

Modification of Cellulose in Conditions of Plastic Flow under Pressure

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SYNOPSIS

The search for new ecologically pure production processes for numerous cellulose derivatives is important technologically. It is well known that under shear deformation in solid substances, various physical and chemical effects may take place. The possibility of production of some cellulose derivatives, such as carboxymethylcellulose and cellulose acetates, is shown under conditions of joint action of high pressure and shear deformation at room temperature. The formation of an easily hydrolyzed fraction of cellulose under these conditions is also investigated. This reaction procedure is of great practical interest, as it makes it possible to reduce the consumption of reagents and to carry out the process in the absence of solvents.

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INTRODUCTION

The natural polymer, cellulose, is one of the most widely used industrial polymers for fibers, films, etc. That is why the investigation and search for new cellulose chemical modifications are of great interest.

Reacting in the solid phase under conditions of plastic flow is an advanced method of production of cellulose derivatives.

For this purpose, the Bridgman's anvil¹ type of apparatus was used, which makes it possible to subject the solid substances to pressure from 0.1 to 1 GPa and to shear deformation. Under joint action of high pressure and shear deformation, material transition to the state of plastic flow takes place, the level of plastic flow (degree of deformation) being practically unlimited. The plastic flow of polymers under pressure has been investigated in some articles (see, for example Refs. 2–4). In these works, flexible polymers were generally studied. In Ref. 5, it was shown that under the joint action of high pressure and shear deformation, the mechanisms of plastic flow in amorphous and semicrystalline polymers are

similar. Hence, basic processes observed in flexible chain polymers may also take place in rigid polymers.

A typical example of such rigid polymers is cellulose. Under the joint action of high pressure and shear deformation on the Bridgman's anvil-type apparatus, the following chemical transformations of cellulose were carried out: (1) the hydrolysis of cellulose in the presence of H₂SO₄; (2) the interaction of cellulose with monochloroacetic acid and solid alkali, resulting in carboxymethylcellulose; (3) the interaction of cellulose with acetic acid, resulting in the formation of acetates of cellulose.

EXPERIMENTAL

Sample Treatment Under Pressure

The treatment of samples under pressure was carried out in an apparatus of the Bridgman's anvil type in a pressure range from 0.5 to 2 GPa at room temperature. Steel anvils with work surface of 20 mm in diameter were used. The samples after treatment under pressure were transparent films, which could be easily separated from the anvils.

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The Determination of an Easily Hydrolyzed Fraction (EHF)

The amount of the easily hydrolyzed fraction (EHF) was determined according to the standard method.⁶ A sample of material to be analyzed was treated with 2% HCl solution. Then the reaction mixture was filtered, and CuSO₄ and Seignette salt (KNaC₄H₄O₆) solutions were added to the filtrate.

The content of glucose in filtrate corresponding to that of hydrolyzed cellulose was calculated on the basis of the amount of reduced copper.

Determination of Degree of Polymerization of Cellulose (DP)

Degree of destruction of cellulose macromolecules was estimated by the change of DP, determined according to the viscosity of cellulose solutions in the ferric sodium tartrate complex (FSTC).

The FSTC solution was prepared by gradually mixing 560 mL of water with 208 g of Na₂(C₄-H₄O₆) · 2H₂O and 121 g of Fe(NO₃)₃. After that, the vessel was placed in an ice bath and a solution of NaOH was added by portions (96 g of NaOH per 200 mL of water). The concentration of cellulose in FSTC depended on DP. Viscosity average molecular weight was calculated by following formula⁶:

$$DP = \frac{[\eta]}{8.14 \times 10^{-4}}$$

where $[\eta]$ = intrinsic viscosity.

X-Ray Analysis of Cellulose Samples

X-Ray patterns of samples were obtained on a DRON-3 diffractometer with a copper anode at 30 kV and 20 mA (Ni-filter).

Analysis of Carboxymethylcellulose

The reaction mass after Bridgman's anvil treatment was dissolved in water, and the soluble portion of CMC was separated from insolubles by centrifugation. Low molecular weight products (Na-glycolate and chloride) were separated from the polymer using the "Amicon" ultrafiltration system with membrane-retaining macromolecules with molecular weight > 2000. CMC was separated by freeze drying clear solutions.

Determination of Degree of Substitution of Carboxymethylcellulose

The degree of substitution of carboxymethyl groups was measured by a method based on the transformation of the salt form (Na-CMC) into the acid form (H-CMC) by treatment of the polymer with 0.02 N HCl in isopropanol. The polymer was quantitatively separated from solution, and the degree of substitution was determined by titration.⁶

Determination of CMC Molecular Weight

Molecular weight of CMC samples was calculated from the intrinsic viscosity in 0.2 M NaCl solution according to the equation⁷:

$$[\eta] = 4.3 \times 10^{-4} \times M_w^{0.74}$$

IR Spectra

The structure of CMC samples was studied by Fourier-transform IR spectroscopy using a FTS-150 Digilab spectrometer with a resolution of 4 cm⁻¹. To improve "signal-noise" ratio repeated scanning was used. Samples were formed into KBr pellets for spectral examination.

Determination of Degree of Substitution of Cellulose Acetates

Analysis of cellulose acetates was based on alkaline saponification of cellulose acetates. The amount of bonded acetic acid was calculated from the amount of alkali used for saponification. A calibration curve (bonded acetic acid vs. degree of substitution) was used for determination of degree of substitution of hydroxyl groups.

RESULTS AND DISCUSSION

The different structural changes in cellulose under the action of shear deformation were investigated by x-ray analysis.

It is well known that cellulose has structural modifications, the most widespread being cellulose I (CI). The grinding of native cellulose in ball mill results in a transition from crystalline structure CI to the amorphous state. Treatment of cellulose with polar liquids results in recrystallization and formation of another structural modification of cellulose—cellulose hydrate (cellulose II, CII).⁸

Results of x-ray analysis of cellulose after the joint action of high pressure and shear deformation

under different conditions are shown in Figures 1 and 2.

X-Ray patterns of cellulose powder after treatment under pressure followed by treatment with different solvents are shown in Figure 1.

These data show that cellulose treatment by high pressure results in the widening of the reflex at $\theta = 10-11^\circ$ (half-width of reflex increases from 14 to 30), indicating formation of the amorphous form of cellulose. The subsequent treatment of cellulose by solvents of different polarity: hexane ($\epsilon = 1.8$), chloroform ($\epsilon = 5.2$), ethanol ($\epsilon = 27.8$), and water ($\epsilon = 80$), results in the narrowing of the reflex at $\theta = 10-11^\circ$. This effect was increased with an increase in solvent polarity. However, unlike mechanical grinding, the treatment of cellulose after the action of high pressure with polar liquids doesn't result in transformation of structure CI to structure CII.

The treatment under pressure of samples with structure CII also results in wide peaks in x-ray patterns, the shape and angle position being analogous

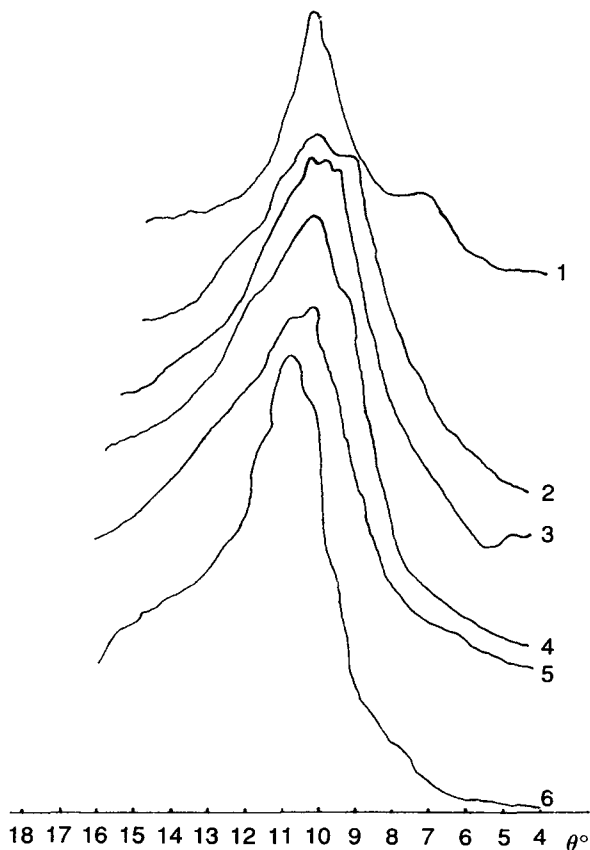


Figure 1 X-Ray pattern of initial powder cellulose (1), powder cellulose after joint action of high pressure and shear deformation (2), and cellulose samples after treatment by pressure (1 GPa) followed by hexane (3), chloroform (4), ethanol (5), and water (6).

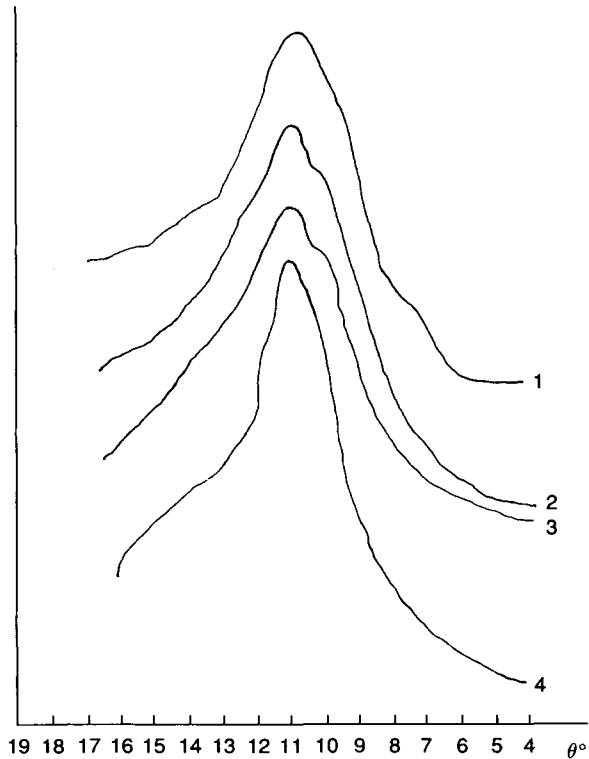


Figure 2 X-Ray pattern of cellulose saturated by hexane (1), chloroform (2), ethanol (3), and water (4) and then treated by pressure (1 GPa).

to peaks obtained after the treatment of samples with structure CI under pressure.

In the next series of experiments, samples of cellulose in modification CI were first saturated with different solvents and were then treated under pressure (Fig. 2). X-Ray patterns of such samples were practically identical to the patterns of samples that were treated with solvents after action of high pressure.

The ability of cellulose to hydrolyze in the presence of acidic catalysts is one of its important properties.

As is known,⁹ the density of macromolecular packing in cellulose is nonuniform. According to the most simple conception of cellulose structure, one may distinguish the amorphous regions, which are easily hydrolyzed by dilute mineral acids, from the crystalline regions, which are hardly accessible for chemical reagents. It is also known that the content of the easy hydrolyzed fraction in cellulose is increased as a result of destruction of close packed structures with the simultaneous lowering of the degree of polymerization.

In destructured cellulose samples, the degree of hydration of macromolecules in water may increase,

resulting in polymer swelling and solution as the degree of polymerization is lowered.

A priori, it should be expected that cellulose treatment under the joint action of high pressure and shear deformation would increase the easily hydrolyzed fraction (EHF) content in samples due to destruction processes, taking place at the plastic flow.

Hence, the investigation of the influence of treatment under the joint action of high pressure and shear deformation on cellulose destruction and changes in hydrolytic capacity was of great interest.

As is known,¹⁰ mechanochemical treatment of cellulose saturated with sulfuric acid results in a large increase in EHF. Hence, cellulose samples containing 0.2–2% H_2SO_4 (based on cellulose mass) were subjected to the joint action of high pressure and shear deformation. The samples were saturated with acid solutions and then were concentrated by heating at 105° for 2–3 h.

The influence of shear deformation on EHF content in samples is shown in Figure 3. The EHF content is increased three to five times as pressure and rotation angle is increased. This dependence is especially apparent in samples containing sulfuric acid; in this case, the EHF content increases up to 80%.

Figure 4 shows the correlation between EHF content and initial content of sulfuric acid in samples under conditions of shear deformation. At these pressures, an increase of acid up to 1% of cellulose mass results in a sharp increase in EHF. Subsequent

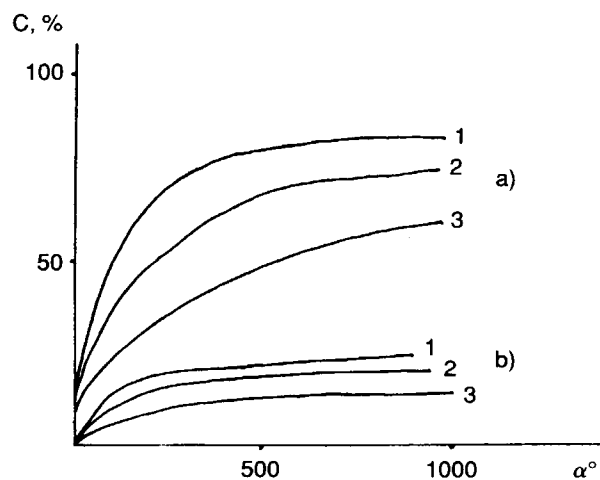


Figure 3 Dependence of yield of easy hydrolyzed products on angle of rotation at different pressures: (a) initial cellulose containing 1% of H_2SO_4 (1—2 GPa, 2—1 GPa, 3—0.5 GPa); (b) cellulose without acid (1—2 GPa, 2—1 GPa, 3—0.5 GPa).

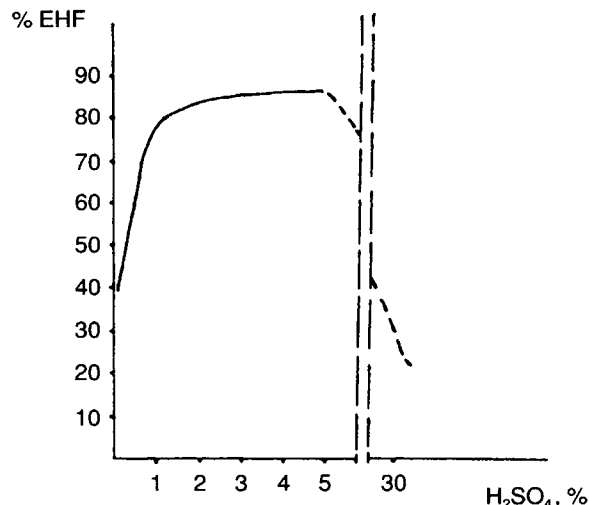


Figure 4 The influence of the amount of acid on EHF output (the angle of anvil rotation was 500° and pressure was 1 GPa).

increases in acid concentration negligibly influenced EHF output.

Determination of degree of polymerization (DP) of samples after the joint action of high pressure and shear deformation shows that during the treatment, an intensive destruction of cellulose macromolecules takes place. Figure 5 shows the dependence of DP change on the angle of rotation of anvils under different pressures. Greater molecular weight loss in the samples containing acid may be explained by more intensive destruction processes in the presence of acid.

In addition to sulfuric acid, the influence of weak organic acids of different acidity on cellulose destruction under conditions of shear deformation was investigated. Oxalic, malonic, and succinic acids from one homologous series were used. The content of oxalic acid was 5% of cellulose mass; other acids were taken in equimolecular ratio to the repeating glucose unit of cellulose.

DP and EHF content in cellulose after saturation of samples by these acids didn't change, and in all cases were: DP = 700, EHF is 2.5%.

The yield of EHF in samples containing acid after treatment under high pressure was higher than in samples without acid, and DP was sharply decreased (Table I). The observed effect was increased, depending on dissociation constant value.

In the case of the weaker succinic acid, a marked effect was achieved only under a pressure of 2 GPa, which may be explained by its low acidity.

Because the acid has no influence on DP and EHF yield in samples that weren't subject to the joint action of high pressure and shear deformation, one

may conclude that acid influences the change of cellulose properties only under the action of pressure and shear deformation. The values of DP in samples containing organic acids are shown in Table I. The data in Table I show that the decrease of DP is higher for samples containing stronger acids.

The Carboxymethylation of Cellulose

Carboxymethylcellulose (CMC) is one of the most important among numerous cellulose derivatives. Water-soluble CMC is widely used in the food, cosmetic, pharmacy, and oil industries.

Usually, CMC is produced by the reaction of cellulose with monochloroacetic acid (MCAA) in the presence of alkali hydroxide in water or water-organic solvents. At the same time, the side reaction of MCAA saponification takes place, resulting in the lowering of its efficiency up to 50%. The extent of this reaction depends on various factors, including the composition of dispersion media.^{8,11}

The saponification of MCAA may be minimized by exclusion of water from the reaction medium, or by conducting the reaction in the solid phase under conditions of shear deformation.

Carboxymethylation of cellulose was carried out using two samples: cotton cellulose (M_w , 162,000) and powder cellulose (M_w , 8,400). The powder cellulose, monochloroacetic acid, and alkali were used in following ratios: (1) 1 : 1 : 2.1; (2) 1 : 0.5 : 1.05; (3) 1 : 1.5 : 3.15; (4) 1 : 1 : 1.05; (5) 1 : 1 : 0.

Because even CMC with a low degree of substitution (0.25–0.50) is completely soluble in water, the water solubility of samples confirms the fact of CMC formation. Almost completely soluble products were obtained in Experiments 1 and 3. In Experiment 2, the product was partially soluble, and in 4 and 5, completely insoluble. Insoluble residue consisted of unreacted cellulose and low substituted CMC. Thus, under conditions of plastic flow at a pressure of 1 GPa in the absence of alkali or under conditions of low alkalinity, as in the case of carboxymethylation in water and water-organic media, CMC formation is not observed.

If sodium monochloroacetate and cellulose is taken in equimolecular ratio, CMC with solubility less than 50% is obtained.

According to the data on CMC samples obtained from powder and cotton cellulose with different initial reagent ratios (Table II), the CMC yield increases with initial content of monochloroacetic acid and alkali in the mixture. The degree of substitution is also increased up to 0.94. The efficiency of the reaction of monochloro acetic acid according this

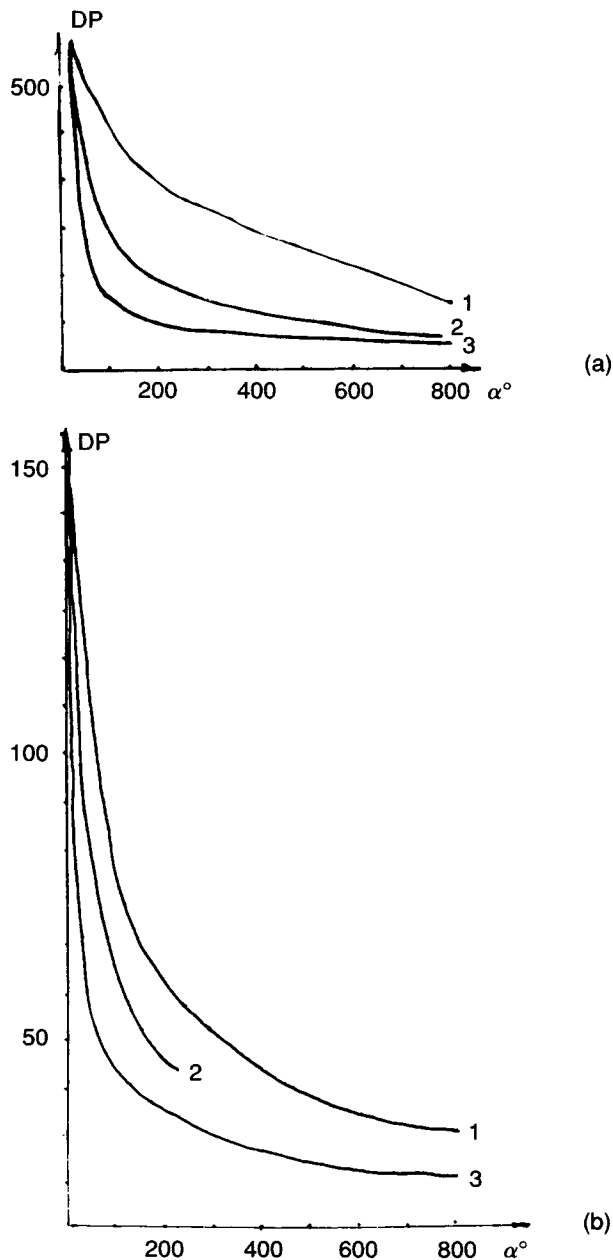


Figure 5 DP of cellulose vs. angle of anvil rotation: (a) cellulose treated under pressure (1—0.5 GPa, 2—1 GPa, 3—2 GPa); (b) cellulose + 1% of H_2SO_4 treated under pressure (1—0.5 GPa, 2—1 GPa, 3—2 GPa).

method of CMC production is 60–70% (compared with 50% in the case of the usual procedure), and it is lowered with increasing monochloroacetic acid content in the initial mixture.

Obviously, powder cellulose has higher reactivity than cotton, and CMC obtained from powder has a higher degree of substitution and solubility.

It is interesting to note that the molecular weight of CMC obtained from powder cellulose is higher

Table I Influence of Weak Organic Acids on DP of Cellulose under Conditions of Joint Action of High Pressure and Shear Deformation (Diameter of Anvils 20 mm, Angle of Rotation 400°).

Sample	pK _a	Pressure GPa	DP	EHF %
Without acid		0.5	270	10
		1	114	20
		2	77	22
With oxalic acid	(I) 1, 27	0.5	62	20
	(II) 4, 27	1	42	30
		2	34	66
With malonic acid	(I) 2, 86	0.5	107	15
	(II) 5, 70	1	38	27
		2	35	49
With succinic acid	(I) 4, 21	0.5	205	10
	(II) 5, 64	1	119	22
		2	96	30

than the M_w of CMC from cotton cellulose, although the initial M_w of cotton cellulose is two times higher than that of powder cellulose. CMC of maximum molecular weight is formed at a reagent ratio 1 : 1 : 2.1. An increase in monochloroacetic acid and alkali content in the initial mixture results in some lowering of CMC M_w . All CMC samples obtained in solid phase carboxymethylation processes under conditions of plastic flow have a lower M_w than CMC obtained by industrial methods.

As shown in Figure 6, the infrared spectrum of CMC obtained under conditions of plastic flow³ is practically identical to that of commercial CMC,⁴ indicating similar chemical structures of these polymers.

It is well known that the viscosity of polyelectrolyte solutions depends on the ionic strength of the solution. For example, the influence of ionic strength on CMC viscosity was investigated in Ref. 12. In this work, the rigidity parameters B for some polyelectrolytes including CMC were calculated.

To compare behavior of commercial CMC samples and CMC samples obtained under conditions of plastic flow, the dependence of viscosity of CMC solutions ($DS = 0.88$) on ionic strength of solution (I) and on $I^{-0.5}$ was investigated (Fig. 7). Parameter B was calculated according the formula:

$$B = \frac{S}{([\eta]_{0.1})^{1.3}},$$

where $[\eta]_{0.1}$ is viscosity of solution with ionic strength 0.1, and S is calculated from the value of slope of line dependence $[\eta]$ vs. $I^{-0.5}$. The B value obtained by this procedure is 0.49, which corresponds to values of B for CMC in Ref. 12. This fact also indicates identical chemical structures of CMC obtained under conditions of plastic flow and commercial samples.

Acetylation of Cellulose

Cellulose acetates are widely used for production of man-made fibers, films, varnishes, and plastics.

Acetylation of cellulose is usually carried out during 4–6 h using acetic anhydride as the acetylating agent and sulfuric acid as the catalyst (in amounts up to 14%) at 35–40°. The ratio of liquid volume to cellulose mass is 7–8.

It is known that cellulose acetates with a high degrees of substitution cannot be obtained by the reaction of cellulose with acetic acid.⁸ The basic fac-

Table II The Characteristics of CMC Samples Obtained under Conditions of Plastic Flow ($p = 1$ GPa)

Sample	Ratio C : MCAA : NaOH mol	Solubility %	Degree of Substitution	Intrinsic Viscosity dL/g	Molecular Weight · 10 ⁻³
Powder Cellulose					
1	1 : 0.5 : 1.05	77	0.39	0.47	13
2	1 : 1 : 2.1	93	0.74	0.81	27
3	1 : 1.5 : 3.15	91	0.94	0.68	21
Cotton Cellulose					
4	1 : 0.5 : 1.05	71	0.35	0.26	5.7
5	1 : 1 : 2.1	76	0.51	0.38	10
6	1 : 1.5 : 3.15	97	0.88	0.32	7

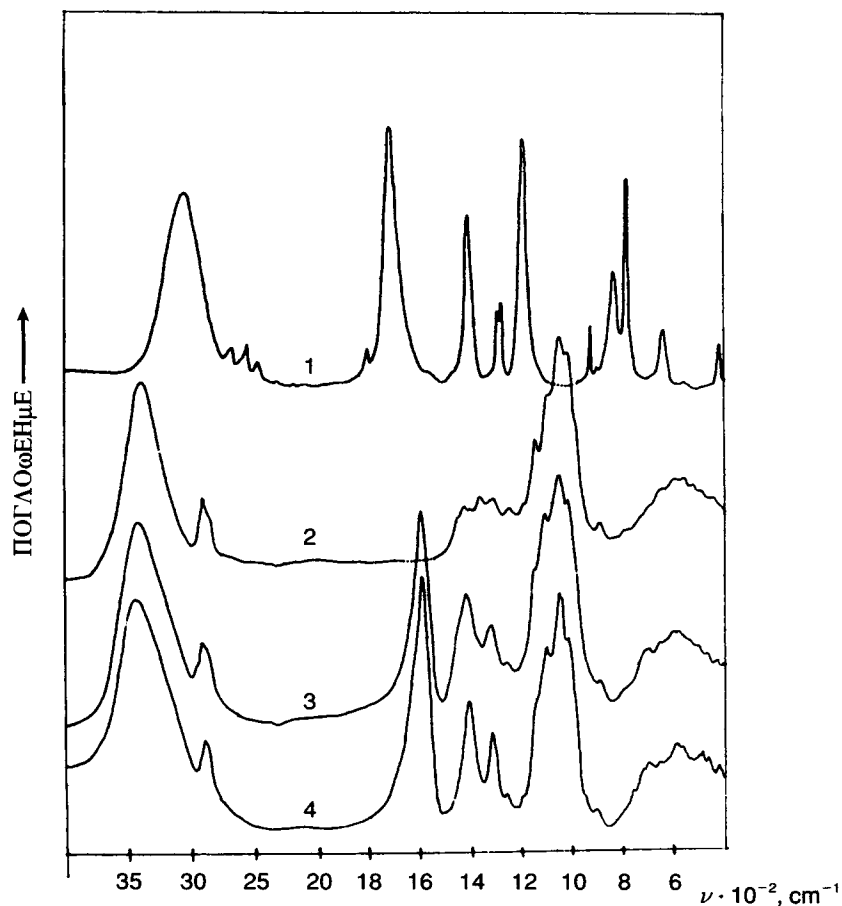


Figure 6 IR Fourier-transform spectra of monochloroacetic acid (1), powder cellulose (2), CMC samples obtained in conditions of plastic flow (3), and in industry (4).

tor preventing the esterification of cellulose hydroxyl groups by acetic acid is strong intermolecular interaction in cellulose due to formation of hydrogen bonds. More complete acetylation of cellulose by acetic acid may be obtained when interaction be-

tween the hydroxyl groups is weakened (for example, acetylation in solution or acetylation of low substituted cellulose esters).

As noted above, the strength of acids is increased under a plastic flow at pressures of 1–5 GPa. Thus,

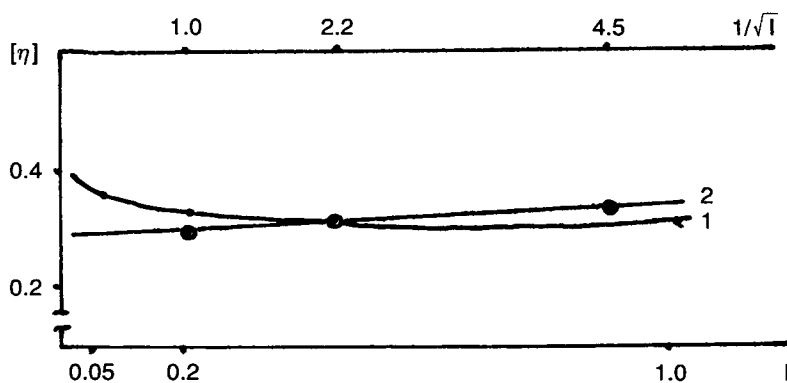
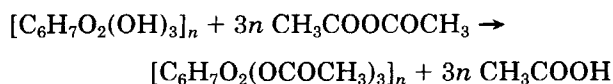


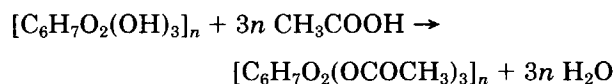
Figure 7 Dependence of intrinsic viscosity (η) of CMC solutions; degree of substitutions is 0.83 on the values of ionic strength of solutions (1) and $I^{-0.5}$ (2); CMC was obtained from powder cellulose.

in Ref. 13, it was established that carboxyl groups of fumaric and maleic acids react with double bonds with formation of esters. The occurrence of this reaction indicates a high mobility of acid protons under plastic flow. In Ref. 14, it was established that joint action of high static pressure and shear deformation results in the mobility of hydrogen atoms taking part in the formation of hydrogen bonds. The increase of mobility of hydrogen atoms of hydroxyl groups of cellulose should, therefore, result in a higher reactivity of cellulose during its interaction with acetic acid under plastic flow.

The acetylation of cellulose with acetic anhydride proceeds according the equation:



and acetylation with acetic acid according the equation:



In our work, the acetylation was accomplished using the following acetylating agents: 66% acetic acid, glacial acetic acid, and acetic anhydride. The cellulose samples saturated by an acetylating agent were subjected to treatment at a pressure of 1 GPa and room temperature. At the same time, cellulose was treated with an acetylating agent for 4 h without pressure. The reagents were used in the following ratios: 1 mol of cellulose to 3 mol of acetic acid or acetic anhydride, and also 1 : 1.5.

The acetylation of cellulose was carried out without a catalyst and also using sulfuric acid in an amount equal to 9 and 14% of the cellulose weight.

Figure 8 shows the dependence of degree of substitution of hydroxyl groups on H_2SO_4 concentration in the mixture in the case of cellulose acetylation under normal conditions and under conditions of the joint action of high pressure and shear deformation.

The data in Figure 8 show that acetates with a low degree of substitution are formed during acetylation by acetic acid under normal conditions.

When cellulose is treated with acetic anhydride, acetates with higher degrees of substitution of hydroxyl groups are formed.

When the process is carried out under conditions of a plastic flow under pressure, an increase in the degree of substitution takes place in all cases. Figure 8 shows that primary acetates are formed during the

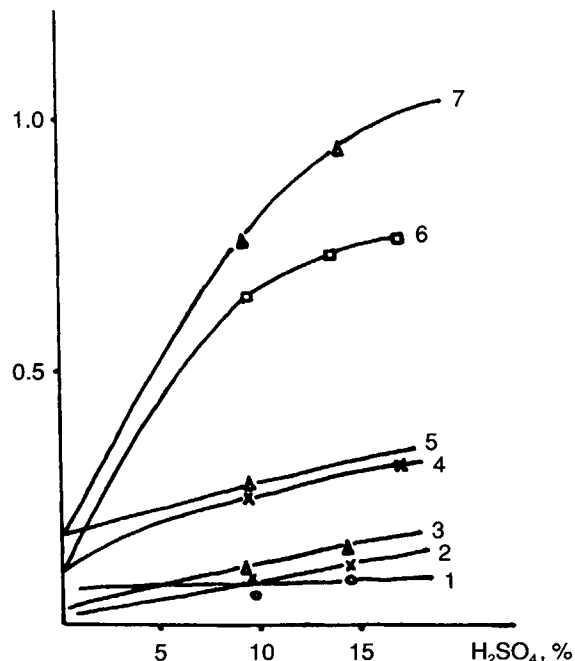


Figure 8 Dependence of the degree of substitution of cellulose hydroxyl groups on H_2SO_4 concentration during acetylation under normal conditions (time of acetylation is 4 h; temperature is 20°C): 1—cellulose + 66% CH_3COOH (1 : 3); 2—cellulose + glacial acetic acid (1 : 3); 3—cellulose + acetic anhydride (1 : 1.5); and under conditions of plastic flow (pressure is 1 GPa): 4—cellulose + glacial acetic acid (1 : 1.5); 5—cellulose + 66% CH_3COOH (1 : 3); 6—cellulose + acetic anhydride (1 : 1.5); and 7—cellulose + glacial acetic acid (1 : 3).

acetylation with glacial acetic acid at a concentration of H_2SO_4 of 14%.

Thus, in this work it was shown that under conditions of the joint action of high pressure and shear deformation, cellulose is subjected to structural transformations that result in changes in its reactivity, thus making it possible to carry out a reaction in the solid phase. This work may help create ecologically pure industrial processes for production of cellulose derivatives using equipment providing the joint action of high pressure and shear deformation.

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