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THE INFLUENCE OF POLYVALENT CATIONS ON THE THERMOSTABILITY OF CELLULOSE

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The influence of some polyvalent cations on the thermostability of cellulose was investigated using both conventional TG analysis and quasi-isothermal treatment at elevated temperatures. It was established that ions of copper, cobalt and iron absorbed in the cellulose fibre surface accelerated the thermal decomposition of cellulose chain molecules, the temperature of the main decomposition decreasing very significantly. Lewis acid type additives (such as $ZnCl_2$) promote the hydrolytic decomposition and hence the temperature of the post-decomposition increases compared with that of the blank sample. Ions of alkaline earth metals (Ca and Ba) do not affect the thermal behaviour of cellulose fibres. From the results of the quasi-isothermal experiments the apparent energy of activation for the decomposition of cellulose in the presence of metal ions was calculated.

There are many papers dealing with the problems of the thermal analysis of cellulose [1–3]. It has been shown that the positions of the peaks in the DTG and DTA curves, as well as the course of the TG curve, greatly depend on the origin of the sample [4], its treatment [5], the heating rate [6], the quantity of sample and the atmospheric conditions in which the thermal analysis is performed [7].

Besides these, the positions and shapes of the peaks in the curves depend on the nature and quantity of the impurities in the cellulose. In the majority of the publications, comparatively high quantities of mineral additives were investigated [8–9].

During the utilization of cellulose in either chemical converting or paper production, in some steps of the technology small amounts of impurities, primarily metal ions dissolved in the process water, might be absorbed on the cellulose fibre surface.

The effects of such small quantities of contaminants on various properties of cellulose have already been dealt with. It was found for example that iron(III) ions in the process water may catalyze the alkaline degradation of rayon cellulose [10], spoil the brightness of paper grade cellulose very significantly [11] and accelerate side-reactions during bleaching [12].

Ions of iron, copper and manganese absorbed on cellulose can accelerate the yellowing and ageing of paper [13] and also promote the catalytic oxidation of SO_2 in the air, the SO_3 formed reacting with water always present in paper to give H_2SO_4, which causes the rapid deterioration of the paper [14].

The present report deals with the effects of some cations, absorbed from the process water or existing in the cellulose ash, on the pyrolysis of cellulose, using the method of thermogravimetry; the depolymerization of cellulose due to these cations during isothermal treatment at 100 – 190° is also investigated.

Experimental

The examined metal ions were divided into three groups. The first group contains those cations which, due to their polyvalency, are capable in our opinion of playing the role of oxygen-transferer and can accelerate oxidative processes: Fe^{3+}, Cu^{2+} and Co^{2+}.

The second group contains ions, the chlorides of which are Lewis acids and can promote dehydration processes: Ti^{4+}, Al^{3+} and Zn^{2+}.

The third group contains the ions of Ba and Ca, which increase the thermostability of cellulose. All of the cations investigated were used in the form of their chlorides, in concentrations of $10^{-3} - 10^{-1}$ mol/l. A paper made from sulphate spruce pulp beaten to 40°SR was used. (In paper terminology beating means the enlarging of specific surface of fibres in order to improve strength properties of paper. The unit of beating is the degree of Schopper – Riegler which varies between 0 – 100. In this respect 40°SR means a medium beaten pulp.) Paper strips were soaked in the salt solutions of appropriate concentration (0.2 g paper per 100 cm^3 solution). After a few minutes of soaking the paper strips were removed from the solutions, pressed between blotters and then dried in an oven at 105°. The amount of cations in the paper was determined by conventional analytical methods. Thermal analysis of the samples was carried out on the Paulik – Paulik – Erdey derivatograph system (MOM). Two series of experiments were made. In the first run the measurement was made under the following conditions: TG: 200 mg, v: 10°/min. In the second run the conditions were as follows: TG: 20 mg v: 5°/min. Ceramic crucible was used. The reason for the two different sample masses was that the higher sample mass (about 200 mg) was suitable for investigation of the endothermic processes, while the lower sample mass (about 20 mg) and the lower heating rate were suitable for investigation of the exothermic processes in analysis of the DTA curves [1].

Quasi-isothermal treatment of the samples in the range 100 – 190° was carried out in an oven. The average DP of the thermally treated samples was calculated from viscosimetric data of cellulose solutions in Cuen.

Results

The decomposition of cellulose containing different kinds of cations began at 80°, when the absorbed water was eliminated. This can be seen in the TG and DTG curves.

After water elimination, the decomposition of cellulose occurred in one step. The initial temperature of the intensive decomposition and the temperature corresponding to the maximum decomposition rate depend to a great extent on the nature of the cations in the cellulose.

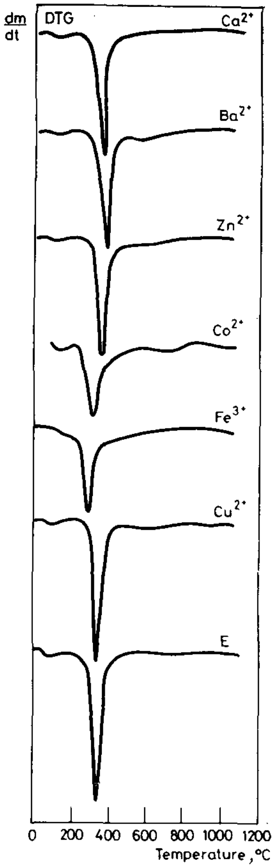

Fig. 1. DTG curves of cellulose treated with metal chlorides. E: untreated sample

The shapes of the DTG curves in the case of different cations can be seen in Fig. 1. From an analysis of the curves it can be stated that the polyvalent cations cause the temperature corresponding to the maximum rate of decomposition to decrease significantly. The temperatures of decomposition calculated from the DTG curves, the amounts and natures of the cations, and the temperatures of the endothermic peaks in the DTA curves are shown in Table 1. From these data it can be seen that polyvalent cations capable of playing the role of oxygen-transfer agents decrease the temperature of decomposition, i.e. the thermostability of the cellulose.

Table 1

Effects of cations on the characteristics of decomposition of cellulose (170 – 180 mg)

Sample	Amount of cation g atom/g × 10^{-5}	In DTG curve		In DTA curve
		beginning of decomposition, °C	temperature of decomposition peak	temperature of endothermic peak, °C
Original sample	—	295	325	350
Sample treated with distilled water	—	260	340	320
Fe^{3+} treated sample	5.46	200	245	—
Cu^{2+} treated sample	6.22	265	310	315, 360
Co^{2+} treated sample	9.24	210	275	—
Zn^{2+} treated sample	6.34	260	305	315
Ca^{2+} treated sample	7.06	260	320	330
Ba^{2+} treated sample	7.10	280	330	325

For example, while the beginning of decomposition in the case of an untreated sample is 295° for a sample extracted with distilled water this value is 260°, in the case of Fe^{3+} it is 200°, in the case of Cu^{2+} it is 265° and in the case of Co^{2+} it is 210°. With samples containing Zn^{2+}, Ca^{2+} and Ba^{2+}, the temperature of initial decomposition did not change. Similarly, the temperature corresponding to the maximum decomposition rate changed very significantly: in the case of Fe^{3+} this

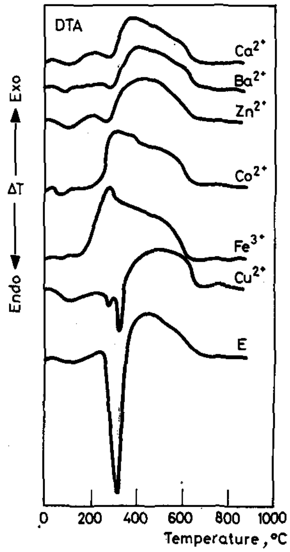

Fig. 2. DTA curves of cellulose treated with metal chlorides. E: untreated sample

temperature was lower than for the untreated sample by 80°, in the case of Cu^{2+} by 15°, and in the case of Co^{2+} by 50°. Zn^{2+} decreased the temperature by 20°, while with Ca^{2+} and Ba^{2+} no changes were observed. The shapes of the DTA curves are shown in Fig. 2.

It can be seen that the well-developed endothermic peak in the DTA curve of the original sample changes its position and size, and even disappears, on the action of the examined cations. The temperatures corresponding to the endothermic peaks are given in Table 1.)

Analysis of the data in Table 1 reveals that in the presence of Zn^{2+}, Ca^{2+} and Ba^{2+} the temperature of the endothermic decomposition reaction decreased; in the case of Cu^{2+} the reaction took place in two steps, at 310° and 360°; while in the case of Fe^{3+} and Co^{2+} no endothermic peaks can be observed. In the investigation of small amounts of samples (18 – 22 mg) in accordance with the literature data two exothermic peaks occur in the DTA curves. The curves recorded in the above experiment are shown in Fig. 3.

The curves show that the cations investigated change not only the temperatures but also the rates and intensities of the two decomposition processes (main decomposition at 300 – 340° and post-decomposition at 400 – 450°.

The temperature of the two exothermic peaks in the DTA curves obtained with small sample weights are given in Table 2.

From the data in Table 2, it can be stated that the temperature of the main decomposition step changes to a smaller extent than the temperature of the post-decomposition process. The untreated sample undergoes the main decomposition reaction at $T_1 = 320°$, the biggest changes to this value being $-15°$ in the case of Fe^{3+} and $+15°$ in the case of Ba^{2+}. Metal ions which are able to catalyze the oxidation decrease the maximum rate of the post-decomposition reaction (T_2) by 25 – 50°, whereas Zn^{2+}, which catalyzes dehydration, increases T_2 by 20°.

The original ratio of the exothermic peaks corresponding to temperatures T_1 and T_2 is not changed in the case of Ca^{2+} and Ba^{2+}, is decreased by Fe^{3+} and Co^{2+}, and is increased by Cu^{2+} and Zn^{2+}.

The thermogravimetric investigations demonstrate that addition of a small amount of different polyvalent cations to cellulose can change the mechanism and kinetics of its thermal decomposition.

The temperatures of dehydration and depolymerization (which compete with each other in the main decomposition process), the rate of decomposition and the thermochemistry of the process all depend on the nature of the cations added to the cellulose. From the points of view of the thermostability and thermal ageing of cellulose and paper, the ions of Fe, Cu and Co are of great significance.

Hence, cellulose treated with chlorides of these metals was subjected to thermal treatment at 100 – 190° and the rate of the depolymerization reaction was measured. The change in the average DP with the temperature and duration of the treatment is shown in Table 3. It can be observed that the DP changes more significantly when the cellulose is treated with cations able to play the role of oxygen-transferer. This can be explained by the decrease of the thermal stability of the glycosidic bond, due to oxidation of the secondary hydroxyl groups on carbon atoms C_2 and C_3 of the pyranosic ring, and the possibility of depolymerization therefore increases.

From the data in Table 3 it can be seen that the catalytic action of Fe^{3+} is the highest, Cu^{2+} and Co^{2+} being somewhat less active. The changes in the DP de-

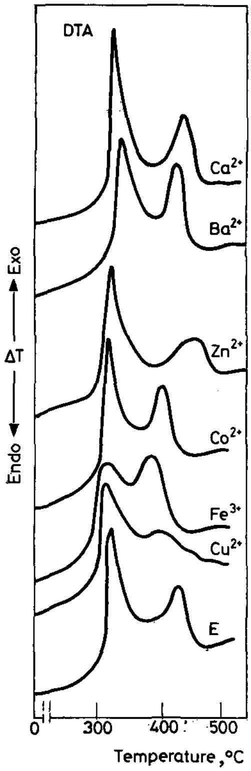

Fig. 3. DTA curves of treated cellulose in the case of a small sample mass (18—22 mg)
E: untreated sample

Table 2

Temperatures of exothermic peak in DTA curve in the case of low sample mass (18—22 mg)

	Original sample	Ion used to treat sample					
		Fe^{3+}	Cu^{2+}	Co^{2+}	Zn^{2+}	Ca^{2+}	Ba^{2+}
Temperature of main decomposition (T_1) °C	320	305	325	315	310	325	335
Temperature of post-decomposition (T_2) °C	430	380	405	405	450	435	415

Table 3

Change* in average DP on thermal treatment in the cases of different metal ions

Sample	Temperature and duration of treatment, °C/h					
	untreated	100/24	130/8	130/16	160/6	190/2
Original	1060	1020	970	920	770	640
Co^{2+}-treated	1060	930	840	730	610	530
Cu^{2+}-treated	1060	800	680	580	490	460
Fe^{3+}-treated	1060	720	580	520	440	390

* DP values are the average values for two samples rounded to the nearest ten.

Table 4

Rate constants of depolymerization reaction in the presence of different metal ions in the temperature range 100 – 190°

Metal ion	$k \times 10^{-6}$			
	100°	130°	160°	190°
–	1.16	9.8	57.0	305
Co^{2+}	5.00	26.5	110.0	467
Cu^{2+}	12.30	55.0	181.0	610
Fe^{3+}	18.40	71.7	220.0	805

monstrate that after thermal treatment for 16 hours at 130°, for example, the DP of the original sample was 920, while in the presence of Fe^{3+}, Cu^{2+} and Co^{2+} this value is only 520, 580 and 730, respectively.

This drop in the DP is very significant if it is taken into account that it was brought about by metal ions in concentrations of only $5-9 \cdot 10^{-5}$ g-ion/g-cellulose.

The data in Table 3 were used to calculate the rate constants of the depolymerization by the method of Battista [15]. The values of the rate constants are given

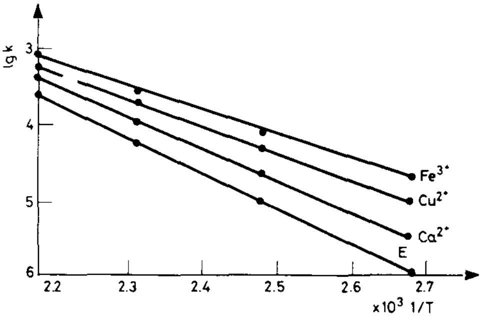

Fig. 4. Rate constants *vs.* $1/T$ for original and treated samples. E: untreated sample

in Table 4. It can be seen that in the presence of metal ions the rate constants were very significantly increased at each temperature.

Plots of the rate constants *vs* $1/T$ according to the Arrhenius equation yielded the curves in Fig. 4, from the slopes of which the apparent energy of activation was calculated. Similarly, the energy of activation was calculated from the H factors by the method of approximation [16]. In this method the most probable value of the activation energy is where the coefficient of variation of the standard deviation (V %) is the smallest, i.e. where the function $V \% = f(E)$ has its minimum (see Fig. 5). The activation energy values calculated by the two different methods (Table 5) are very near to each other.

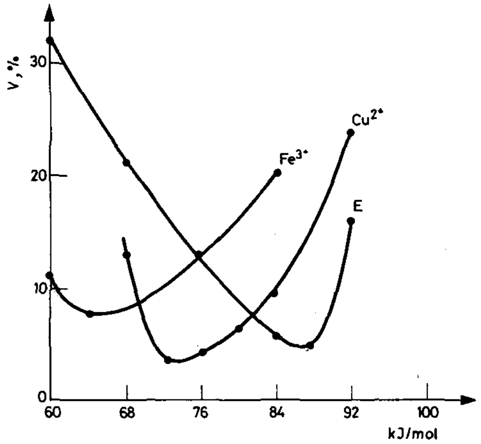

Fig. 5. Coefficients of variation (V%) *vs*. energy of activation for original and treated cellulose. E: untreated sample

The data in Table 5 definitely reveal the catalytic action of the metal ions. The energy of activation in the case of untreated sample is 87.8 kJ/mol; after treatment with Co^{2+}, this decreases to 73.2 k,/mol, and after treatment with Cu^{2+} or Fe^{3+}

Table 5

Apparent activation energy of depolymerization (E)

Metal ion in sample	Activation energy (E), kJ/mol	
	from Arrhenius equation	from H-factor
—	87.8	86.6
Co^{2+}	72.0	73.2
Cu^{2+}	62.0	62.7
Fe^{3+}	60.2	62.7

to 60–63 kJ/mol. The decrease in the activation energy definitely indicates catalysis.

Since the structural-mechanical properties of a paper are in close correlation with, among others, the average DP of the cellulose fibres, it can be assumed that the strength properties responsible for the durability of paper are spoiled to the same extent in the presence of the above-mentioned cations. For this reason, cations able to form a redox system and adsorbed on cellulose may decrease not only the thermostability but also the durability of paper.

References

1. G. A. Petropavlovszkij and G. H. Mihajlov, Cell. Chem. and Techn., 6 (1972) 213.
2. B. Philipp, J. Baudisch and H. Ruscher, TAPPI, 82 (1969) 693.
3. C. D. Kay, Forest Prod. J., 18 (1969) 71.
4. M. Kosik, V. Reiser and I. Michlik, Papir a Celuloza, 28 (1973) 29.
5. J. Györe and S. Faragó, Magyar Kém. Folyóirat, 81 (1975) 36.
6. N. Hurduc, I. A. Schneider and Cr. Simionescu, Cell. Chem. and Techn., 2 (1968) 569.
7. O. P. Golova and R. G. Krilova, Dokl. AN SSSR, 116 (1957) 419.
8. O. P. Golova, Uspk. Khim., 44 (1975) 1454.
9. W. K. Jany and W. K. Neill, J. Pol. Sci., C6 (1964) 65.
10. D. M. MacDonald, TAPPI, 48 (1965) 708.
11. S. Hernádi, Papíripar, 14 (1970) 8.
12. J. H. E. Herbst, TAPPI, 45 (1962) 833.
13. T. P. Cziepel, TAPPI, 43 (1960) 289.
14. W. H. Langwell, TAPPI, 38 (1955) 190A.
15. O. A. Battista, Ind. and Eng. Chem., 42 (1950) 502.
16. A. Hernádi, Svensk Papperstidn., 79 (1976) 418.

Résumé — L'influence de plusieurs cations polyvalents sur la stabilité thermique de la cellulose a été étudiée par TG conventionnelle et traitement quasi-isotherme à températures élevées. On a établi que les ions cuivre, cobalt et fer adsorbés à la surface de la fibre de cellulose accélèrent la décomposition thermique des molécules de la chaine de cellulose et que la température de la décomposition principale diminue de manière très appréciable. Les additifs du type acides de Lewis (comme $ZnCl_2$) facilitent la décomposition hydrolytique et c'est pourquoi la température de la décomposition ultérieure augmente, comparée à celle du témoin. Les ions alcalino-terreux (Ca et Ba) n'exercent pas d'action sur le comportement thermique des fibres de cellulose. A partir des données obtenues par les examens quasi-isothermes on a calculé l'énergie d'activation apparente de la décomposition de la cellulose en présence d'ions métalliques.

Zusammenfassung — Der Einfluß einiger mehrwertigen Kationen auf die Temperaturbeständigkeit von Zellstoffen wurde unter Anwendung der konventionellen Thermogravimetrie und der quasi-isothermen Behandlung bei höheren Temperaturen, untersucht. Es wurde festgestellt, daß an der Oberfläche der Zellstoff-Faser adsorbierte Kupfer-, Eisen- und Kobalt-Ionen die thermische Zersetzung der Kettenmoleküle des Zellstoffes beschleunigen, wodurch die Temperatur des Hauptvorganges wesentlich herabgesetzt wird. Zusätze vom Typ der Lewis-Säuren(z.B. $ZnCl_2$) begünstigen die hydrolytische Zersetzung, wodurch die Temperatur nach der Zersetzung im Vergleich mit der Blindprobe ansteigt. Die ionender Erdalkalimetalle (Ca und Ba) haben keine Wirkung auf das Verhalten von Zellstoff-Fasern. Aus den Ergebnissen der quasi-isothermen Behandlung wurde die scheinbare Aktivierungsenergie der Zellstoffzersetzung in Anwesenheit von Metallionen berechnet.

Резюме — С помощью обычного ТГ анализа и квазиизотермической обработки при повышенных температурах исследовано влияние некоторых многовалентных катионов на термоустойчивость целлюлозы. Установлено, что адсорбированные на поверхности целлюлозного волокна ионы меди, кобальта и железа ускоряют термическое разложение цепных молекул целлюлозы и при этом температура главного процесса разложения значительно понижается. Добавка льюисовских кислот (например, $ZnCl_2$) ускоряет гидролитическое разложение, вследствии чего температура последующего разложения увеличивается по сравнению с образцом сравнения. Ионы щелочно-земельных металлов (Ca и Ba) не оказывают влияния на термическое поведение целлюлозных волокон. На основании данных квазиизотермических измерений вычислена кажущаяся энергия активации реакции разложения целлюлозы в присутзтвии ионов металлов.