

ACCESSIBILITY AND CRYSTALLINITY OF CELLULOSE

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The accessibility of cellulose samples having various degrees of crystallinity was studied with respect to molecules of water, lower primary alcohols, and lower organic acids. It was found that small water molecules have full access to non-crystalline domains of cellulose (accessibility coefficient $\alpha = 1$). Molecules of the lowest polar organic liquids (methanol, ethanol, and formic acid) have partial access into the non-crystalline domains ($\alpha < 1$), and with increasing diameter of the organic molecules their accessibility to cellulose structure decreases. Accessibility of cellulose samples to molecules of various substances is a linear function of the coefficient α and the content of non-crystalline domains. The relationship between crystallinity (X) and accessibility (A) of cellulose to molecules of some liquids has been established as $A = \alpha (1-X)$. The water molecules were found to have greater access to cellulose samples than the molecules of the investigated organic liquids. The obtained results permit use of accessibility data to estimate the crystallinity of cellulose, to examine the structural state of non-crystalline domains, and to predict the reactivity of cellulose samples toward some reagents.

Keywords: Celluloses; Structure; Accessibility; Crystallinity; Reactivity

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INTRODUCTION

Accessibility of cellulose samples to some low-molecular mass substances is used for estimation of structure and reactivity of the cellulose. Accessibility of cellulose has been studied by means of water vapor sorption, water retention value, iodine and dye sorption, deuteration, acid hydrolysis, and others methods (Ott et al. 1955; Jeffries et al. 1969; Bikales et al. 1971; Schleicher et al. 1991; Krässig 1993; Inglesby et al. 1996; Bertran et al. 2003). Many researchers have tried to establish correlations between accessibility and content of non-crystalline domains in order to determine crystallinity of cellulose samples. Hermans and some other researchers found direct correlation between accessibility of water vapor and the content of non-crystalline regions in cellulose samples, and such results have been used as a basis for calculation of crystallinity (Hermans 1949; Papkov et al. 1976). However, if other substances were used for accessibility testing, then different crystallinity values have been obtained. For instance, the crystallinity of cotton cellulose as estimated by the iodine sorption method was 0.87, by interaction with formic acid it was 0.79, and by cellulose deuteration it was 0.58 (Jeffries et al. 1969). Some researchers came to the conclusion that accessibility methods generally are not suitable for determination of cellulose crystallinity (Schleicher et al. 1991). It seems that this conclusion is too categorical.

The main purpose of the present article is to carry out additional investigations in order to find correlations allowing use of accessibility data in structural investigations of cellulose samples and for predicting the reactivity of cellulose toward some reagents.

EXPERIMENTAL

Materials

The following cellulose samples were investigated:

- Microcrystalline cellulose (MCC) Avicel-PH102 of FMC BioPolymer Co.
- Pure chemical grade cotton cellulose (COC) of Hercules Co.
- Prehydrolyzed and bleached Kraft chemical pulp (KCP) of Weyerhaeuser Co.
- Bleached high-pure sulfite wood cellulose (SFI) of Weyerhaeuser Co.
- Mercerized cellulose (MEC) prepared by treatment of cotton cellulose with 20% NaOH and following washing and drying
- Amorphized cellulose (AMC) obtained by cotton cellulose treatment with liquid ammonia and following recrystallization with water and drying
- Regenerated cellulose (REC) - viscose fibers of Rayonier, Inc.

Methods

X-Ray

Diffraction

A Rigaku-Ultima Plus diffractometer ($\text{CuK}\alpha$ – radiation, $\lambda=0.15418$ nm) was used for X-ray investigations. Diffractograms were recorded in the $\varphi=2\theta$ angle range from 5 to 80°. After recording of the diffractograms, the background was separated, corrections for Lorentz factor, polarization, and intensity of primary beam were made, and X-ray patterns were normalized. Then, diffraction intensities from crystalline and non-crystalline regions were separated by computerized method (Vonk 1973). The procedures allowed calculate the degree of crystallinity (X) according to equation,

$$X = \int J_c d\varphi / \int J_o d\varphi \quad (1)$$

where J_c and J_o are corrected and normalized diffraction intensities for crystalline regions and sample respectively. The content of non-crystalline domains (Y) in cellulose sample was calculated as:

$$Y = 1-X \quad (2)$$

Detailed description of the X-ray diffraction method for determination of cellulose crystallinity can be found in the papers of Ioelovich et al. (1987, 1992, 1994).

Electron spin resonance (ESR)

Dry cellulose samples were irradiated by γ -rays of ^{60}Co up to a dose 1 kGy. Then the samples were immersed into medium of various liquids (water, alcohols, formic acid and some others), followed by vacuum drying at room temperature up to constant weight.

The concentration of macroradicals in initial and immersed irradiated samples was measured by an ESR-spectrometer MS-100 using DPPH as a standard.

As is known, a high-energy irradiation causes cleavage the hydrogen atoms and hydroxyl groups from the anhydroglucose units of cellulose both in non-crystalline and crystalline regions (Jett and Arthur 1966). The macroradicals formed in dry cellulose are kinetically stable because of the glassy state of the non-crystalline domains. Molecules of water and some other polar low-molecular substances penetrating into accessible regions of non-crystalline domains lead to decreasing of their glass transition point to below room temperature due to a plasticizing effect. As a result, a kinetic mobility of macroradicals in accessible non-crystalline domains increases, resulting in the disappearance of the macroradicals due to recombination and disproportion processes (Hinojosa et al. 2007; Ioelovich et al. 1997; Plotnikov et al. 1977). After penetration of water molecules, the residual, kinetically stable macroradicals remain in crystalline regions only, while after penetration of molecules other polar liquids the stable macroradicals can remain both in crystalline regions and also in inaccessible regions of non-crystalline domains. The accessibility degree of non-crystalline domains for various substances can be calculated according to equation,

$$\alpha_o = (C_o - C_x)/(C_o - C_w) \quad (3)$$

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

Sorption of vapor

Sorption of water vapor and vapor of the lowest primary alcohols (methanol and ethanol) and the lowest organic acid (formic acid) by cellulose samples was measured at 25 °C and relative vapor pressure $p/p_o = 0.8$ using a vacuum Mac-Ben apparatus having helical spring quartz scales.

The effective diameter of molecules was calculated as,

$$d = 2(s/\pi)^{1/2} \quad (4)$$

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

$$s \text{ (m}^2\text{)} = 1.53 \times 10^{-20} (M/\rho)^{2/3} \quad (5)$$

where M is the molecular weight and ρ is the specific weight.

Reactivity

The reactivity of cellulose was investigated by weight loss due to hydrolysis with boiling 2.5N hydrochloric acid for 1h, alkalization with 2N sodium hydroxide at room temperature for 24 h, esterification with formic acid at 35 C for 24 h, and oxidation with

10% solution of nitrogen tetroxide (N₂O₄) in carbon tetrachloride at room temperature for 24h.

RESULTS AND DISCUSSION

Typical X-ray diffractograms of cellulose sample are shown in Fig. 1. Samples of natural celluloses have well resolved peaks, while X-ray peaks of mercerized, regenerated, and amorphized celluloses are less resolved due to decreasing in crystallinity degrees and sizes of crystallites (Bikales and Segal 1971; Hindeleh and Johanson 1972; Jeffries 1968).

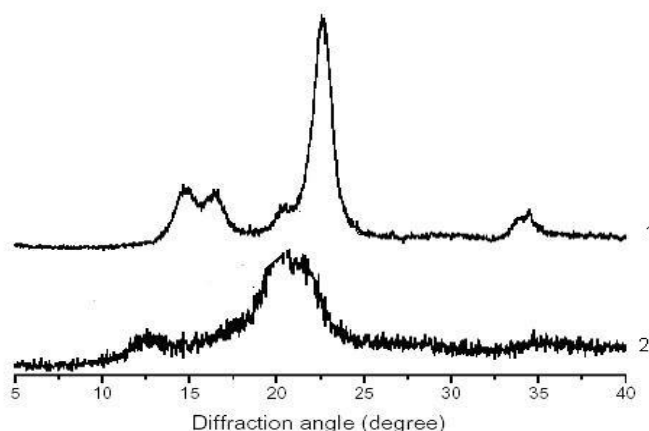


Fig.1. X-ray diffractograms of cotton (1) and regenerated cellulose (2)

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

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

Note: CI and CII are crystalline polymorphs of cellulose having different parameters of elementary crystalline cell (Bikales and Segal 1971). CI polymorph is transformed into CII polymorph during mercerization of native cellulose or regeneration from cellulose solutions.

The obtained values of crystallinity degree of cellulose samples have been confirmed by independent investigations of some other researchers (Hermans 1949, 1951; Jayme 1964, 1975).

The results of this work showed that crystallinity of cellulose does not change with sorption vapors of water, alcohols, or formic acid. Such results provide evidence that these low-molecular substances don't penetrate into the crystalline phase, but only into non-crystalline domains.

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

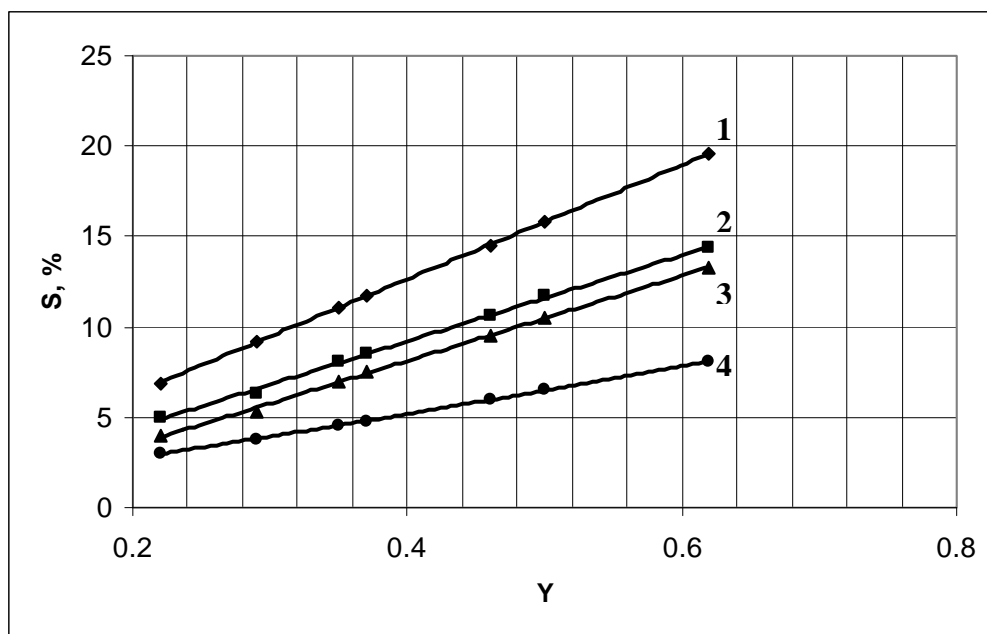


Fig. 2. Dependence sorption (S) vapor of water (1), formic acid (2), methanol (3), and ethanol (4) on content of non-crystalline domains (Y) in cellulose

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

$$A = \alpha_o S / S_o \quad (6)$$

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 $Y=1$; and α_o is the degree of accessibility of non-crystalline domains.

As follows from the ESR results (Table 2), the degree of accessibility of non-crystalline domains for water was $\alpha_o=1$. This provides evidence that water molecules are fully accessible to the non-crystalline domains of cellulose. However for molecules of organic substances, α_o was less than 1; such results indicate that the non-crystalline domains of cellulose are partially accessible for molecules of these substances.

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 x 10 ⁻²¹ , spin/kg	α_o -value
Water	1.6	1
Formic acid	2.9	0.80
Methanol	3.1	0.77
Ethanol	3.7	0.67

*Note: Concentration of macroradicals in dry irradiated cotton cellulose $C_0 = 8 \times 10^{21}$ spin/kg

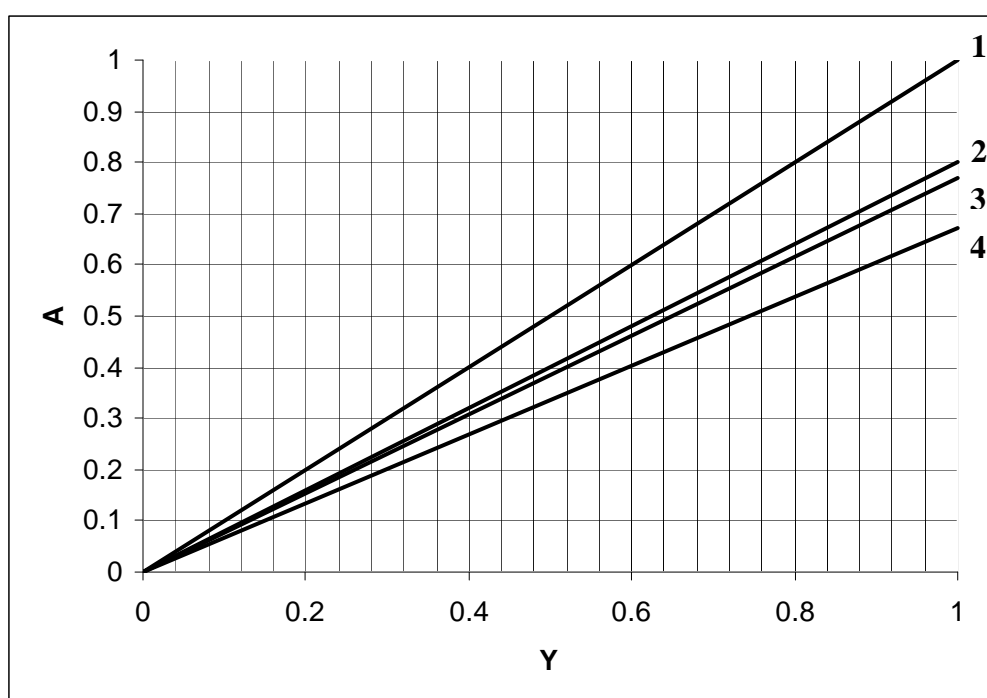


Fig. 3. Accessibility (A) of cellulose samples with different content of non-crystalline domains (Y) to vapor of water (1), formic acid (2), methanol (3), and ethanol (4)

Accessibility of cellulose samples to vapor of various substances was found to be a linear function of the content of non-crystalline domains (Fig. 3). The water vapor is more accessible to cellulose than the vapor of the investigated organic liquids. The following regularity was observed: with increasing diameter (d) of molecules their accessibility to cellulose structure decreased. Moreover, the multiplication factor, $K = \alpha_o \times d$, was approximately constant (Table 3).

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	0.77	0.48	0.37
Ethanol	0.67	0.54	0.36
			Average $K_a = 0.37$

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

$$A = K_a Y/d \quad (7)$$

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

Table 4. Experimental (A_e) and Calculated (A_c) Accessibility Value for Cotton Cellulose

Substance	A_e	A_c
Water	0.30	0.30
Formic acid	0.25	0.24
Methanol	0.23	0.23
Ethanol	0.19	0.20

Between crystallinity (X) and accessibility (A) of cellulose, the relationship is given by equation (6):

$$X = 1 - (Ad/K_a) \quad (8)$$

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

$$X = 1 - A \quad (9)$$

The dependence X on A is shown in Fig. 4.

Thus, small polar water molecules are fully accessible to non-crystalline domains of cellulose. However, molecules of the lowest polar organic liquids are only partially accessible into the domains, and with increasing diameter of the organic molecules, their accessibility to cellulose structure decreases. This is connected with non-uniform structure of non-crystalline domains caused by a distribution in packing density of the domains (Ioelovich et al. 2002). Molecules of lowest organic polar substances can be introduced only into loose-packed regions of the domains having low energy of hydrogen bonds, while small and high-polar water molecules penetrate into regions of non-crystalline domains having both loose and dense packing.

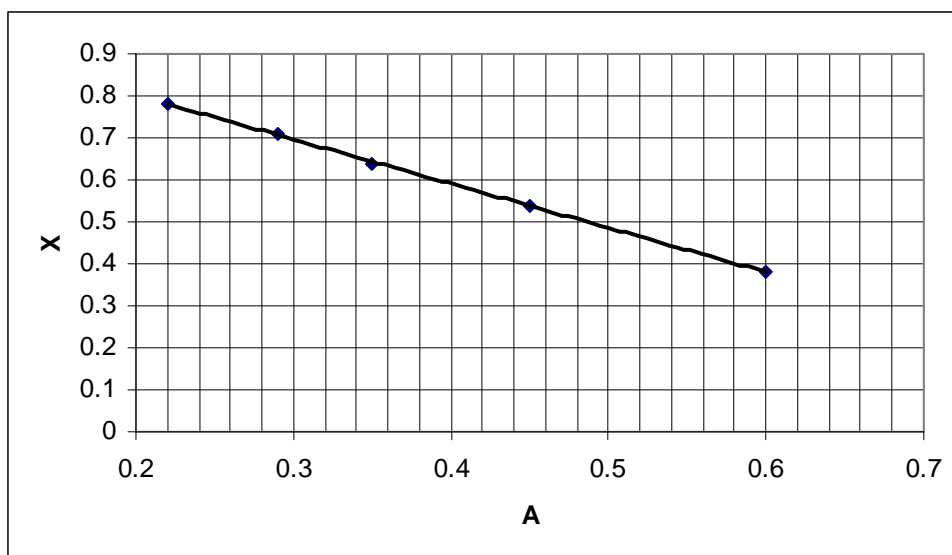


Fig. 4. Relationship between crystallinity and accessibility of cellulose samples to water molecules

Based on the accessibility value, the reactivity of cellulose to some reagents can be predicted. The good correlations between cellulose accessibility to water molecules and reactivity during hydrolysis, alkalization, esterification with formic acid, and oxidation are shown in Table 5.

Table 5. Accessibility to Water Molecules and Reactivity of Cellulose Samples

Sample	Accessibility	¹ Weight loss, %, at hydrolysis	² Alkalization, mole/kg	³ Substitution degree, mole/kg	⁴ Oxidation degree, 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

Note: 1-Hydrolysis with boiling 2.5N HCl for 1h;

2- Alkalization with 2N NaOH at room temperature for 24h;

3- Esterification with formic acid at 35 °C for 24h;

4- Oxidation with 10% N₂O₄ solution in CCl₄ at room temperature for 24h.

The relationship between reactivity and accessibility to water molecules can be described by the correlation equations shown in Table 6.

Table 6. Correlation Equations between Accessibility (A) and Reactivity (R)

Reaction	Reactivity parameter (R)	Equation	Correlation coefficient
Hydrolysis with boiling 2.5N HCl	Weight loss, %	$R = 0.6A - 0.1$	0.88
Alkalization with 2N NaOH	Content of hydroxyl anions, mole/kg	$R = 6.17A$	0.96
Esterification with formic acid	Content of formic groups, mole/kg	$R = 21.5A - 3.0$	0.90
Oxidation with N_2O_4	Content of carboxyl groups, mole/kg	$R = 5.68A$	0.93

CONCLUSIONS

1. Accessibility of non-crystalline domains of cellulose samples having various crystallinity degree to molecules of water, lower primary alcohols, and lower organic acids was investigated by the methods of sorption, X-ray, and ESR.
2. Small water molecules are fully accessible to non-crystalline domains of cellulose. However, molecules of the lowest polar organic liquids are only partially accessible into the domains, and with increasing diameter of the organic molecules, their accessibility to cellulose structure decreases.
3. The correlation $X = \alpha_o(1-A)$ between crystallinity (X) and accessibility (A) of cellulose to molecules of some polar liquids was established. In the case when penetrating agents are molecules of the lowest organic polar substances, the accessibility coefficient α_o was less than 1, while for water molecules $\alpha_o = 1$.
4. Relationships between accessibility and reactivity cellulose to some reagents were established. These relationships make it possible to predict the reactivity of cellulose based on its accessibility value.

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