AMORPHOUS CELLULOSE – STRUCTURE AND CHARACTERIZATION

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Amorphous cellulose was obtained from different types of celluloses (microcrystalline cellulose, dissolving pulp and cotton cellulose), by regeneration with ethanol from their solutions in an SO_2-diethylamine-dimethylsulfoxide (SO_2-DEA-DMSO) solvent system. Different techniques, X-ray diffraction (XRD), FTIR spectroscopy and differential scanning calorimetry (DSC) were used to estimate the crystallinity degree. The values obtained for amorphous celluloses were compared with those of the initial samples and correlated with their supramolecular structures. Viscosity measurements have shown that little or no depolymerization occurs during dissolution.

Keywords: cellulose I, dissolution, regeneration, amorphous cellulose, XRD, FTIR, DSC

INTRODUCTION

As generally known, cellulose is a very important and fascinating biopolymer and an almost inexhaustible and renewable raw material. The trend towards this kind of resources and the tailoring of innovative products for science, medicine and technology has led to a global renaissance of interdisciplinary cellulose research and to the extended use of this abundant organic polymer over the last decade.[1]

In any chemical reaction, the accessibility of cellulose molecules to the reagent is highly important in the process and efficiency of modification. The premise for obtaining any derivative regards the contact of the reactants with each other. In the case of cellulose, this process is more difficult, due to its biphasic structure.

Most cellulosic materials consist of crystalline and amorphous domains, in varying proportions, depending on both source and history. The physical properties of cellulose, as well as their chemical behavior and reactivity, are strongly influenced by the arrangement of the cellulose molecules with respect to each other and to the fiber axis, as well. Most of the reactants penetrate only the amorphous regions and it is only in these regions with a low level of order and on the surface of the crystallites that the reactions can take place, leaving the intracrystalline regions unaffected. Starting from this, the behavior of both regions has been extensively studied to elucidate the micro and macro responses of the cellulose material to thermal, hydrothermal and chemical treatments.[2-5]

Interactions between solid cellulosic materials with water, enzymes or other reactive or adsorptive substances occur first in the noncrystalline domains and/or on the surface of cellulose crystallites. Thus, the secondary and tertiary structures of the noncrystalline domains in cellulose, their properties and their distribution states should be significant for understanding the behavior of cellulosic materials under various conditions. The distribution of noncrystalline domains in cellulose is related to DP leveling-off, which has always been observed in the acid hydrolysis of cellulose samples of higher plants, but has never been detected as periodic units by microscopic observations. The noncrystalline domains include liquid crystalline and nematic ordered cellulose and do not necessarily indicate amorphous cellulose. Amorphous cellulose samples have been often used for model experiments to understand the behavior of the noncrystalline domains in cellulose under various conditions.

The amorphous cellulose model samples, or cellulose samples with a 100% amorphous structure, are prepared by cellulose ball-milling,[6] deacetylation of cellulose acetate under nonaqueous alkaline conditions,[7] regeneration of cellulose from solutions into nonaqueous media,[8,9] or regeneration of cellulose solution in aqueous media.[10] The obtained samples present flat X-ray diffraction patterns, typical Raman spectra over the 300-600 cm^{-1} range, and typical solid-state ^{13}C-NMR spectra with relatively broad resonances.[11] However, the structures of conventional amorphous cellulose samples are unstable in the presence of water or moisture; they usually form partially crystalline cellulose II. In this respect, such amorphous cellulose samples may have amorphous structures somewhat different from those of native cellulose fibers. Recently, amorphous cellulosic materials stable even under aqueous media have been obtained.[10]

The aim of this paper has been to investigate the structure of amorphous cellulose obtained from different native celluloses with various morphological structures. X-ray diffraction (XRD) was used to reveal the modification in the supramolecular structure of celluloses, occurring after the dissolution/regeneration process. Fourier transform infrared spectroscopy (FTIR) was performed to investigate the differences of crystallinity and hydrogen bond of the fiber cellulose. Differential scanning calorimetry (DSC) was used to establish the dehydration heat and to estimate crystallinity.

EXPERIMENTAL

Materials

Microcrystalline cellulose, AI (Avicel HP-101), purchased from Fluka, was used in air-dry state. Cotton cellulose, BI (Arshad Enterprises, Pakistan), was extracted in a Soxhlet extractor with ethanol and benzene mixture, for 8 h. The cellulose sample was then boiled in 1% NaOH solution for 6 h, washed with distilled water, immersed in 1% CH_3COOH, washed with water, and finally air-dried. Spruce dissolving pulp, EI, was supplied by Extranier F, Rayonier, France, and was used without any purification. All other chemicals used were of the highest commercially available purity.

Preparation of amorphous cellulose

The process was based on the SO_2-DEA-DMSO system for cellulose dissolution. To produce regenerated cellulose, the regeneration media used consisted of ethanol.[10,12] The obtained amorphous samples were coded as A am, B am and E am, respectively.

Preparation of SO_2 solutions in DMSO

The procedure consisted in bubbling SO_2 gas into DMSO for about 20 min. After cooling to room temperature, the SO_2 solution was diluted with distilled water in a ratio of 1:100.

Preparation of cellulose solution

Depending on the desired concentration of the cellulose solution, dry cellulose and DMSO were placed together. The mixture was stored for a few hours or heated at 60 °C for 10 min, to assure sufficient penetration of DMSO into cellulose. An amount of the previously prepared SO_2 solution containing 1.19 g SO_2/g cellulose was added to the mixture, followed by 1.35 g diethylamine (DEA), after which the flask was shaken vigorously.

Regeneration of cellulose

When cellulose was completely dissolved in the solvent system, the solution was poured into an excess of a regeneration medium, such as ethanol. Dry regenerated celluloses were obtained by solvent exchange, followed by air-drying.

Methods

Degrees of cellulose polymerization (DP) were measured by the viscosity method, in 0.5 mol Cuen.[13]

X-ray diffraction method (XRD)

X-ray diffraction patterns of the samples were collected on a RIGAKU RINT 2500 apparatus, equipped with a transmission type goniometer using nickel-filtered, CuKα radiation. The resulting diffraction patterns exhibited peaks deconvoluted from a background scattering by means of Lorenzian functions, while the diffraction pattern of an artificially amorphicized sample was approximated by a Gaussian function curve fitting analysis. The deconvolution of the peaks from diffractograms was performed with the PeakFit 4.11 software.

The surface method estimates the crystallinity index of the cellulose samples, by the following equation:[14]

$$\text{Cr.I. } (\%) = (Sc / St) \cdot 100 \quad (1)$$

where: Sc – area of the crystalline domain, St – area of the total domain.

FTIR spectroscopy

FTIR spectra of the cellulosic samples were measured on a FTS 2000 spectrometer Series DIGILAB. A total of 24 cumulative scans were taken, with a resolution of 4 cm^{-1}, in the frequency range of 4000-400 cm^{-1}, in transmission mode.

The ratio of crystallinity was determined by two methods:[15]

- the absorbance ratio from 1372 cm^{-1} (A_{1372}) and 2900 cm^{-1} (A_{2900}) bands:

$$Cr.R._1 = A_{1372} / A_{2900} \quad (2)$$

- the absorbance ratio from 1430 cm^{-1} (A_{1430}) and 893 cm^{-1} (A_{893}) bands:

$$Cr.R._2 = A_{1430} / A_{893} \quad (3)$$

The energy of the hydrogen bonds (E_H, kJ) was calculated with the following equation:[16]

$$E_H = (1/K)\cdot[(\nu_0 - \nu)/\nu_0] \quad (4)$$

where: ν_0 – standard frequency corresponding to the free OH groups (cm^{-1}), ν – frequency of the bonded –OH groups (cm^{-1}), $K = 1.6\cdot 10^{-2}$ $Kcal^{-1}$.

The asymmetric index (a/b) is the ratio between segment widths at half height of the OH adsorption band.[17]

Differential scanning calorimetry (DSC)

The DSC curves of celluloses were recorded on a Mettler DSC 12E at a heating rate of 5 ºC/min. To obtain a 2.5% relative humidity for the cellulosic materials, they were stored in a desiccator containing $CaCl_2$ at 25 ºC, until constant mass was reached. The same samples were also conditioned at a constant relative humidity of 65% and a temperature of 25 ºC, until constant mass was achieved.

Cellulose crystallinity (C.C.) was determined by the DSC method, as the ratio between the heat of dehydration of a preconditioned sample at constant relative humidity and the dehydration heat of the completely amorphous cellulose, preconditioned under the same conditions.[18]

RESULTS AND DISCUSSION

In the present study, amorphous cellulose was obtained by dissolution in an SO_2-DEA-DMSO system and by regeneration from ethanol media, because of the retention occurring even after extended soaking in aqueous media, at room temperature.

Amorphous celluloses were obtained from different celluloses with crystalline organization forms, such as cellulose I, microcrystalline cellulose (A am), cotton cellulose (B am) and spruce dissolving pulp (E am).

X-ray diffraction measurements

The X-ray diffractograms obtained for the initial samples are presented against the amorphous ones, in Figures 1, 2 and 3, respectively.

The cellulosic samples regenerated in ethanol medium gave diffractograms, which clearly indicate an amorphous structure. This character is demonstrated by the absence or strong reduction of all peaks corresponding to planes (101), ($10\bar{1}$) and (002), to values of the Bragg angle characteristic to cellulose I.

The X-ray diffractograms also prove that these samples are amorphous, irrespective of the molecular mass of the original cellulose samples.

Moreover, by comparing the X-ray diffraction patterns of the initial celluloses with those of the obtained amorphous samples, it may be remarked that the areas under the diffraction curves permit the application of the surface method for calculating the crystallinity index. In this respect, the obtained samples can be successfully used as an internal amorphous standard.

Table 1 presents the required times for dissolution of the cellulosic samples and the crystallinity degrees of the studied samples, both before and after dissolution and regeneration.

A strong decrease of the crystallinity degree, to values of around 20%, may be observed for all amorphous cellulosic samples. Thus, for microcrystalline cellulose, crystallinity decreases by 77%, while for cotton cellulose, the value is 74% lower. This fact can be explained by a reduction in the intra- and intermolecular hydrogen bonds, occurring during the continuous transformation of cellulose I into amorphous cellulose.

Table 1
Dissolution time and crystallinity index of cellulosic samples

Sample	Time of dissolution	Cr.I., %	
		Initial	After dissolution
AI	< 10 s	83.83	19.08
BI	< 50 min.	71.11	18.11
EI	< 10 min.	65.47	15.75

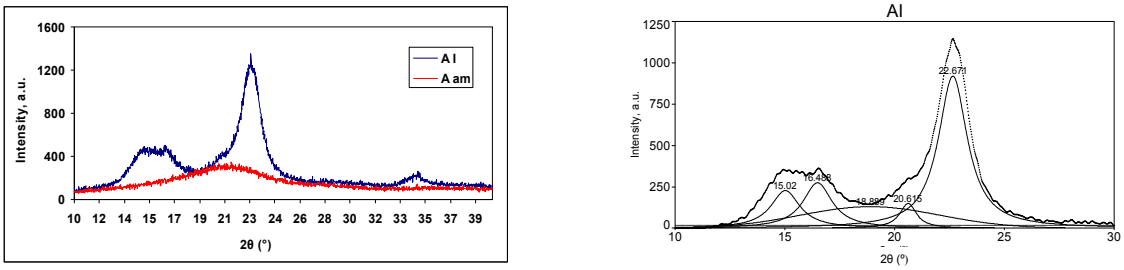


Figure 1: X-ray diffractograms of AI and A am samples

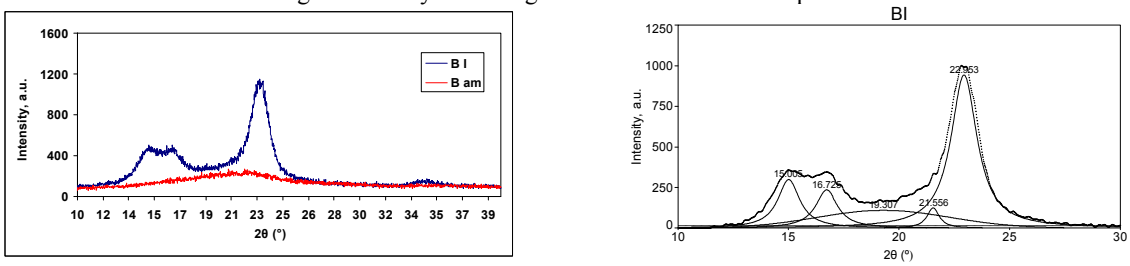


Figure 2: X-ray diffractograms of BI and B am samples

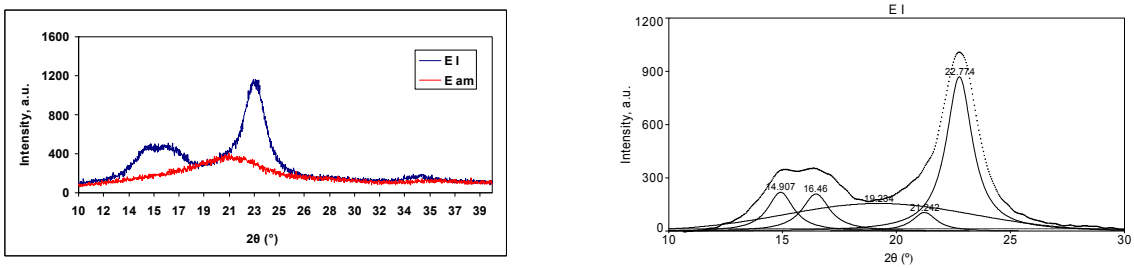


Figure 3: X-ray diffractograms of EI and E am samples

Table 2
Polymerization degree of cellulosic samples

Sample	DP	
	Initial	After dissolution
AI	183	178
BI	1458	1335
EI	3078	2820

The dissolution time directly depends on the supramolecular and morphological structure of each cellulosic sample. Microcrystalline cellulose was dissolved within half a minute, after the addition of SO_2 and DEA. For the samples with a higher degree of polymerization and a more compact structure, dissolution requires a longer period of time. Thus, the complete dissolution of cotton required over 30 min, while spruce pulp was dissolved within 10 min. Dissolution also depends on the power of DMSO to penetrate the sample.

An important observation is that, during dissolution and regeneration, the cellulosic samples suffer no significant depolymerization (Table 2), which is in contrast with the effects of the procedures commonly used for obtaining amorphous cellulose.

These results are very important, permitting the possible preparation of amorphous celluloses of well-defined molecular mass, by selecting the appropriate source of cellulose for dissolution in a specific system for regeneration purposes.

FTIR measurements

FTIR spectroscopic investigations evidenced the capacity of different absorption bands to characterize the ordering degree of the cellulosic polymers (Figs. 4, 5 and 6).

An alteration of the crystalline organization leads to a significant simplify-cation of the spectral contour through reduction in intensity or even disappearance of the bands characteristic of the crystalline domains.

The broad band in the 3600-3100 cm^{-1} region, which is due to the OH-stretching vibration, gives considerable information concerning the hydrogen bonds. The peaks characteristic of hydrogen bonds from the spectra of amorphous celluloses became sharper and with lower intensity, compared to the initial cellulosic samples, which can be correlated with the scission of the intra- and intermolecular hydrogen bonds. Also, in the case of amorphous samples, the peak shifted to higher wavenumber values (Table 3).

The presence of amorphous cellulosic samples can be further confirmed by the shift of the band from 2900 cm^{-1}, corresponding to the C–H stretching vibration, to higher wavenumber values and by the strong decrease in the intensity of this band.

The adsorption bands from the 1500-899 cm^{-1} region are strongly reduced in intensity, or even absent.

In addition, the FTIR absorption band at 1430 cm^{-1}, assigned to a symmetric CH_2 bending vibration, decreases. This band is also known as the "crystallinity band", indicating that a decrease in its intensity reflects reduction in the degree of crystallinity of the samples. The FTIR absorption band at 898 cm^{-1}, assigned to C–O–C stretching at β-(1→4)-glycosidic linkages, is designed as an "amorphous" absorption band, an increase in its intensity occurring in the amorphous samples, compared to the initial ones – as actually plotted in Figures 4 to 6.

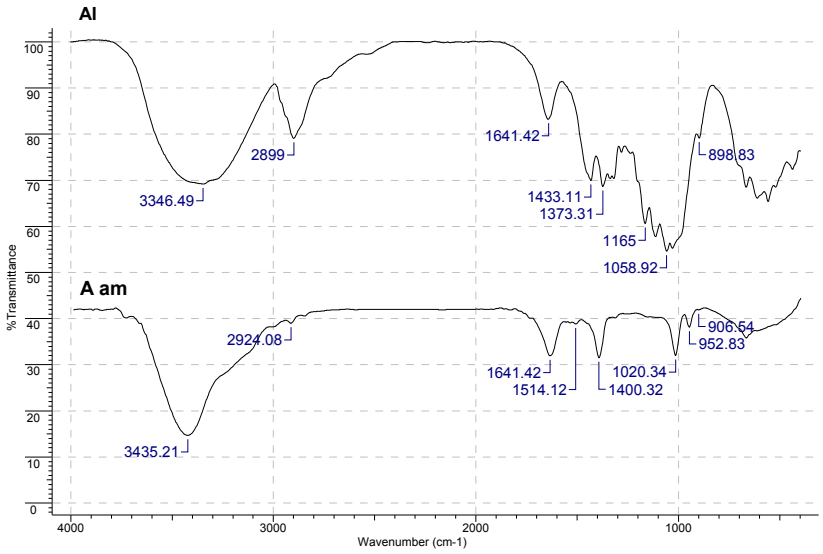


Figure 4: FTIR spectra of original and amorphous microcrystalline celluloses

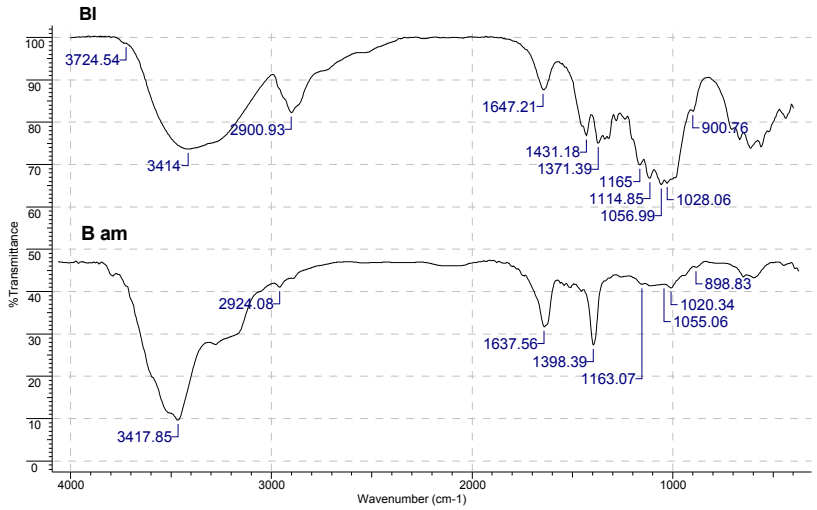


Figure 5: FTIR spectra of original and amorphous cotton celluloses

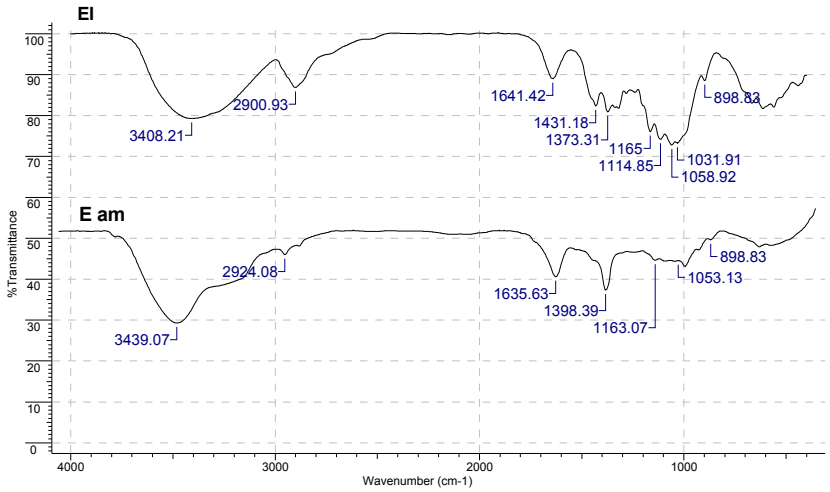


Figure 6: FTIR spectra of original and amorphous dissolving pulp

Table 4 shows that the initial cellulosic samples have the highest energy of the hydrogen bonds (E_H), decreasing values being recorded for the corresponding amorphous samples, which indicate a decrease in the number of hydrogen bonds and, consequently, changes in the crystalline structure of cellulose – namely, a reduction in the degree of crystallinity.

The index of asymmetry (a/b) characterizes the uniformity of the cellulosic samples. The values tending to 1.0 indicate the most uniform samples, characteristic of the initial celluloses, while the less uniform samples are those corresponding to amorphous cellulosic ones.

The ratios of crystallinity obtained from FTIR spectra ($Cr.R._1$ and $Cr.R._2$) agreed with the crystallinity indices presented in Table 1, as established by X-ray diffraction.

DSC measurements

Starting from the idea that thermal degradation is influenced by the supramolecular structure of cellulosic materials, the effect of the structural organization form of celluloses on their thermal behavior was analyzed. The samples were first conditioned for 72 h in a desiccator containing $CaCl_2$ (2.5% relative humidity) at 25 °C, until constant mass was reached.

The endothermic peaks characteristic of native cellulose, occurring in the 50-150 °C region of the DSC curves, are presented in Figure 7a.

A shift of the maximum temperature of the dehydration process to higher values may be observed with the decrease of the crystallinity degree. Thus, in the case of AI, the maximum temperature of the peak appears at 68 °C, followed by BI at 72 °C, and EI at 80 °C.

The same effect is also noticed for the 250-400 °C region (not shown), which corresponds to the scission of the glucosidic bonds, with laevoglucose formation. This behavior is explained by the fact that the thermal degradation reaction starts in the amorphous domain of the cellulosic materials by statistical degradation of cellulose. In the present case, the amorphous content increases from microcrystalline cellulose to cotton cellulose and spruce dissolving pulp.

The effect of the structural organization form over dehydration heat was also investigated for amorphous cellulose by the DSC method. Figure 7b plots the DSC curves of the amorphous cellulose obtained under the same conditions applied to native cellulose, namely 2.5% relative humidity and 25 °C.

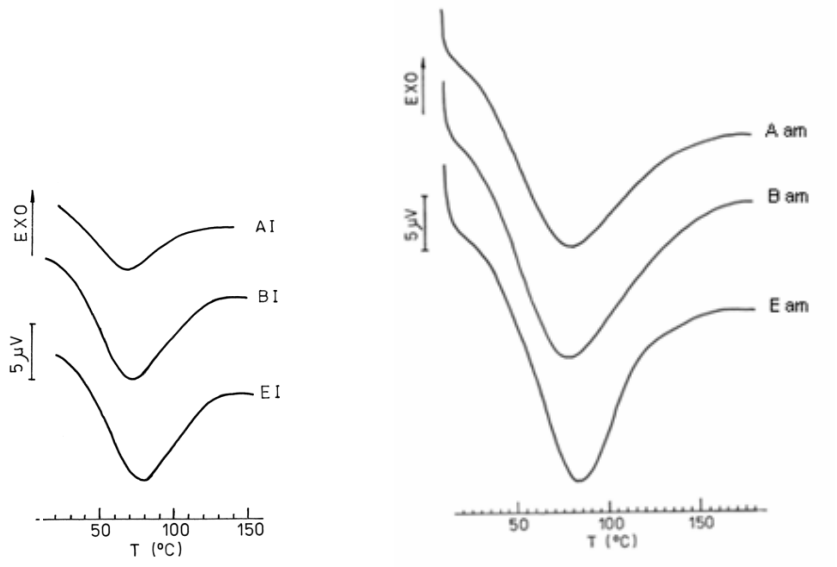
To establish the dependence of dehydration heat on the conditions of sample preparation, the cellulosic samples were conditioned at a higher relative humidity (65%) and at 25 °C, up to constant mass. The results obtained lead to the conclusion that dehydration heat increases considerably when the samples are previously conditioned at a higher relative humidity (Fig. 8).

Table 3
Main FTIR absorption band assignments for initial and amorphous celluloses

Wavenumber, cm^{-1}	Sample					
	AI	A am	BI	B am	EI	E am
ν_{OH}	3346	3435	3414	3418	3408	3439
ν_{CH}	2899	2924	2901	2924	2901	2924
H_2O absorbed	1641	1641	1647	1637	1641	1636
δ_{CH2}	1433	-	1431	-	1431	-
δ_{CH}, ν_{COO}	1373	-	1371	-	1373	-
ν_{C-O}, δ_{OH}	1165	-	1165	1163	1165	1163
ν_{C-O}	1059	-	1057	1055	1059	1053
δ_{CH2}	899	906	900	899	899	899

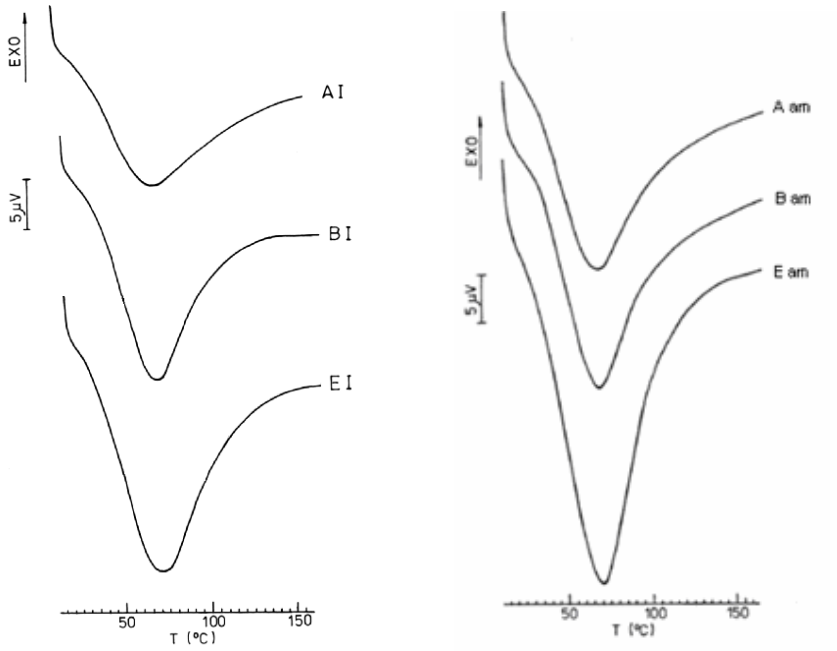
Table 4
Energy of hydrogen bonds and asymmetry index for native and amorphous samples

Sample	E_H, kJ	a/b	$Cr.R._{.1}$, %	$Cr.R._{.2}$, %
A	5.197	0.538	0.967	0.971
A am	3.677	0.923	-	-
B	4.041	0.444	0.957	0.974
B am	3.975	1.04	-	-
E	4.144	0.471	0.944	0.973
E am	3.612	0.875	-	-



(a) (b)

Figure 7: DSC curves registered in the 25-150 °C temperature range for native (a) and amorphous cellulose (b) obtained at a relative humidity of 2.5% and 25 ºC



(a) (b)

Figure 8: DSC curves registered in the 25-150 °C temperature range for native (a) and amorphous cellulose (b) obtained at a relative humidity of 65% and 25 ºC

Passing from AI to EI induces an increase of the endothermic peak, explained by the sorption of a higher amount of water, which demonstrates a higher accessibility of the studied samples. The dehydration heat was determined by measuring the areas of the endothermic peak corresponding to each sample.

It can be observed that sample conditioning at a higher relative humidity also determined the shift of the maximum temperature of the endothermic peak, characteristic of dehydration, to higher values, with the increase in the amorphous content in the samples.

As generally known, the capacity of cellulose for water absorption depends largely on the availability of the free hydroxyl groups. It has been generally considered that water absorption occurs almost entirely in the amorphous regions of cellulose, neglecting the free hydroxyl groups that may be present on the surfaces of crystallites. Therefore, as water sorption occurs almost totally in the amorphous domain of cellulose, the area of the endothermic peak is directly related, due to the loss of absorbed water, to the amorphous fraction of cellulose.

Table 5 lists the dehydration heat values, determined by the DSC method, of the cellulosic samples conditioned up to a relative humidity of 2.5 or 65% and a temperature of 25 °C.

Table 5
Dehydration heat at different relative humidity values (2.5% and 65%) for native and amorphous celluloses

Sample	Air relative humidity (R.H.)			
	2.5%	65%	2.5%	65%
	ΔH, J/g		C.C., %	
AI	25.39	86.46	80.37	78.98
A am	129.35	411.29	-	-
BI	45.03	120.29	71.75	70.56
B am	159.39	408.57	-	-
EI	47.72	152.67	67.23	64.83
E am	145.64	434.13	-	-

The crystallinity index (Cr.I.) values for native and amorphous celluloses conditioned to 2.5 or 65% relative humidity and 25 ºC, estimated by DSC, are also given in Table 5. A comparison of these data with those from Table 1 shows the excellent agreement between the cellulose crystallinity values obtained by the DSC method and those determined by the X-ray diffraction technique. One may remark that, at a relative humidity of 65%, the ΔH values are higher than those obtained for a relative humidity of 2.5%, which suggests a direct dependence between the amount of amorphous material and the relative humidity of the samples. Thus, it is obvious that the DSC method can be used as an alternative means to estimate the crystallinity of allomorphic forms of cellulose.

An important contribution of this work refers to the attempt of using some simple methods, permitting to evaluate cellulose crystallinity.

CONCLUSIONS

It was demonstrated that the SO_2-amine forms a complex with cellulose hydroxyls, sufficiently strong to cause the rapid dissolution of different cellulose samples with various supramolecular structures and to permit the obtaining of the amorphous celluloses by regeneration in ethanol medium. XRD investigations reveal typical shapes for amorphous samples and a strong decrease of their crystallinity indices. Viscosity measurements have shown that a slight depolymerization occurs during dissolution. The alteration of the crystalline organization in the obtained amorphous celluloses leads to an important simplification of the FTIR spectral shape through the reduction in intensity or even disappearance of the bands characteristic of the crystalline domains. The effect of the structural features of amorphous celluloses on their dehydration heat was also evaluated by differential scanning calorimetry (DSC). The endothermic peaks detected in the DSC curves of celluloses are in a linear relationship with the percent value of the amorphous material from their crystalline structure. The crystallinity values of the cellulose samples determined by XRD, FTIR and DSC methods showed a very good relationship.

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