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Physicochemical methods for determination of cellulose crystallinity

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Abstract : Two physicochemical methods for determination of crystallinity degree of cellulose have been developed. The first method was to study the sorption of water vapor (A), and second was to measure the enthalpy of wetting (ΔH). These methods are based on mechanism of interaction between cellulose and molecules of water, which is carried out in the amorphous domains of the polymer. Thus, increase in content of amorphous domains and decrease in degree of crystallinity leads to rise of water sorption and enthalpy of wetting. As a result, an equation for calculation of the crystallinity degree (X) of cellulose was proposed: $X=1-(Z/Z_0)$, where Z is a physicochemical parameter (A or ΔH) of the sample,

and Z_0 is a theoretical parameter calculated for amorphous cellulose. Both physicochemical methods give similar values of crystallinity degree. For example, crystallinity degree of MCC samples was 0.72 to 0.75. It was shown that the independent physicochemical methods for determination of cellulose crystallinity are free of shortcomings inherent to physical methods such as XRD and NMR; therefore the proposed method can be used to determine the actual degree of crystallinity of cellulose samples.

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Keywords : Cellulose; Sorption of water; Enthalpy of wetting; Degree of crystallinity.

INTRODUCTION

Cellulose is a semicrystalline polysaccharide and the most abundant organic matter on Earth^[1]. This polysaccharide is present in all terrestrial plants and algae; cellulose of the tunicin type forms a shell of certain marine creatures, and it is also synthesized by some microorganisms^[2, 3]. To isolate the cellulose, a feedstock is heated within closed vessels under pressure in the presence of caustic soda (soda process), mixture of sodium hydroxide with sodium

sulfide (kraft process), or sulfurous acid and salts thereof (sulfite process)^[4, 5]. Organosolv, oxidative, and some other delignification methods are also used, but at a lower scale^[6, 7]. To obtain chemically pure cellulose, the delignified sample is subjected to additional bleaching procedure.

Since cellulose contains crystalline and non-crystalline (amorphous) domains, an important characteristic of the cellulose sample is its crystallinity, i.e. the content of crystalline portion in the sample. Crystallinity affects various properties of cellulose

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materials such as stiffness, specific gravity, specific volume, specific heat capacity, thermal expansion coefficient, wetting enthalpy, sorption of various substances, reactivity and some other properties^[3].

Currently, main methods used to determine the crystallinity of cellulose are X-ray diffraction (XRD) and solid state ¹³C-NMR^[8-10]. Unfortunately, these physical methods do not measure the absolute crystallinity degree, but gives an estimating parameter - so called crystallinity index, that shows the comparative content of the crystalline fraction in investigated cellulose samples^[3]. There are several reasons that impede the measurement of the absolute (actual) crystallinity degree by XRD and NMR methods. First, it is the absence of completely crystalline and amorphous standards. Second, it is the absence of standard protocols for preparation of the samples for investigations. Third, it is the use of various structural models that do not describe adequately the structure of real cellulose samples. Fourth, it is the use of different mathematical func-

tions and programs. These and some other unsolved problems give different values even of crystallinity index for the same sample, if different methods of preparation or calculation are used.

Therefore, it is advisable to develop other independent methods for determination of the actual crystallinity degree of cellulose without shortcomings inherent to the mentioned physical methods. For this purpose, in this article physicochemical methods are proposed such as study of sorption of water vapor and wetting enthalpy.

EXPERIMENTAL

Materials

The following cellulose samples were investigated (TABLE 1):

- Microcrystalline celluloses (MCC) Avicel PH-301 (MCC-1) and PH-101 (MCC-2) of FMC BioPolymer Co.
- Pure chemical grade cotton cellulose (CC) of

TABLE 1: Characteristics of the samples

Sample	α -Cellulose, %	DP	CrI
MCC-1	88	170	0.71
MCC-2	89	220	0.69
CC	98	2700	0.67
CCM	99	2100	0.51
KCP	97	1200	0.62
SFI	95	1100	0.60
CF	-	360	0.38
VF	-	250	0.36

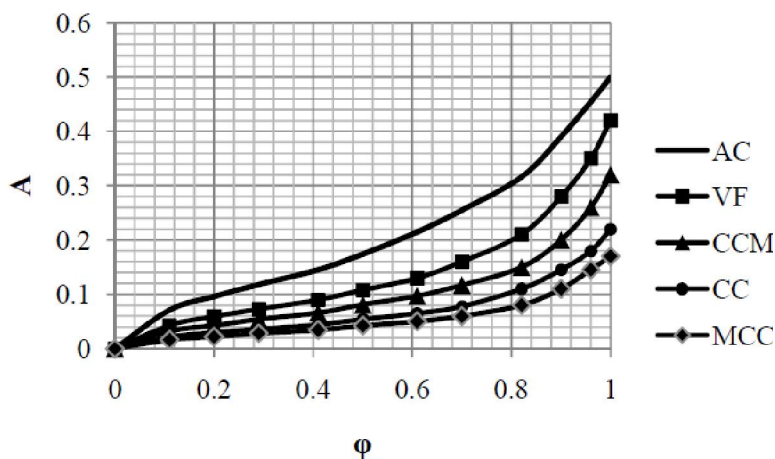


Figure 1 : Isotherms of water vapors sorption by various cellulose samples and sorption isotherm of amorphous domains of cellulose (AC)

Hercules Co.

- Mercerized cotton cellulose (CCM) prepared by treatment with 20% NaOH and following washing and drying.
- Bleached Kraft pine chemical pulp (KCP) of Weyerhaeuser additionally refined by treatment with a cold solution of 8% NaOH and following washing and drying.
- Bleached high-pure sulfite spruce pulp (SFI) of Weyerhaeuser Co.
- Mercerized sulfite cellulose (SFM) prepared by treatment with 20% NaOH and following washing and drying.
- Regenerated cellophane film (CF) of Celulozon Co.
- Regenerated viscose fibers (VF) of Rayonier Inc.

METHODS

Chemical analysis

The content of α -cellulose was tested after treatment of the samples with 17.5% NaOH at 20 °C for 1h. The average degree of polymerization (DP) was measured by the viscosity method using diluted cellulose solutions in Cadoxen^[11].

X-ray diffraction

X-ray investigations of samples were carried out with a Rigaku-Ultima Plus diffractometer (CuK_α – radiation, $\lambda=0.15418$ nm) in the 2Θ -angle range from 5 to 50°. The crystallinity index was evaluated by method of Jayme and Knolle^[12]. Three diffractograms were recorded for the each cellulose sample to calculate average CrI and its standard deviation that was in the range ± 0.02 .

Sorption of water vapor

The sorption experiments were carried out at 25°C in a *vacuum Mac-Ben apparatus* having helical spring quartz scales. Prior to starting of the experiments the samples were dried at 105 °C up to constant weight and additionally degassed in the sorption device. Three of the same samples were tested to calculate an average sorption value and standard deviation that was in the range ± 0.002 g/g DM.

Enthalpy of wetting

The enthalpy of cellulose wetting with water (ΔH) was studied at 25°C by the method of micro-calorimetry at 25 °C using a TAM III calorimeter^[13-15]. Three of the same samples were tested to calculate an average enthalpy value and standard deviation that was in the range ± 0.02 J/g DM.

RESULTS AND DISCUSSION

Sorption method to determine the degree of crystallinity

Sorption of water vapors is usually described through isotherms having various shapes that express the relative amount of water in the cellulose (A , g/g) as a function of relative vapor pressure ($\varphi=P/P_0$) at a constant temperature, 25°C. The experimental results revealed that isotherms of water vapor sorption by cellulose samples have a sigmoidal form (Figure 1). The lowest sorption was observed for crystalline MCC Avicel PH-301 ($\text{CrI} = 0.71$), whereas the samples of low-crystalline regenerated cellulose VF ($\text{CrI}= 0.36$) showed the higher sorption. Since the real mechanism of sorption is absorption of water molecules into amorphous domains of cellulose, the amorphous sample must have the highest sorption ability.

Unfortunately, amorphous or amorphized cellulose cannot be used for sorption of water due to its recrystallization in conditions of the experiment^[16]. However, the isotherm of water vapor sorption (absorption) by amorphous cellulose (AC) can be calculated with a high accuracy using the theory of additive functions for sorption of water molecules by various functional groups of amorphous polymers^[17]. The calculated theoretical isotherm can be expressed in a linear form by an exact thermodynamic equation^[18]:

$$1/A_{\text{am}} = 1/A_{\text{am},0} - (K/A_{\text{am},0}) \ln \varphi \quad (1)$$

where $A_{\text{am},0}$ is maximal absorption value for AC at $\varphi=1$; K is coefficient.

From the linearized isotherm (Figure 2) the following sorption parameters were obtained: $A_{\text{am},0} = 0.5$ g/g and $K=2.61$. This makes it possible to calculate the sigmoidal isotherm of absorption of wa-

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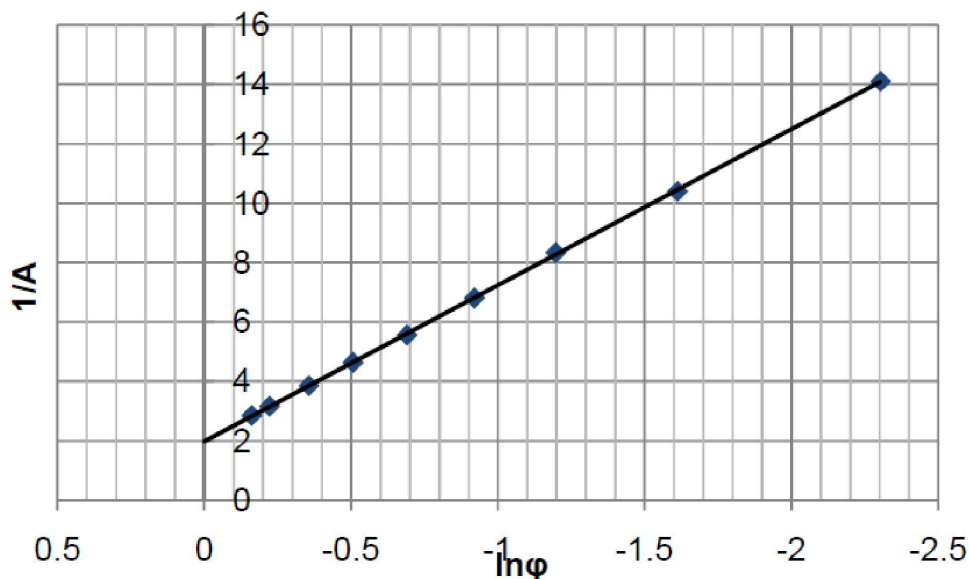


Figure 2 : Linearized isotherm of water vapors absorption by amorphous cellulose

TABLE 2 : Sorption characteristics of the samples

Sample	A_0 , g/g	$A_{0.7}$, g/g	X
MCC-1	0.125	0.064	0.75
MCC-2	0.140	0.073	0.72
CC	0.150	0.078	0.70
CCM	0.225	0.117	0.55
KCP	0.173	0.091	0.65
SFI	0.185	0.096	0.63
CF	0.290	0.150	0.42
VF	0.311	0.161	0.38
AC*	0.500	0.260	0

*Note: Calculated characteristics of AC

ter vapor by AC using the equation:

$$A_{am} = A_{am,0} / (1 - K \ln \phi) \quad (2)$$

For semicrystalline cellulose sample, the sorption (absorption) isotherm of water vapor can be described by the equation:

$$A = A_0 / (1 - K \ln \phi) \quad (3)$$

where A_0 is maximal sorption value for the sample at $\phi=1$ (TABLE 2).

Taking in consideration that absorption of water vapor by semicrystalline sample is directly proportional to content of amorphous domains (Y), the maximal sorption value for the sample can be obtained as: $A_0 = A_{am,0} Y$.

Thus, it can be derived the following equation of sigmoidal isotherm of the sample:

$$A = 0.5 Y / (1 - 2.61 \ln \phi), \text{ or} \quad (4)$$

$$A = 0.5(1 - X) / (1 - 2.61 \ln \phi) \quad (5)$$

where $X = (1 - Y)$ is crystallinity degree.

Finally, from the equation (5), the crystallinity degree of the cellulose can be calculated:

$$X = 1 - 2A(1 - 2.61 \ln \phi) \quad (6)$$

Since the obtaining of complete isotherm is a laborious and long procedure, it is convenient to measure the sorption value at the one relative pressure of vapors, e.g. at $\phi=0.7$, in order to determine the crystallinity degree from the sorption experiment:

$$X = 1 - 3.85 A_{0.7} \quad (7)$$

where $A_{0.7}$ is sorption value at $\phi=0.7$ (TABLE 2).

Using of enthalpy of wetting to determine the degree of crystallinity

As is known, interaction of water molecules is carried out in the amorphous domains of cellulose and accompanied by the exothermic heat effect – enthalpy of wetting (ΔH), which is directly propor-

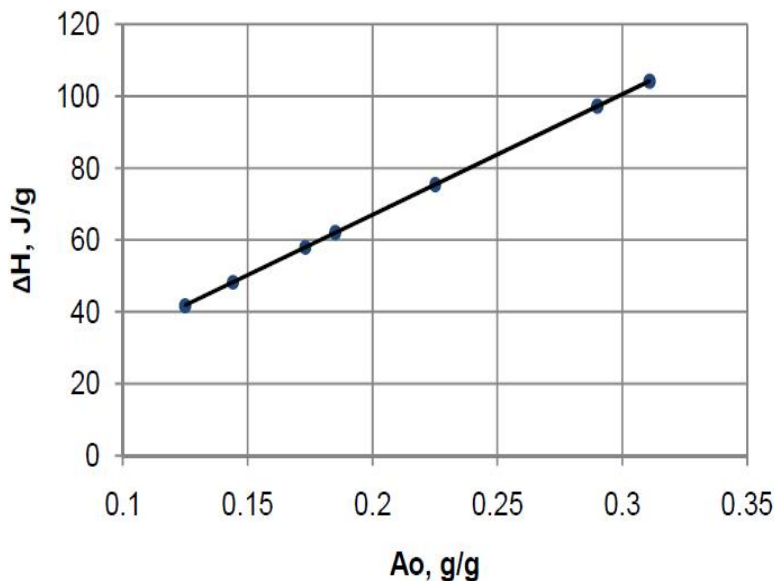
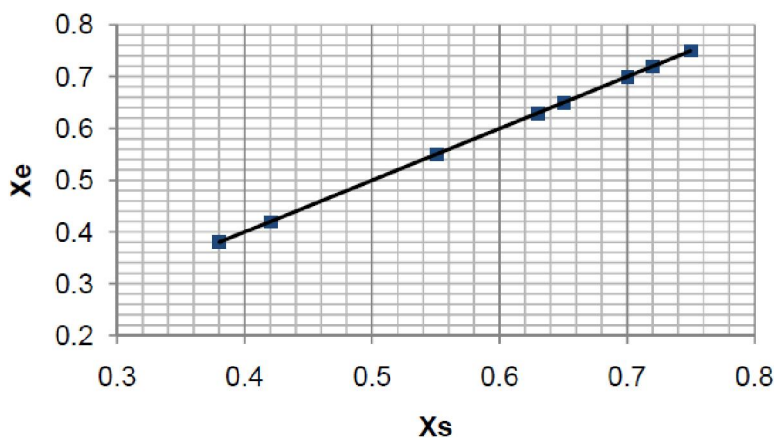


Figure 3 : Dependence enthalpy of wetting on maximal sorption value

TABLE 3 : Maximal water sorption and value of wetting enthalpy

Sample	A ₀ , g/g	-ΔH, J/g	-Δh, J/g H ₂ O
MCC-1	0.125	41.8	334.4
MCC-2	0.140	46.9	335.0
CC	0.150	50.3	335.3
CCM	0.225	75.4	335.1
KCP	0.173	58.0	335.2
SFI	0.185	62.1	335.6
CF	0.290	97.2	335.2
VF	0.311	104.1	334.7
AC*	0.500	167.5	335.0
	Average:		335.0

Note: Calculated characteristics of AC

Figure 4 : Correlation between values of crystallinity degree obtained by method of water sorption (X_s) and enthalpy of wetting (X_e)

tional to content of amorphous domains (Y) in the sample^[3, 15], i.e.

$$\Delta H = \Delta H_{am} Y \quad (8)$$

$$\text{Thus, } Y = \Delta H / \Delta H_{am} \quad (9)$$

$$X = 1 - (\Delta H / \Delta H_{am}) \quad (10)$$

The experimental results for various cellulose

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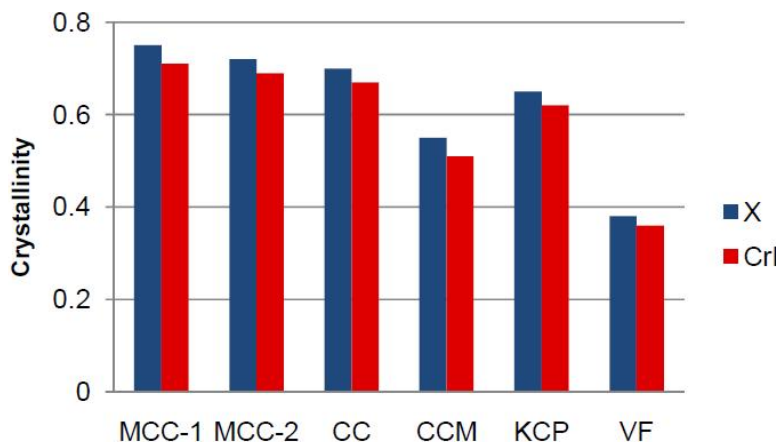


Figure 5 : Comparison of crystallinity values obtained by physicochemical methods (X) and XRD (CrI)

samples showed that with increase the maximal sorption value (A_o) the linear rise of exothermic enthalpy of wetting (ΔH) was observed (Figure 3); i.e. the specific enthalpy $\Delta h = \Delta H/A_o$ is constant. As it follows from calculations, $\Delta h \approx -335$ J/g water (TABLE 3). Considering that amorphous sample has the maximal sorption value $A_{am,o} = 0.5$ g/g, it can be calculate the enthalpy of wetting for completely amorphous cellulose (AC),

$$\Delta H_{am} = h A_{am,o} = -167.5 \text{ (J/g AC)} \quad (11)$$

Finally, the value of $\Delta H_{am} = -167.5$ J/g is used to calculate the crystallinity degree of cellulose samples by the equation (10).

It has been found that the measurement of enthalpy of wetting gives values of crystallinity degree similar to those obtained by the study of water sorption (Figure 4). For example, the crystallinity degree of MCC samples was 0.72 to 0.75, whereas the crystallinity degree of regenerated cellulose samples was 0.38 to 0.42. It was also discovered that the physicochemical methods show a higher crystallinity value than the crystallinity index obtained by XRD method of Jayme and Knolle (Figure 5).

CONCLUSION

Two physicochemical methods for determination of crystallinity degree of cellulose have been developed. The first method was based on the study of sorption of water vapor (A), and second - on the measurement of enthalpy of wetting (ΔH). As is known, molecules of water absorb by amorphous domains of cellulose, which is accompanied by the

exothermic heat effect –enthalpy of wetting. Thus, increase in content of amorphous domains and decrease in degree of crystallinity leads to rise of the obtained physicochemical parameters. As a result, an equation for calculation of the crystallinity degree (X) of cellulose was derived: $X = 1 - (Z/Z_o)$, where Z is a physicochemical parameter (A or ΔH) of the sample, and Z_o is a theoretical parameter calculated for amorphous cellulose. Both physicochemical methods give similar values of crystallinity degree. For example, the crystallinity degree of MCC samples was 0.72 to 0.75, whereas the crystallinity degree of regenerated cellulose samples was 0.38 to 0.42. It was also discovered that the physicochemical methods show a higher crystallinity value than the crystallinity index obtained by XRD method of Jayme and Knolle.

Currently, main methods used to determine the crystallinity of cellulose are XRD and solid state ^{13}C -NMR. Unfortunately, these physical methods do not measure the absolute crystallinity degree, but gives an estimating parameter - crystallinity index (CrI), that shows only the comparative content of the crystalline fraction in investigated cellulose samples. There are several reasons that impede the measurement of the absolute (actual) crystallinity degree by XRD and NMR methods. First, it is the absence of completely crystalline and amorphous standards. Second, it is the absence of standard protocols for preparation of the samples for investigations. Third, it is the use of various structural models that do not describe adequately the structure of real cellulose samples. Fourth, it is the use of dif-

ferent mathematical functions and programs. These and some other unsolved problems give different values even of crystallinity index for the same sample, if different methods of preparation or calculation are used. For example, XRD CrI of textured sample is significantly higher than of non-textured sample. Moreover, the reflection and transmission XRD modes give different values of CrI. The difference in density and thickness of the sample has a great impact on the XRD CrI value. On the other hand, adding of signals of paracrystalline layers of crystallites and amorphous domains in the NMR method leads to decrease of final CrI value.

The independent physicochemical methods for determination of cellulose crystallinity are free of shortcomings inherent to physical methods such as XRD and NMR. The proposed physicochemical methods are simple and do not require difficult mathematical calculations and programs. The samples used for these methods can possess various allomorphs; moreover, they can be non-textured or textured, have different thickness, density and shape. There are only two main requirements for preparation of samples: they must be dry and chemically pure. After meeting these requirements, the developed physicochemical method can be used to determine the actual degree of crystallinity of cellulose samples.

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