CELLULOSE CHEMISTRY AND TECHNOLOGY

ACCESSIBILITY AND SUPERMOLECULAR STRUCTURE OF CELLULOSE

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The accessibility of cellulose samples with various crystallinity degrees to molecules of water, lower primary alcohols and lower organic acids was studied. It was found out that small water molecules have full access to the non-crystalline domains of cellulose (accessibility coefficient $\boldsymbol{\alpha} = 1$). The molecules of the lowest polar organic liquids have partial access to these domains ($\boldsymbol{\alpha} < 1$), while, with an increasing diameter of the organic molecules, their access to the cellulose structure decreases. The accessibility of cellulose samples to molecules of various substances is a linear function of coefficient $\boldsymbol{\alpha}$ and of the content of non-crystalline domains. The relationship between the crystallinity (X) and accessibility (A) of cellulose to the molecules of some liquids was established as $A = \boldsymbol{\alpha}(1-X)$. The water molecules were found to have greater access to the cellulose samples than the molecules of the investigated organic liquids. The obtained results permit the use of accessibility coefficient values to estimate cellulose crystallinity, to examine the structural state of the non-crystalline domains and to predict the reactivity of cellulose samples towards some reagents.

Keywords: cellulose, structure, accessibility, crystallinity, reactivity

INTRODUCTION

The accessibility of cellulose samples to some low-molecular substances has been studied by water vapor sorption, water retention value, iodine and dye sorption, deuteration, acid hydrolysis and other methods[1-7] in order to estimate the structure and reactivity of cellulose. It has been noted that the weight loss of the cellulose samples during hydrolysis with boiling diluted acids is related to the dissolution ability of the oligomeric fractions of the hydrolyzed non-crystalline domains, and not to the accessibility of acid ions to the cellulose structure. Many researchers[8,9] have tried to establish correlations between accessibility and the content of non-crystalline domains to determine the crystallinity of the cellulose samples; a direct correlation between the accessibility of water vapors and the content of non-crystalline regions from the cellulose samples was found, which permitted the calculation of crystallinity. However, if other substances were used in accessibility tests, different crystallinity values were obtained. For instance, the crystallinity[2] of cotton cellulose, as estimated by the iodine sorption method, was of 0.87, by interaction with formic acid, it equalled 0.79, and by cellulose deuteration – 0.58. Some researchers[5] came to the conclusion that, generally, accessibility methods are not suitable for determining cellulose crystallinity. It is seems that this conclusion is too categorical.

The main objective of the present study is to carry out additional investigations to find possible correlations, allowing the use of accessibility data for structural investigations on cellulose samples and for predicting the reactivity of cellulose towards some reagents.

EXPERIMENTAL

Materials

The following cellulose samples were investigated:

- microcrystalline cellulose (MCC) Avicel-PH102, from FMC BioPolymer Co.;
- pure chemical grade cotton cellulose (COC), from Hercules Co.;
- prehydrolyzed and bleached Kraft chemical pulp (KCP), from Weyerhaeuser Co.;
- bleached sulfite wood cellulose (SFI), from Weyerhaeuser Co.;
- mercerized cellulose (MEC) prepared by treating cotton cellulose with 20% NaOH, followed by washing and drying;
- amorphicized cellulose (AMC) obtained by cotton cellulose treatment with liquid ammonia, followed by recrystallization with water and drying;
- regenerated cellulose (REC) – viscose fibers of Rayonier, Inc.

Methods

X-Ray Diffraction

A Rigaku-Ultima Plus diffractometer (CuK_α – radiation, $\lambda = 0.15418$ nm) was used for X-ray investigations. Diffractograms were recorded in the 2Θ angle range – from 5 to 80°. The degree of crystallinity (X) and content of non-crystalline domains (Y = 1-X) were calculated according to improved calculation methods.[10-12]

Electron spin resonance (ESR)

Dry cellulose samples were irradiated by γ-rays of ^{60}Co up to a dose 1 kGy, then immersed into various liquids (water, methanol and formic acid), followed by vacuum drying at room temperature, until reaching a constant weight. The concentration of macroradicals in the initial and immersed irradiated samples was measured on an ESR-spectrometer MS-100 (X-band), with DPPH as a standard.

As known, a high-energy irradiation causes cleavage of the hydrogen atoms and hydroxyl groups from the anhydroglucose units of cellulose, both in non-crystalline and crystalline regions.[13] The macroradicals formed in dry cellulose are kinetically stable due to the glassy state of the non-crystalline domains. Molecules of water and of some other polar low-molecular substances penetrating the accessible regions of the non-crystalline domains lead to the decrease of their glass transition point below room temperature, due to a plasticizing effect. As a result, the kinetic mobility of macroradicals in accessible non-crystalline domains increases, resulting in the disappearance of the macroradicals, as due to recombination and disproportion processes.[14-15] After the penetration of water molecules, residual, kinetically stable macroradicals remain only in the crystalline regions, while, after the molecules' penetration into other polar liquids, the stable macroradicals can remain both in the crystalline regions and in the inaccessible regions of the non-crystalline domains. The accessibility degree of the non-crystalline domains for various substances can be calculated according to equation:

$$\boldsymbol{\alpha_o} = (C_o - C_x)/(C_o - C_w) \qquad (1)$$

where C_x and C_w represent the concentration of residual macroradicals remaining after the immersion of the irradiated cellulose into various liquids and water, respectively, and C_o is the concentration of macroradicals in the dry, irradiated cellulose.

Vapor sorption

The sorption of water vapors and of the vapors of the lowest primary alcohol (methanol) and lowest organic acid (formic acid) from the cellulose samples was measured at 25 °C and relative vapor pressure $p/p_o = 0.8$, using a *vacuum Mac-Ben apparatus* with helical spring quartz scales.

The effective diameter of the molecules was calculated as:

$$d = 2(s/\pi)^{1/2} \qquad (2)$$

where s is the surface of the molecule cross-section, defined as:

$$s\ (m^2) = 1.53 \times 10^{-20}\ (M/\rho)^{2/3} \qquad (3)$$

where M is molecular weight and ρ is specific weight.

Reactivity

The reactivity of cellulose was investigated by weight loss, due to the hydrolysis with boiling 2.5N hydrochloric acid for 1 h, alkalization with 2N sodium hydroxide at room temperature for 24 h, esterification with formic acid at 35 °C for 24 h, and oxidation with a 10% solution of nitrogen tetroxide (N_2O_4) in carbon tetrachloride, at room temperature for 24 h.

RESULTS AND DISCUSSION

The typical X-ray diffractograms of the cellulose samples are shown in Figure 1. The samples of natural celluloses evidence well-resolved peaks, while the X-ray peaks of mercerized, regenerated and amorphized celluloses are less resolved, due to decreasing crystallinity degrees and crystallite sizes.

The calculated values of the crystallinity degree (*X*) and content of non-crystalline domains (*Y*) in the cellulose samples are shown in Table 1.

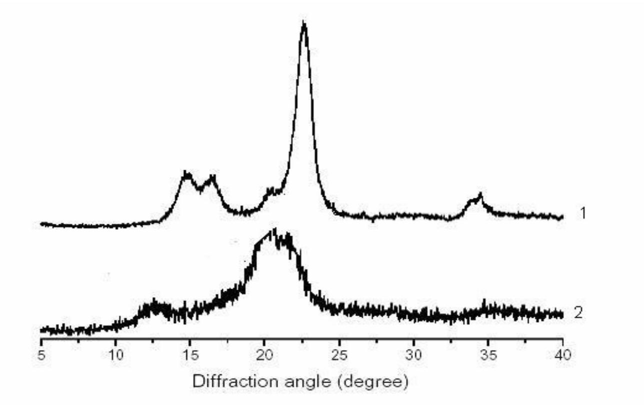

Figure 1: X-ray diffractograms of cotton (1) and regenerated cellulose (2)

Table 1
Crystalline modification (CM), crystallinity degree (X) and content of non-crystalline domains (Y) for various cellulose samples

Sample	CM	X	Y
MCC	CI	0.78	0.22
COC	CI	0.71	0.29
KCP	CI	0.65	0.35
SFI	CI	0.63	0.37
MEC	CII	0.54	0.46
AMC	CI	0.50	0.50
REC	CII	0.39	0.61

The results of the present investigation showed that cellulose crystallinity does not change with sorption of water, methanol or formic acid vapors. At the same time, such results evidence that these low-molecular substances do not penetrate the crystalline phase, but only the non-crystalline domains.

The sorption value of the vapor in the studied low-molecular substances was found to be proportional to the content of non-crystalline domains (Fig. 2).

The cellulose sample accessibility towards molecules of various low-molecular substances was calculated from sorption experiments as:

$$A = \alpha_o S/S_o \qquad (4)$$

where S_o is the sorption value related to non-crystalline domains; to obtain S_o, the function S = f(Y) was extrapolated to the sorption value at Y = 1; α_o is the degree of accessibility of the non-crystalline domains.

As shown by ESR results (Table 2), the degree of accessibility of the non-crystalline domains for water was $\alpha_o = 1$, which evidences that the water molecules have full access to the non-crystalline domains of cellulose.

However, for the molecules of the investigated organic substances, α_o was less than 1, which indicates that the non-crystalline domains of cellulose are partially accessible to the molecules of these substances.

The accessibility of cellulose samples to the vapors of various substances was found to be a linear function of the content of non-crystalline domains (Fig. 3). The access of water vapors to cellulose is higher than that of the vapors of the organic liquids under investigation. The following regularity was observed: with an increasing diameter (d) of the molecules, their access to the cellulose structure decreases. Moreover, the multiplication factor, $K = \alpha_o \times d$, was approximately constant (Table 3).

Therefore, the accessibility values of the cellulose samples to vapors of water and of the studied organic substances can be calculated by a simple equation:

$$A = K_a\, Y/d \qquad (5)$$

As follows from Table 4, the calculated accessibility values were in good agreement with the experimentally obtained accessibility values.

Table 2

Concentration of macroradicals in immersed cotton cellulose (*C*) and degree of accessibility of non-crystalline cellulose (α_o) for molecules of various low-molecular substances*

Substance	$C \times 10^{-21}$, spin/kg	α_o-value
Water	1.6	1
Formic acid	2.9	0.80
Methanol	3.1	0.76

*Note: Concentration of macroradicals in dry irradiated cotton cellulose $Co = 8 \times 10^{21}$ spin/kg

Table 3

Multiplication factor, $K = \alpha_o \times d$, for various substances

Substance	α_o	d, nm	K, nm
Water	1	0.37	0.37
Formic acid	0.80	0.47	0.38
Methanol	0.76	0.48	0.36

*Average: $K_a = 0.37$ nm

Table 4

Experimental (**A_e**) and calculated (**A_c**) accessibility value of cotton cellulose

Substance	A_e	A_c
Water	0.30	0.30
Formic acid	0.25	0.24
Methanol	0.23	0.23

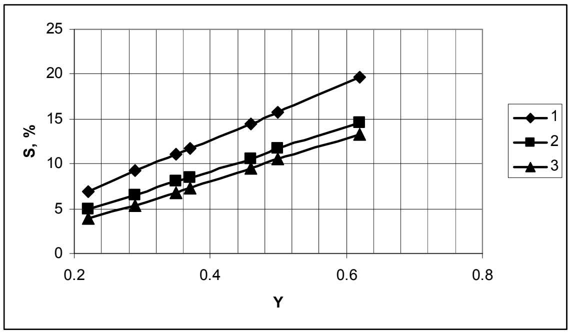

Figure 2: Dependence of sorption (S) of water (1), formic acid (2) and methanol (3) vapors on the content of non-crystalline domains (Y) in cellulose

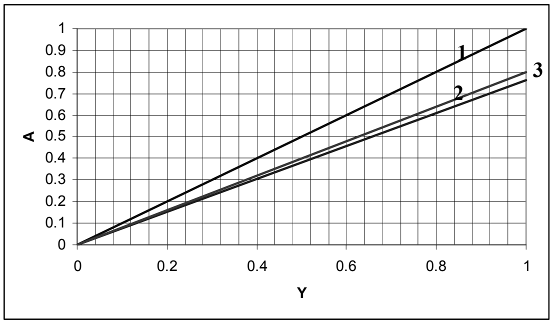

Figure 3: Accessibility (**A**) of cellulose samples with different contents of non-crystalline domains (**Y**) to water (1), formic acid (2) and methanol (3) vapors

The relationship between the crystallinity (*X*) and accessibility (A) of cellulose is given by equation (6):

$$X = 1 - (Ad/K_a) \qquad (6)$$

If sorption of water vapors is used for investigating cellulose accessibility, then $K_a \approx d$, and the crystallinity degree of the cellulose samples can be calculated by a simple equation:

$$X = 1 - A \qquad (7)$$

The dependence of X on A is graphically plotted in Figure 4.

Consequently, the non-crystalline domains of cellulose are fully accessible to low and polar water molecules. However, the access of the molecules of lower polar organic liquids to the domains is limited and, with increasing the diameter of the organic molecules, cellulose accessibility to these molecules decreases. This is related with the non-uniform structure of the non-crystalline domains, caused by distribution in the packing density of the domains.[16] Molecules of organic liquids such as methanol and formic acid can be introduced only into the loosely packed regions of the domains with low energy of the hydrogen bonds, while the low- and high-polar water molecules penetrate the regions of the non-crystalline domains with both loose and dense packing.

The correlation between cellulose accessibility to water molecules and reactivity during hydrolysis, alkalization, esterification with formic acid and oxidation was established (Table 5).

The experimental results evidence a linear regression (8) between reactivity (R) and accessibility (A) to water molecules:

$$R = n\,A + C \qquad (8)$$

where n and C – regression coefficients listed in Table 6.

Thus, based on the accessibility value, the reactivity of cellulose to some reagents can be predicted.

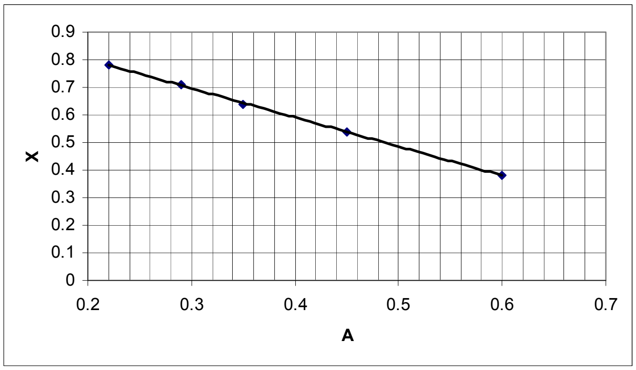

Figure 4: Relationship between crystallinity and accessibility of the cellulose samples to water molecules

Table 5
Accessibility of cellulose samples to water molecules and their reactivity

Cellulose sample	Accessibility value	Weight loss,[1] %, at hydrolysis	Alkalization,[2] mole/kg	Substitution degree,[3] mole/kg	Oxidation degree,[4] mole/kg
MCC	0.23	1	1.4	2.0	1.3
COC	0.30	8	1.8	3.4	1.7
KCP	0.35	11	2.2	4.5	2.0
SFI	0.37	12	2.3	4.9	2.1
MEC	0.46	18	2.8	6.8	2.6
AMC	0.50	20	3.0	7.7	2.9
REC	0.60	27	3.8	10.0	3.4

[1] Hydrolysis with boiling 2.5N HCl for 1 h;
[2] Alkalization with 2N NaOH at room temperature for 24 h;
[3] Esterification with formic acid at 35 ºC for 24 h;
[4] Oxidation with a 10% N_2O_4 solution in CCl_4 at room temperature for 24 h

Table 6
Coefficients of linear regression

Reaction	Reactivity parameter (R)	n	C	Correlation coefficient
Hydrolysis with boiling 2.5N HCl	Weight loss, %	0.6	-0.1	0.88
Alkalization with 2N NaOH	Content of hydroxyl anions, mole/kg	6.17	0	0.96
Esterification with formic acid	Content of formic groups, mole/kg	21.5	-3	0.90
Oxidation with N_2O_4	Content of carboxyl groups, mole/kg	5.68	0	0.93

CONCLUSIONS

For testing the accessibility of the non-crystalline domains of cellulose, a limited group of polar liquids, namely water, the lowest primary alcohol, the lowest organic acid, and some other substances can be used. Water solutions of iodine and some dyes, as well as heavy water also penetrate the non-crystalline domains. Small water molecules have full access to the non-crystalline domains of cellulose. Cellulose accessibility to the molecules of the lower polar organic liquids is limited and, with increasing the diameter of the organic molecules, their access to the cellulose structure decreases. This may be related to the non-uniform structure of the non-crystalline domains, caused by the distribution of packing density of the domains. Molecules of lower polar organic substances can be introduced only into the loosely packed regions of the domains with low energy of the hydrogen bonds, while the low and high-polar water molecules penetrate the regions of the non-crystalline domains with both loose and dense packaging.

Correlation $X = 1 - (A/\alpha_o)$ between the crystallinity (X) and accessibility (A) of cellulose to molecules of some liquids was established. If the penetrating agents are molecules of the lowest organic polar substances, *e.g.* methanol or formic acid, the accessibility coefficient α_o was below 1 while, for water molecules, $\alpha_o = 1$. The relationships between the accessibility and reactivity of cellulose to some reagents were established, thus permitting to predict the reactivity of cellulose based on its accessibility value.

However, molecules of non- or low-polar organic liquids, such as olefins, ethers, esters, ketones, highest alcohols and acids (M.W. ≥ 60) and some others cannot penetrate the non-crystalline domains of cellulose; these organic liquids can only fill the pores and capillaries of the cellulosic materials.

REFERENCES

[1] E. Ott, H. M. Spurlin and M. W. Grafflin (Eds.), "Cellulose and Cellulose Derivatives", III, 2nd Ed., Interscience, New York, 1955, 556 pp.

[2] R. Jeffries, D. M. Jones, J. G. Roberts, K. Selby, S. C. Simmens and J. O. Warwicker, *Cellulose Chem. Technol.*, **3**, 255 (1969).

[3] N. Bikales and L. Segal, "Cellulose and Cellulose Derivatives", Wiley-Intersciences, New York, 1971, 600 pp.

[4] H. A. Krässig, "Cellulose – Structure, Accessibility and Reactivity", edited by M. B. Huglin, Gordon & Breach Science Pub., Yverdon, 1993, 376 pp.

[5] H. Schleicher, J. Kunze and H. Lang, *Wood Chem.*, **2**, 38 (1991).

[6] M. K. Inglesby and S. H. Zeronian, *Cellulose*, **3**, 165 (1996).

[7] M. S. Bertran and B. E. Dale, *J. Appl. Polym. Sci.*, **32**, 4241 (2003).

[8] P. H. Hermans, "Physics and Chemistry of Cellulose Fibers", Elsevier Publ. Co., Amsterdam, 1949, 543 pp.

[9] S. P. Papkov, and E. Z. Fainberg, "Interaction of Cellulose and Cellulosic Materials with Water", Khimija, Moscow, 1976, 232 pp.

[10] M. Ioelovich and G. Veveris, *Wood Chem.*, **5**, 72 (1987).

[11] M. Ioelovitch, *Acta Polym.*, **43**, 110 (1992).

[12] M. Ioelovich and M. Gordeev, *Acta Polym.*, **45**, 121 (1994).

[13] C. Jett and J. Arthur, *Text. Res. J.*, **36**, 630 (1966).

[14] M. Ioelovich, T. Dizhbite and O. Plotnikov, *Cellulose Chem. Technol.*, **31**, 291 (1997).

[15] O. Plotnikov, A. Mikhailov and E. Rajavee, *High-Molecular Substances*, **19**, 2528 (1977).

[16] M. Ioelovich and M. Laka, *J. SITA*, **4**, 90 (2002).