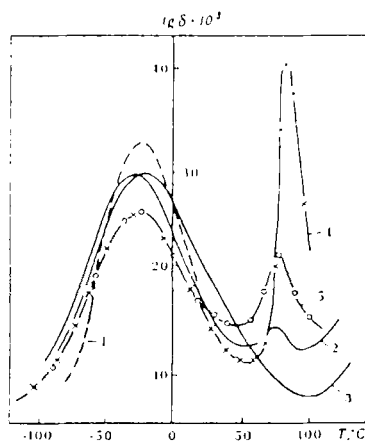


Fig. 1.  $\tan \delta$  of primary cellulose hydroxides vs. temperature: 1) starting Baikalsk cellulose; 2) mechanical mixture of cellulose + 1% MMO; 3) activated mixture of cellulose + 1% MMO; 4) mechanical mixture of cellulose + 5% MMO; 5) activated mixture of cellulose + 5% MMO.

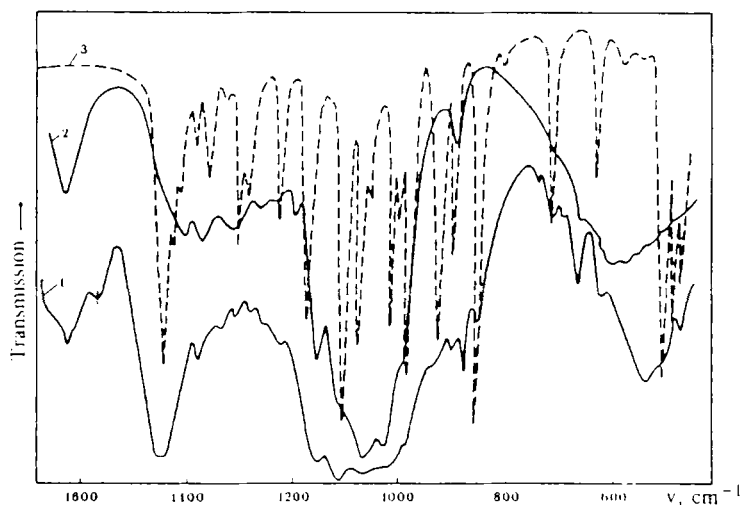


Fig. 2. Section of the IR spectra of a 50% "solid solution" of cellulose in MMO (1) and its starting components — powdered cellulose (2) and MMO (3).

Cellulose is dissolved in MMO according to a direct mechanism. MMO is a strongly polar solvent of the donor type, and the degree of its reaction with respect to cellulose is limited by the concentration of water in the MMO. For a concentration of water in MMO greater than 28% (dihydrate form of MMO, melting point  $mp = 38^\circ C$ ), it can only cause swelling of the cellulose. The monohydrate form of MMO (13.3% concentration of water,  $mp = 76^\circ C$ ), which combines relatively high dissolving power with a comparatively low  $mp$ , is used most widely. A further decrease in the concentration of water in MMO, accompanied by an increase in its melting point ( $mp$  of MMO anhydride is  $182^\circ C$ ) increases its dissolving power. However, despite the high dissolving power of MMO, the stage of preliminary activation of the cellulose precedes the stages of dissolution in the MMO process. To facilitate access of the molecules of solvent to the functional groups in the cellulose and accelerate the dissolution process, it is treated with a 30-60% aqueous solution of MMO with continuous stirring until a homogeneous suspension is formed. In the process developed by the German investigators [11], hydrothermal

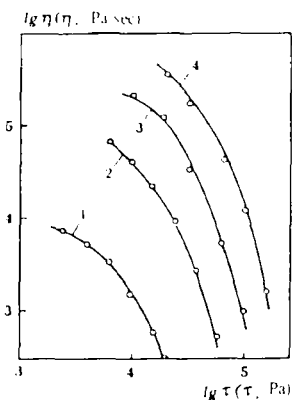


Fig. 3. Viscosity vs. shear stress at 100°C for solutions of cellulose in MMO in the concentration of 15 (1), 20 (2), 25 (3), and 30% (4).

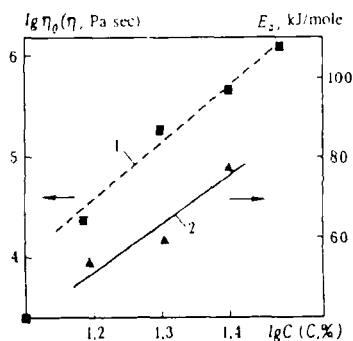


Fig. 4. Highest Newtonian viscosity (1) and activation energy of viscous flow (2) vs. concentration of a solution of cellulose in MMO.

treatment of the cellulose at 130-150°C for 3 h precedes the activation stages. The excess water is removed from the pulp in vacuo to a 15-18% concentration of water. The solution is then placed in a screw conveyor where more water is removed to a 6-10% concentration under the simultaneous effect of temperature and vacuum and the cellulose is dissolved, with formation of solutions containing 10-15 wt. % cellulose according to patent data. The next stages are filtration, spinning, and washing off of MMO, which is purified and concentrated in a closed cycle and is then fed in the form of an aqueous solution to the spinning bath and to the first stage of homogenization and formation of cellulose pulp.

This is the technological scheme for the new, ecologically clean process of processing cellulose from solutions in MMO.

The cellulose fibres obtained by the new method are characterized by high degrees of crystallinity and fibrillizability and have a high strength and modulus of elasticity. As the data reported in Table 1 suggest, the new fibre should probably be considered a special type of cellulose fibres with higher strength than even natural cotton when wet.

Extensive studies of the cellulose–MMO system have been conducted at VNIIPV since the beginning of the 1980s, ranging from a study of the structure, properties, and phase state of the starting objects to determination of the characteristics of the spinning process and properties of the fibres obtained [14-24].

Great attention has been focused on the electron donor–acceptor mechanism of reaction of direct organic solvents of the donor type with hydroxyl-containing compounds, and primarily with cellulose, to define the criteria which determine their maximum dissolving power. Despite the fact that of all systems investigated, only MMO has the unique combination of the required parameters which ensure high efficiency of the reaction with cellulose and total realization of the dissolving power

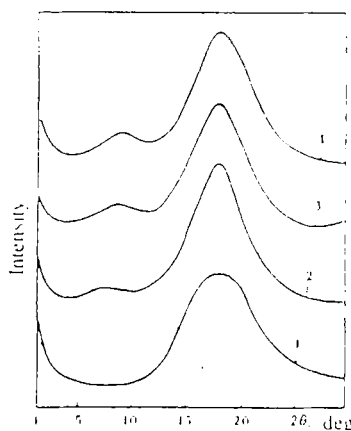


Fig. 5. Diffractograms of 50% solution of cellulose in MMO at 20 (1), 81 (2), 103 (3), and 124°C (4).

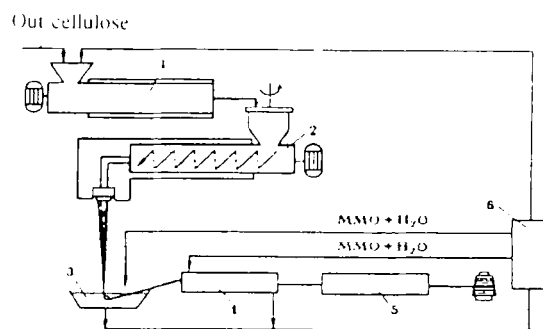


Fig. 6. Diagram of the solid-phase process of processing cellulose into fibres from highly concentrated solutions in MMO: 1) pulverizer for preparation of powdered cellulose and highly concentrated solid solutions; 2) single-screw extruder with spinning unit for preparation of spinning solutions and spinning of the fibre; 3) spinning bath; 4) fibre washing circuit; 5) fibre finishing and drying circuit; 6) MMO regeneration circuit.

of MMO, and obtaining highly concentrated solutions in the conditions of the traditional MMO process is almost impossible due to the low thermal stability of MMO. The heat of decomposition of MMO is 159 kJ/mole [25, 26]. The basic difficulties of the process are due to the fact that the mp of the most reactive anhydrous form of MMO, which has two free unshared electron pairs at the oxygen atom of the semipolar N→O bond and can react with the protons of two hydroxyl groups, is close to the temperature of active thermal degradation. The use of thermodynamically poorer melts of the hydrate forms of MMO with a high concentration of water and correspondingly a lower mp for preparation of highly concentrated solutions of cellulose makes it necessary to use special equipment and to significantly increase the duration of dissolution, which also causes extremely high thermochemical degradation of MMO.

In decomposition of MMO, whose mechanism was investigated in some detail in [27-29], simultaneous breaking of the hydrate bond between molecules of MMO and molecules of water and the amine oxide bond of the MMO molecules directly takes place. In solutions of cellulose, the processes of decomposition of MMO can take place with a high intensity with formation of morpholine, formaldehyde, N-formylmorpholine, and formic acid, in addition to methylmorpholine. The atomic oxygen liberated during degradation of MMO causes active degradation of cellulose. To inhibit oxidative degradation of cellulose, antioxidants of different natures are added to the solutions, and gallic acid propyl ester is one of the most effective. However, despite the efficiency of the thermostabilizing additives incorporated in the system, the conditions of pre-

TABLE 4. Basic Technological Parameters of the MMO Process

Parameters	Tencel	Newcell	Lyocell	ALCERU	According to H. Chanzy	Orcel <sup>®</sup>
Concentration of cellulose, %	10-14	14	10-13	5-20	13	25
DP of cellulose	600-5000	787	750-1400	400	600-2000	500-800
$T_d$ , °C	90-140	100	60-100	85-90	100	100
Stabilizer*	+	++	+	+	+	+
Additional additives				Tenside	NH <sub>4</sub> Cl, CaCl <sub>2</sub>	
Water content, %	60		40	40-60	40	
Extruder $T$ , °C	115-120	115-120	75-115	75-95	110-130	110-125
Air space, cm	30		1-3.5	0.2-2.0	10-15	10-30
Spinneret hole diameter, $\mu$ m	32-250		50, 70-1500	50-70	300-500	150-500
Number of holes			500, 1000-2000	160 cm <sup>2</sup>	1	
Spinning bath	H <sub>2</sub> O	H <sub>2</sub> O, ROH		5-50%		10-40%
H <sub>2</sub> O/MMO (its temperature)				(5-10 °C)		
Rate of taking fibre off godet, m/min	140, 220		100-200	60-200	20, 200, 400	50-150

\*Propyl gallate (0.5-1.5%), except for the "Newcell" process, where ascorbic acid was the stabilizer.

paration of highly concentrated solutions according to the traditional scheme are so harsh that it is not promising to conduct research in this direction.

Detailed studies of the characteristics of the reaction of cellulose with MMO revealed a new solution for the problem of direct dissolution of cellulose, namely, by preliminary solid-phase treatment of cellulose in high-melting MMO hydrates in conditions of shear strains and pressure. The solutions obtained contain up to 50% cellulose. This solution is protected by a 1989 patent [30].

For creating a general notion of solid-phase processing of cellulose and fabrication of the new Orcel<sup>®</sup> fibre, the results of the studies conducted are generalized and systematized according to the following basic directions:

- characteristics of the solid-phase reaction of cellulose and MMO which takes place in conditions of shear strains and pressure;
- the properties, structure, and phase transitions of highly concentrated "solid solutions" of cellulose in MMO;
- the major technological scheme for processing of highly concentrated "solid solutions" of cellulose, and the properties and structural characteristics of the new cellulose fibre Orcel<sup>®</sup>.

## CHARACTERISTICS OF THE SOLID-PHASE REACTION OF CELLULOSE AND MMO IN CONDITIONS OF SHEAR STRAINS AND PRESSURE

There are very few published studies of solid-phase reactions of polysaccharides and they basically concern modification of cellulose, i.e., conducting chemical reactions with formation of cellulose esters [31, 32]. The high efficiency of the solid-phase reaction of cellulose suggests the possible occurrence of reactions of a lower energetic order in conditions of shear — direct "solid-phase dissolution" of cellulose. In solid-phase processing of cellulose and high-melting MMO containing from 0.5 to 8% water, finely disperse powders are formed in laboratory grinders; when heated, they melt, turning into homogeneous solutions containing up to 50% cellulose [22, 33].

The maximum temperature of the dissolution unit for a given duration of the dissolution process (2 min) was set as the melting point. The completeness of dissolution was monitored by polarization microscopy and the turbidity spectrum. As Table 2 shows, solid-phase processing, most effective when highly reactive hydrate forms of MMO with a water content of less than 8% are used, increases the reactivity of MMO monohydrate as well. In melting of a cellulose—MMO monohydrate mixture containing under 20% cellulose, a homogeneous solution is formed after 1-2 min with small shear stresses.

The decrease in the melting point and correspondingly dissolution of mixtures undergoing solid-phase processing in comparison to the melting point of the oxide used when the concentration of cellulose in the mixture is increased merits special attention. These dependences are in agreement with the data in [2] and [34] except that in the given case, the temperature depression is more pronounced. Although increasing the concentration of cellulose from 3 to 15% in the case of MMO monohydrate decreases the mp of the solution by 2-6°C, as demonstrated in [2], and by 6-13°C according to the data

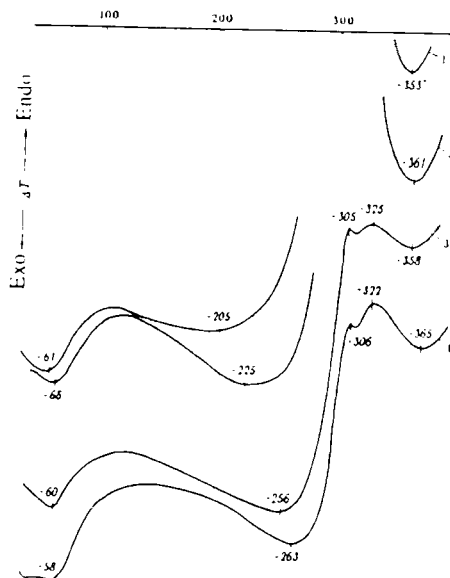


Fig. 7. DTA results for samples of fibres: 1) viscose textile fibre; 2) viscose cord thread; 3) Orcel® fibre.

obtained in [34], mixtures based on MMO with mp of 170 and 150°C containing 30% cellulose melt with formation of a solution at 130°C, i.e., the temperature depression is equal to 40 and 20°C, respectively.

The decrease in the melting–dissolution point which takes place as a result of treating cellulose and MMO in conditions of pressure and shear stress can be due to either the indirect effect of the dissolution process on macrokinetic factors (accessibility of any of its segments to reaction with the solvent which enters the most inaccessible interfibrillar spaces with such high dispersion) or a reaction on the molecular level.

Comparative physicochemical studies of the starting reagents, mixtures of cellulose with MMO, exposed to shear and pressure and mechanical mixtures of the same composition, i.e., treated separately in the same conditions and then homogenized, were conducted to establish the nature of the high reactivity of solid-phase treatment of mixtures of cellulose with MMO.

Using a computer method based on determination of the degree of crystallinity with standard areas of amorphous scattering of x-rays (Germans–Weidinger method), it was shown that grinding of cellulose significantly reduces its crystallinity and causes accumulation of paracrystalline perturbations and a change in the state of ordering in the amorphous phase. The qualitative evaluation of the size of crystal grains in treated mixtures by the discrete spot method showed that in contrast to cellulose, the size of MMO particles does not change during solid-phase treatment and ranges from 25 to 43  $\mu\text{m}$  in different directions.

Interesting information on the processes that take place between cellulose and MMO under the effect of shear and pressure was obtained in studying the reaction of activated and mechanical mixtures containing from 3 to 25% cellulose with water by the calorimetric method [35]. As the data in Table 3 show, a tendency toward an increase in the heat effect of the reaction of the mixtures with water, common to both systems, was observed when the concentration of cellulose in the mixtures was decreased, probably caused by the difference between the heats of the reaction of MMO and cellulose with water. However, despite the fact that the enthalpy of the reaction of mechanical mixtures with water was significantly higher than the heats of the reaction of activated mixtures with water, the difference in the enthalpies was almost constant and equal to 222 J/g. This difference is almost the same as the enthalpy of dissolution of cellulose in MMO melt (224 J/g), which indicates the same nature of the reactions that take place between cellulose and MMO in the solid phase and in direct contact of solid cellulose with liquid MMO. These dependences suggest that "solid-phase dissolution" with formation of highly concentrated "solid solutions" of cellulose takes place during solid-phase treatment of cellulose and MMO in conditions of simultaneous exposure to shear strain and pressure.

The molecular mechanism of the initial stages of dissolution of cellulose in MMO, i.e., the reaction of the solvent molecules with the cellulose hydroxyl groups, was investigated by dielectric spectroscopy in [36]. The temperature curves of

the dielectric loss tangent  $\tan \delta$  for the starting cellulose, mechanical mixtures, and mixtures undergoing solid-phase processing with a different concentration of cellulose in MMO are shown in Fig. 1. The intensity of the peak at  $-40^\circ\text{C}$ , corresponding to the dielectric absorption caused by reorganization of cellulose primary OH groups, decreases with an increase in the concentration of MMO in the sample. In addition to the peak at  $-40^\circ\text{C}$ , when MMO is added to cellulose, a dielectric loss peak appears at  $80^\circ\text{C}$ , probably corresponding to the mp of the hydrate form of MMO. As we see, the character of the dielectric loss curves changes as a function of the history of the sample. In going to activated samples, the changes are insignificant in the  $-40^\circ\text{C}$  region, while an important decrease in the value of  $\tan \delta_{\text{max}}$  is observed in the  $80^\circ\text{C}$  region. As a consequence, the phase composition of the system changes as a result of the activation treatment, the complex phase remains unchanged, and the free MMO phase decreases. The decrease in the concentration of the free MMO phase is probably caused by the occurrence of reactions of a higher order during solid-phase activation, i.e., MMO forms complexes not only with the primary hydroxyl groups of the cellulose but also with secondary groups.

The results of these studies are in good agreement and confirm the probability of the occurrence of reactions with a high degree of efficiency during solid-phase treatment of cellulose and MMO in conditions of shear stresses. Based on the nature of cellulose and MMO, these reactions are electron donor–acceptor (EDA) reactions. In the  $\text{Cel}-\text{OH}\cdots\text{O}\leftarrow\text{NR}_3$  complex, the hydroxyl group of the cellobiose unit in the cellulose macromolecules is the electron acceptor, so that if we rigorously characterize this type of reaction, it is a H complex. However, EDA complexation even causes an increase in the dipole moment and electron density on the oxygen atom of the  $\text{N}\rightarrow\text{O}$  bond in the case of MMO monohydrate. The asymmetry of the coordination bond in the molecule of anhydrous MMO should be even stronger, i.e., the H complex formed in conditions of shear strains probably has a certain proportion of charge transfer.

An attempt was made to separate and study the H complex formed by IR spectroscopy in [37] to confirm the validity of the proposed mechanism of the solid-phase reaction of cellulose and MMO which would allow realizing the maximum reactivity of the high-melting hydrate forms of MMO and converting up to 50% of the cellulose into solution. Since the spectra of a 50% "solid solution" are unsolvable due to overlapping of the signals of MMO and cellulose, free MMO not bound with cellulose was separated from the system by sublimation in a deep vacuum. The comparative analysis of the section of the spectra of the isolated H complex and the individual components of this system (Fig. 2) shows the absence of additivity in the spectrum of the complex. The appearance of additional absorption bands in the spectrum of the complex, in particular, a band at  $670\text{ cm}^{-1}$  in the region of torsional vibrations of the OH group and at  $870\text{ cm}^{-1}$  (this region characterizes the supermolecular state of cellulose according to the published data) is the most important criterion of the reaction in this system. Important changes are also correlated with the significant change in the character of the bands of both MMO and of cellulose in the  $1200\text{--}1350\text{ cm}^{-1}$  region.

According to the published data, such changes in this region of the spectrum of cellulose are most probably caused by substituted primary hydroxyl groups. The set of additive deviations in the spectrum of this sample can thus be considered direct confirmation of EDA solid-phase complexation which takes place when the cellulose–MMO system is exposed to shear stresses and pressure.

## PROPERTIES, STRUCTURE, AND PHASE TRANSITIONS IN HIGHLY CONCENTRATED SOLUTIONS OF CELLULOSE IN MMO

Under the simultaneous effect of temperature and a velocity gradient, "solid solutions" of cellulose in MMO melt and are converted into highly concentrated flowing solutions with a relatively high degree of homogeneity. The size of the heterogeneous particles in solutions containing 20–50% cellulose, determined by the optical method of the turbidity spectrum, varies from  $r < 0.1\ \mu\text{m}$  to  $r > 1.6\ \mu\text{m}$ .

The rheological studies of solutions containing 15–40% cellulose conducted by capillary viscometry with a constant load on a MV-3M microviscometer showed that large highly elastic deformations which lead to perturbation of laminar flow develop in solutions containing 30% cellulose. In studying solutions containing 15–30% cellulose, their thermal stability at  $100^\circ\text{C}$  was revealed [38], and the viscosity remained unchanged for 2 h. However, repeated passage of the solution through a capillary caused a significant decrease in the viscosity, especially with an increase in the applied shear stress. All solutions studied are non-Newtonian liquids whose viscosity  $\eta$  decreases with an increase in the shear rate or stress  $\tau$  (Fig. 3). Similar curves were also obtained at other temperatures. The degree of the viscosity anomaly, as examined above, significantly increases in going to solutions containing more than 30% cellulose.



Based on the data in Fig. 3, the highest Newtonian viscosity of the solutions was determined by extrapolation to a zero value of  $\tau$ . As Fig. 4 shows, a power dependence of  $\eta_0$  on the concentration is observed for the solutions investigated:

$$\eta_0 \sim C^\alpha \text{ for } \alpha = 4.8.$$

The values of the activation energy of viscous flow  $E_a$  obtained with the Arrhenius dependence of  $\eta_0$  on the temperature in the 15-25% region of concentrations of cellulose also do not change when the viscosity is measured with different shear stresses.

The change in the viscoelastic characteristics of solutions when the concentration of cellulose is increased to 28% does not exhibit any anomalies either with respect to the rate of increase in the modulus of elasticity and the losses or in their absolute values [39]. The data obtained indicate that solutions containing under 30% cellulose behave at 100°C similarly to isotropic solutions of polymers.

Preparation of superconcentrated solutions allowed conducting directed studies to determine the possibility of realization of liquid-crystalline (LC) order in them. The LC state of cellulose in solutions of MMO was found for the first time by French investigators based on data on the appearance of birefringence (BR) in solutions containing 20-25% cellulose [40, 41], but due to the difficulty of preparing the highly concentrated solutions, this research was not pursued. The properties and structural and phase transformations in solutions containing 20-50% cellulose with DP of 300 and 600 in the 20-180°C temperature range were investigated by polarization microscopy, scanning calorimetry, and x-ray structural analysis to solve the problem of the transition of cellulose to the LC state.

As demonstrated in [42, 43], the solutions studied are optically anisotropic, but the stability of the anisotropy is a function of the concentration of cellulose in the solution. When solutions containing up to 40% cellulose are heated, the anisotropy totally disappears at 80-90°C and is not recovered on cooling. Highly viscous, rubber-like solutions containing more than 45% cellulose do not lose optical anisotropy in repeated and prolonged thermostating at high temperatures up to thermal degradation. The BR is probably preserved due to the inhomogeneity of the phase composition of the highly concentrated solutions and the presence of regions of swollen cellulose in them. However, even when the overall picture of BR is preserved in individual sections of the sample investigated, pronounced changes in the texture are observed — a decrease in the BR on cooling and an increase on heating.

The presence of a blurred endothermic peak in the 80-84°C temperature region appeared on the DSC thermograms of solutions containing 20-30% cellulose. The thermogram of a 50% solution is more complicated in the 80-95°C region. The analysis of the character of the change in the heat of the transition at 80-84°C as a function of the temperature-time effect using a system containing 25% cellulose showed that the orientation of highly concentrated solutions of cellulose is formed during their preparation in conditions of shear stresses. The relatively high viscosity of the solutions caused by both the high viscosity of the solvent and the structural features of the system — a dense network of intermolecular bonds — stabilizes the induced orientation and results in an extremely low relaxation rate.

The x-ray structural studies confirmed the validity of the dependences. Solutions containing up to 40% cellulose are amorphous. Their diffractograms only contain a diffuse maximum in the 16-20°C region corresponding to short-range order in the system. Studies of 50% solutions of cellulose in MMO conducted for large and small diffraction angles revealed a new reflection,  $2\theta = 9^\circ$  at 80°C (Fig. 5), which indicates the appearance of long-range order in the system with laminar interchain periodicity. When the temperature increased to 124°C, the intensity of the reflection increased.

It was not possible to establish the upper temperature of the transition of the solution to the isotropic state, since it is probably in the region of active breakdown of the cellulose solution.

Summarizing all of these studies made it possible to conclude that a thermodynamically equilibrium anisotropic state is realized in solutions containing more than 45% cellulose. The anisotropy of solutions containing under 45% cellulose is due to kinetic factors, namely slow relaxation of the induced orientation formed during their preparation under the effect of shear stress.

## **TECHNOLOGICAL SCHEME FOR PROCESSING HIGHLY CONCENTRATED "SOLID SOLUTIONS" OF CELLULOSE. PROPERTIES AND CHARACTERISTICS OF THE STRUCTURE OF ORCEL® FIBRE**

The dependences of the temperature of dissolution  $T_d$  on the melting point of MMO for several concentrations of the spinning solution and the properties of the solutions obtained were analyzed to select the parameters for processing highly con-

centrated solid solutions and correspondingly dissolution of cellulose. Based on the decrease in the temperature of dissolution with an increase in the concentration of cellulose in "solid solutions" in using the high-melting hydrate forms of MMO, MMO with  $m_p = 130-150^\circ\text{C}$  was used as the most suitable hydrate forms in the process developed.

The technological characteristics of the new solid-phase amine oxide process were investigated in solutions containing 25% cellulose. The use of efficient extrusion equipment allowed decreasing the temperature of processing 25% "solid solutions" of cellulose to  $100-125^\circ\text{C}$ .

The decrease in  $T_d$  combined with the high rates of dissolution and correspondingly brief time the solution remains in the high-temperature zone significantly slows degradation of MMO and cellulose. As the studies showed, the change in the degree of polymerization (DP) of the cellulose during its processing, including the stage of solid-phase processing and dissolution, does not exceed 10-15%.

The technological diagram of solid-phase processing of cellulose from highly concentrated solutions in MMO shown in Fig. 6 includes the following stages: preparation of powdered cellulose and highly concentrated solid solutions; dissolution and spinning; washing, finishing, and drying.

The process, which is essentially continuous, can also be periodic if necessary, since it is possible to process and store the intermediate products — the powdered cellulose and solid cellulose solution.

The basic elements of the technology and equipment used are a pulverizer for preparing the powdered cellulose and highly concentrated solid solutions, a single-screw extruder of the melt type for processing the "solid solutions" on spinning, and spinning-finishing benches for continuous spinning, washing, and finishing of cellulose fibre. As in the existing MMO process, dry-wet spinning in a spinning bath containing an aqueous solution of MMO is used. The fibre obtained with the new technology is called "Orcel<sup>®</sup>" and has been registered as a trade mark.

The basic technological parameters of the new process and the MMO processes of leading foreign firms generalized in [5] are compared in Table 4. Unfortunately, there are no data in Table 4 on the duration of dissolution of the cellulose, but according to different patents [44, 45], it is 1.5-2 h in existing MMO processes, while it does not exceed 5-10 min in the new process. The main differences in the first two stages of the new process virtually do not alter the spinning process. The basic orientational and structural transformations in the fibre take place under the effect of shear (in the spinneret channel), longitudinal (under the effect of drawing) strains, and the temperature gradient in the air space. The orientation realized is basically fixed and the cellulose is crystallized in the spinning bath.

The x-ray structural studies of the character of the change in the texture of the fibre as a function of the stages of its preparation revealed elements of long-range order and the presence of axial orientation in the fibre after the spinning bath. The reflections observed in the x-ray picture characterize the long-range order in the layer. The interchain period in the layer coincides with the interplanar distance of 010 in the crystal lattice of the cellulose. There is no periodicity between layers, and interchain contacts between layers are probably realized by molecules of the solvent. The dependences obtained indicate the interfacial structure of the precipitated fibre gel.

The anisotropy and high viscosity of the spun fibre cause a significant decrease in the diffusion coefficient ( $D = 0.4 \cdot 10^{-8} \text{ cm}^2/\text{sec}$ ), low rates of decomposition into phases, and consequently, formation of a dense, homogeneous structure of the fibre formed, characterized by high orientation and crystallinity. A preliminary indirect estimation of the degree of crystallinity of Orcel fibre by sorption of water vapors demonstrated its agreement with the degree of crystallinity of polynosic cellulose fibre: 45 and 48%, respectively. The degree of orientation of the new fibre is also closest to polynosic fibre:

Fibre type	Angle of disorientation $\varphi$ , deg	Degree of crystallinity, %
Textile fibre	14.30	35
Cord thread	11.30	38
Polynosic fibre	9.80	48
Orcel	7.25	45

The electron microscopic study of the geometric shape of Orcel<sup>®</sup> fibre showed that it has a round cross section. The morphology of the fibre is homogeneous, with distinct fibrillation, and the size of the microfibrils is 0.08-0.1  $\mu\text{m}$ . Such a fine structure results in close packing and is virtually not seen in cross sections.

The sorption study of the structure of cellulose fibres prepared by different methods indicates the denser structure of Orcel<sup>®</sup> fibre in comparison to viscose and polynosic fibres, and its specific surface area is almost one order of magnitude less than for viscose fibre.

Interesting information on the structure of Orcel<sup>®</sup> fibre was obtained in studying its thermal stability by DTA and TGA. The DTA curves in Fig. 7 show that Orcel fibre (curves 3 and 4) is characterized by a less active region of thermooxidative degradation, manifested on the curve as a double-hump exothermic peak in comparison to viscose fibre (curves 1 and 2). The onset of degradation (inflection in the endothermic region) lies higher on the temperature scale (256-263°C) than for viscose fibre (205-232°C). The same tendency is observed in the TGA curves. The highest temperature of the inflection of the TGA curve is in the region of intense weight loss (264°C) for Orcel<sup>®</sup> fibre. In addition, a lower rate of weight loss in the linear segment of intense degradation is characteristic of this fibre, and extension of this interval on the temperature scale to 16-18°C is observed (this temperature interval is equal to 12°C for viscose fibres). Very significant weight loss is also observed at 360°C: 53-54% for Orcel<sup>®</sup> fibre and 61-65% for viscose fibre.

The results of the DTA and TGA studies once more confirm the high density of the structure of Orcel<sup>®</sup> fibres, which leads to lower thermal accessibility and lower rates of heat transfer, which is an extremely important characteristic in fabrication of carbon fibres for technical applications.

High strength equal to 45-50 kg/mm<sup>2</sup> (440-490 MPa) and high moduli of elasticity, 30-40 GPa, are characteristic of Orcel<sup>®</sup> fibre and fibres spun by the existing MMO process.

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