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THE THERMAL BEHAVIOUR OF CELLULOSE SAMPLES WITH DIFFERENT STRUCTURE

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In this work the thermal characteristics of cellulose samples with different structure were investigated. The samples were prepared by reacting the cellulose with ethanolic hydroxide solution. Depending on the time of alkaline treatment, the intensity of cellulose transformation differed. Starting from cellulose I structure, with the highest degree of crystallinity, the other samples consisted of mixed structures of cellulose I and II, or were completely transformed to cellulose II structure with the lowest degree of crystallinity. The thermal behaviour of the samples was studied by using a Perkin Elmer TGS–2 and DSC–2 instruments. The kinetic parameters of dehydration and degradation were determined from non-isothermal TG–data (Nitrogen-inert atmosphere and a heating rate of 20 deg/min). The thermal effects of water evolution (heating rate of 80 deg/min) of the cellulose samples were found to depend on the structural characteristics and the crystallinity of the samples. The activation energy and frequency factor were in correlation with the structural changes.

Keywords: cellulose, structural characteristics

Introduction

In spite of the application of modern measurement techniques which require the use of expensive equipment, as well as complex procedures, the problems related to the synthesis and structure of native cellulose and its structural transformation have still not been resolved [1–4].

Cellulose consists of varying degrees of order which continuously transform from the one into the other, therefore constituting a polyphase system. The phase boundaries can be set only by definition, for example by means of a certain method, with the phase boundaries dependent on the method applied. In these investigations the X-ray diffraction method was primarily used. Cellulose is approximated as a two-phase system in which the ordered regions, which give sharp X-ray signals, differ from the less ordered or amorphous regions [5].

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In chemical reactions cellulose participates as a heterogeneous system with its ordered and disordered regions or as a homogeneous system when cellulose is in solution. Topochemical reactions in which reactions occur only on certain surfaces or in disordered regions are also characteristic of cellulose.

Cellulose most commonly participates in a reaction as a heterogeneous system so its behaviour in chemical reactions is determined by structural characteristics such as the system of inter- and intramolecular bonds, the position of cellulose chains in fibriles or their larger units, the cross-section of elementary fibriles, the degree of order or index of crystallinity, as well as the existence of interfibrilal accessible holes and pores, which are defined by the length of the elementary crystallites or fibrile aggregates and their degree of orientation [6, 7].

During the structural transformation of cellulose I (native cellulose) into cellulose II, it is assumed that the form of the crystalline lattice is changed, which brings about a change in the fraction of accessible regions in the fibriles. In native celluloses the fraction of accessible regions is small and can be compared to dislocations in defect crystals. Fibres of the cellulose II structure, especially those with low crystallinity, have much larger accessible regions (specific internal surface), in other words the micropore volume is much greater [7, 8].

Various method are used to investigate the system of pores in cellulose materials [9–12]. The goal of this study was to follow the structural transformations and changes in the system of pores, which occur as a consequence of the intracrystalline swelling of cellulose, by investigating the kinetics and enthalpy of dehydration by TG and DSC.

Experimental

Dissolved beechwood (DP_o 712) and eucalyptus (DP_o 815 and DP_o 1585) cellulose samples were used in these investigations.

The alkaline treatment of cellulose fibers consisted of the intensive stirring in a Loedge batch reactor. The cellulose samples were treated with sodium hydroxide solution at 25° in an ethanol-water mixture in the following way:

I Series B – Beechwood (DP_o 712): Molar ratio cellulose: NaOH = 1:2.13 for 70 min in 52.82 mass % (wt) ethanol (cellulose: ethanol liquor ratio 1:1.68).

II Series E_1 – Eucalyptus (DP_o 815): Molar ratio cellulose: NaOH = 1:2.30 for 60 min in 42.26 mass % (wt) ethanol (cellulose: ethanol liquor ratio 1:2.0)

III Series E_2 – Eucalyptus (DP_o 1585): Molar ratio cellulose: NaOH = 1:2.23 for 45 min in 53.31 mass % (wt) ethanol (cellulose: ethanol liquor ratio 1:1.24).

After alkaline-ethanol treatment the samples were regenerated from alkali cellulose.

Table 1 Some structural characteristics of the alkali treated samples

Beechwood cellulose series B

	Starting sample	Treated 15 min	Treated 30 min		Treated 45 min		Treated 60 min	Treated 70 min
X-RAY DATA								
Crystal. forms	I	I	I	II	I	II	II	II
R, %	1.10	1.12	1.84		0.98		1.54	2.2
Crystallinity, %	66.1	67.5	46.0	20.6	27.0	32.0	35.4	34.2
Partial crystallinity, %								
$\alpha_{(101)}$	10.6	11.3	9.1	0.9	5.7	1.9	1.9	1.0
$\alpha_{(10\bar{1})}$	11.4	8.9	8.2	1.7	5.5	26.5	15.5	14.4
$\alpha_{(002)}$	44.8	47.3	28.9	13.7	16.1	3.8	17.4	15.4
$\frac{\alpha_{(101)}}{\alpha_{(10\bar{1})}}$	0.93	1.27	1.11	0.55	1.04	0.07	0.12	0.07
$\frac{D_{(101)}}{D_{(10\bar{1})}}$	0.91	1.06	1.57	0.75	1.57	0.76	0.76	0.77
VISCOMETRIC DATA (DP)	712	685	678		650		620	618

Eucalyptus cellulose series E_1

	Starting sample	Treated 15 min	Treated 30 min		Treated 45 min	Treated 60 min
X-RAY DATA						
Crystal. forms	I	–	I	II	II	II
R, %	0.66	–	1.06		2.05	1.47
Crystallinity, %	69.0	–	42.6	14.8	35.3	35.2
Partial crystallinity, %						
$\alpha_{(101)}$	10.1	–	6.8	0.2	0.3	0.6
$\alpha_{(10\bar{1})}$	10.6	–	7.2	14.2	17.3	21.9
$\alpha_{(002)}$	32.5	–	28.6	0.5	18.6	13.7
$\frac{\alpha_{(101)}}{\alpha_{(10\bar{1})}}$	0.95	–	0.95	0.01	0.02	0.03
$\frac{D_{(101)}}{D_{(10\bar{1})}}$	1.00	–	1.00	0.31	0.42	0.40
VISCOMETRIC DATA (DP)	815	745	600		515	485

Table 1 Continuous

Eucalyptus cellulose series E_2

	Starting sample	Treated 15 min	Treated 30 min	Treated 45 min	
X-RAY DATA					
Crystal. forms	I	I	I	I	II
R, %	1.22	1.29	1.59	1.60	
Crystallinity, %	70.1	66.4	64.5	36.4	26.8
Partial crystallinity, %					
$\alpha_{(101)}$	9.34	7.3	15.9	3.9	1.5
$\alpha_{(10\bar{1})}$	10.85	12.00	9.3	12.4	5.1
$\alpha_{(002)}$	39.81	41.35	32.3	20.1	20.2
$\frac{\alpha_{(101)}}{\alpha_{(10\bar{1})}}$	0.86	0.61	1.71	0.31	0.29
$\frac{D_{(101)}}{D_{(10\bar{1})}}$	0.80	0.74	0.96	0.96	1.74
VISCOMETRIC DATA (DP)	1585	1441	1452	1192	

Methods of investigation

The samples for X-ray powder diffraction studies were prepared in the form of lightly (2 to 5 MPa) pressed pellets ($d = 2$ cm; $m = 0.2$ g).

The diffraction data were obtained on a Philips PW 1051 diffractometer using CuK$_\alpha$ (graphite monochromator) radiation. The structural characteristics of the samples before and after alkaline treatment, calculated from data obtained by PEAK [13] program are presented in Table 1. The degree of polymerization was determined by the SCAN-C15-62 method, Table 1.

The kinetic parameters of the dehydration and degradation of cellulose samples were determined by application of the dynamic method in a flowing atmosphere with a Perkin Elmer TGS-2 apparatus. The heating rate was 20 deg/min and the nitrogen flow rate 35 ml/min. The sensitivity setting of the TG measurements for 8 mg sample was 1 mg (dehydration) or 10 mg (thermal degradation).

The enthalpies of cellulose dehydration were determined by the dynamic method with a Perkin Elmer DSC-2 apparatus. The heating rate was 80 deg/min, the DSC range for 6–8 mg samples was 0.5 mcal/s and the nitrogen pressure 1.5 atm.

The results of the TG and DSC measurements are shown in Tables 2.

The samples for X-ray, TG and DSC measurements were left in a constant humidity atmosphere (over a saturated $Ca(NO_3)_2$ solution) to achieve an equal content of absorbed water.

Discussion

As already stated in the introduction, the possibilities of applying TG for following the structural transformations of alkali-treated cellulose samples was investigated in this study. Keeping in mind that the structural transformations of cellulose I into cellulose II occur with an increase in the amount of micropores, which is reflected in the percent of total bound water, the measurements were mostly oriented towards investigating the dehydration process.

Due to the high sensitivity of the TG instrument, the results obtained enable observations of the influence of structure on the thermal behaviour of samples in the temperature range 25° to 140°C. For example, the conversion curves of only the initial samples and of samples after the longest alkali treatment time are shown in Fig. 1. All the other conversion curves lie between the curves presented (Table 2). These results primarily indicate the gradual increase of temperature of maximal water evolution rate (T_{max}) as a function of alkalization time, i. e. the 'prehistory' of the sample (pretreatment conditions) (Fig. 2). The amount of water released more easily at lower temperatures (w_L) are shown in the same figure. The amounts of water released more easily or with greater difficulty were obtained for all the samples by drawing tangents to the corresponding conversion change curve and reading off the fraction that is evolved at the same rate (Fig. 1). The fractions of water released with the greatest difficulty probably originate from water molecules are bound to the free hydroxyl groups of the cellulose chains. These amounts correspond to the lowest values on the sorption curve.

The values of the activation energy (E) and pre-exponential factor (A) of the corresponding dehydration processes are given in Table 2 as a function of sample type and 'prehistory'. The activation energy ranged from 33.2 to 53.6 kJ/mol.

It is characteristic of the TG changes that they are closely correlated with the crystallinity changes, i.e. to the decrease in crystallinity of the investigated samples, which is caused by the alkali treatment of samples. The increase of the amorphous fraction of the investigated samples (Am) is shown in Fig. 2 as a function of alkalization time (τ). In the case of the beechwood sample (series B) and the eucalyptus sample having a lower degree of polymerization (series E_1), more significant changes in the structure correspond to greater changes in the total water content (w_{TOT}) and the amount of water that is more easily released (w_L), Fig. 2. In the case of an eucalyptus sample with a higher degree of poly-

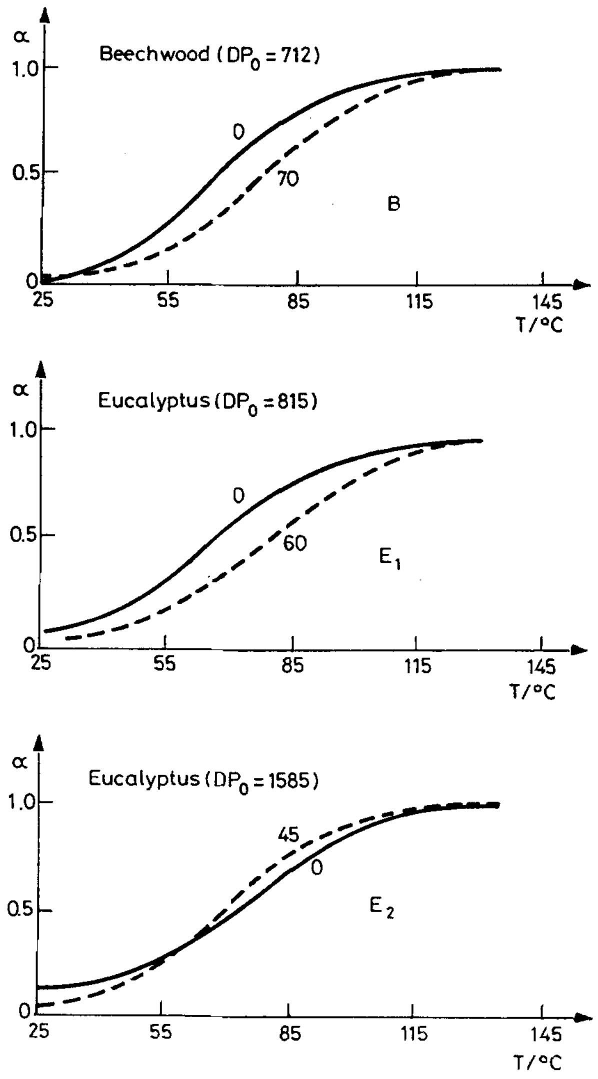

Fig. 1 The dependence of the properties of samples on temperature,
B – beechwood cellulose (DP_0 712) before (——) and after 70 minutes of alkali treatment (– – –),
E_1 – eucalyptus cellulose (DP_0 815) before (——) and after 60 minutes of alkali treatment (– – –).
E_2 – eucalyptus cellulose (DP_0 1585) before (——) and after 45 minutes of alkali treatment (– – –)

merization (series E_2), which is much more resistant to structural transformations, the changes were much less pronounced. Only after 45 minutes was a certain transformation achieved and a partial transition from cellulose I to cellulose II. Accordingly, changes in the system of pores are slight, which is reflected in the small values of the total bound water (Fig. 2).

The values of the corresponding dehydration enthalpies ΔH, (Table 2) also support the above observations. In the case of samples that are structurally more transformed, i.e. with a higher amount of cellulose II, or are completely transformed into the form of cellulose II, the enthalpy increases considerably, which also corresponds to an increase in the total water.

Table 2 Thermal dehydration of alkali treated samples

Sample	Alkalization times	Kinetic parameters of dehydratation 30°–90°C Free water		Endothermic peak 62°–180°C
	τ / min	E / kJ/mol	A / s^{-1}	J/g
Series B				
	0	47.3	$2.0\cdot10^5$	113.4
	15	47.4	$1.2\cdot10^5$	130.0
Beechwood	30	48.3	$1.2\cdot10^5$	151.1
(DP = 712)	45	–	–	192.5
	60	–	–	207.9
	70	47.4	$5.6\cdot10^4$	–
Series E_1				
	0	43.1	$2.0\cdot10^4$	120.2
Eucalyptus	15	48.6	$1.2\cdot10^5$	125.7
(DP = 815)	30	63.6	$1.3\cdot10^7$	142.8
	45	50.3	$1.7\cdot10^5$	181.7
	60	50.2	$1.3\cdot10^5$	165.2
Series E_2				
	0	33.2	$3.8\cdot10^2$	159.0
Eucalyptus	15	41.2	$8.2\cdot10^3$	148.5
(DP = 1585)	30	48.4	$9.6\cdot10^4$	162.4
	45	44.2	$2.3\cdot10^4$	179.5

This is the case with the beechwood cellulose samples and the eucalyptus samples with a lower degree of polymerization (series E_1). A smaller enthalpy increase was found in the case of the eucalyptus samples with a higher degree of polymerization (series E_2), which are structurally more stable, when after 45 minutes of alkalization only a small decrease in the degree of crystallinity was determined. There are various values of the dehydration enthalpy in the literature [14, 15].

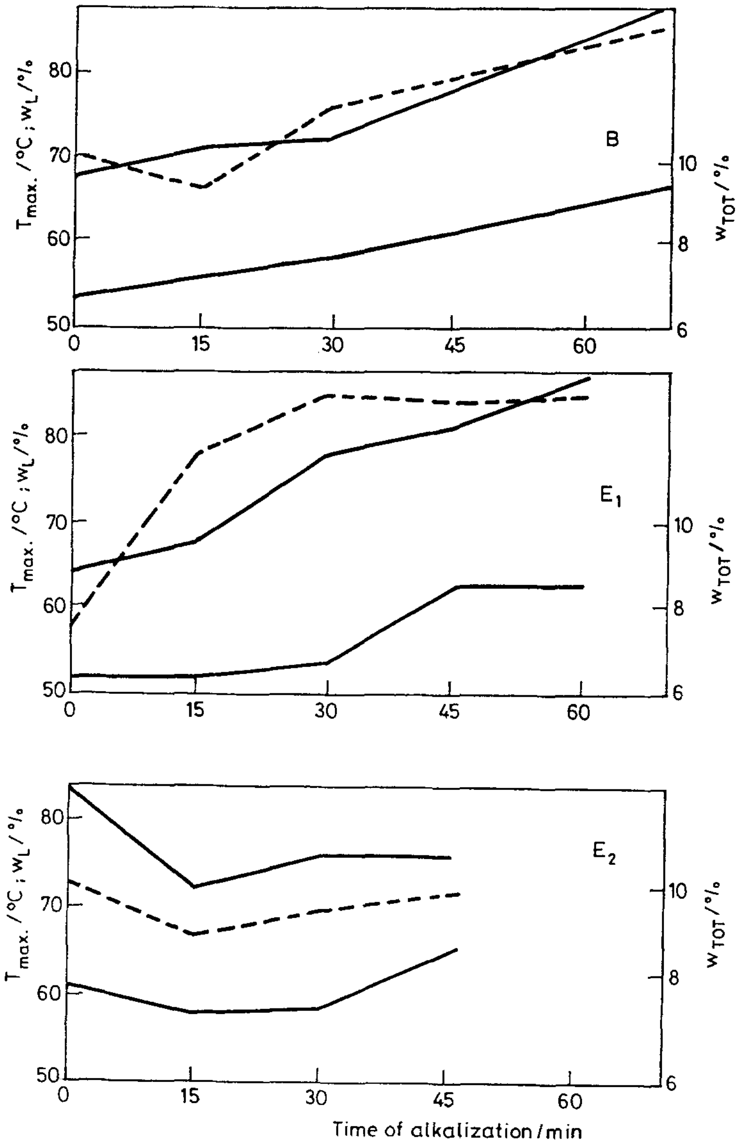

Fig. 2 The total bound water (W_{TOT}), the 'free water' (W_L) and the temperature of maximal water evolution rate (T_{max}) as a function of 'prehistory' of the samples (alkalization time)

The endothermal effects of the degradation of the investigated samples at temperatures greater than 180°C were not analysed because of a strong shift in the baseline which occurs with the onset of degradation, thus complicating the calculation and bringing into doubt the reliability of the results obtained.

Conclusions

On the basis of all the results obtained by TG and DSC, which were applied to follow the structural transformations of cellulose samples of different origin and various histories, the following conclusions may be drawn:

By TG measurements in the region of water evolution from cellulose samples, it is possible, on the basis of the shapes of the curves, to separate the amounts of water which evolve at various rates, i.e. at various temperatures.

Depending on the degree of structural transformation a shift towards higher temperatures was registered in the temperature of the maximal water evolution rate, as well as an increase in the amount of water bound by weaker bonds to the sorbent cellulose. This fraction of water attains its highest values when the cellulose is completely transformed to the cellulose II form.

Starting from samples of cellulose I structure to samples completely transformed to cellulose II, the dehydration energies ranged from 33 to 62.3 $kJ \cdot mol^{-1}$ while the dehydration enthalpies varied from 113.4 to 207.9 J/g.

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Zusammenfassung — Die thermischen Eigenschaften von Zelluloseproben unter-schiedlicher Struktur wurden untersucht. Die Proben wurden durch Einwirkung von ethanolischen Hydroxidlösungen auf Zellulose hergestellt. Die Intensität der Zellulos-eumwandlung ist abhängig von der Einwirkungszeit der alkalischen Lösung. Ausgehend von der Zellulosestruktur I mit dem höchsten Kristallinitätsgrad bestehen die anderen Proben aus einem Strukturengemisch aus Zellulose I und II oder werden vollständig in die Zellulosestruktur II mit dem niedrigsten Kristallinitätsgrad umgewandelt. Das ther-mische Verhalten der Proben wurde mit Geräten vom Typ Perkin Elmer TGS-2 bzw. DSC-2 durchgeführt. Die kinetischen Parameter der Dehydratation und der Spaltung wurden anhand nichtisothermer TG-Daten (inerte Stickstoffatmosphäre, Aufheizgeschwindigkeit 20 K/min) ermittelt. Der thermische Effekt der Wasserfreisetzung (Aufheizgeschwindigkeit 80 K/min) der Zelluloseproben ist eine Funktion ihrer Struktureigenschaften und ihrer Kristallinität. Aktivierungsenergie und Frequenzfaktor stehen in Übereinstimmung mit den strukturellen Veränderungen.