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Cellulose sorbents obtained by the action of Lewis acids

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Abstract - An investigation has been carried out of the mechanism of the destruction of cellulose in anhydrous media in the presence of aprotic acids, such as $TiCl_4$, $SbCl_5$, $SnCl_4$, $AlCl_3$, of the type (MX_n) [1]. This enables us to determine the conditions for the formation of cellulose with a maximum degree of polymerization. On the basis of these results methods have been developed for producing a new type of cellulose powder modified by Lewis acids. This cellulose is different from that obtained by hydrolysis to a maximum degree of polymerization in the presence of protic acids as the catalyst. The difference lies in the complex structural nature of the cellulose powder.

Cellulose powder (CP), modified by Lewis acids in the thermocatalytic destruction process with aprotic acids of the type MX_n ($TiCl_4$, $SbCl_5$, $SnCl_4$, $AlCl_3$, etc) in organic solvents [1, 2], differs from microcrystalline (MC) cellulose obtained by hydrolysis to a maximum degree of polymerization in the presence of protic acids. The difference consists in the complex structural characteristics of CP.

Scanning electron microscopic studies of CP have shown the presence of numerous deep fissures in and transverse fractures of the fibers (Fig. 1). The surface of the fibers has only a weakly defined structure; the separation of fibers into more elementary formations are not typical. The fracture site is as a rule in an irregular tapered form characteristic of a brittle destruction.

This makes it possible to describe the destruction process on the basis of the mechanism of polymer destruction due to the external load. Such destruction involves the simultaneous fracturing of numerous glucoside bonds through all the sections of the fiber. According to a widely held concept, the fracturing of macromolecules under the action of a mechanical load results from the accumulation of a critical concentration of thermal energy acting on the chemical bond (the thermofluctuation hypothesis [3]). Since under the conditions of thermocatalytic destruction the external mechanical load is absent we can assume that the internal stretching serves as a source of stress. This stress lowers the energy barrier of the degradation process in the macromolecule. The internal stretching can be explained as follows.

As is known, the crystalline and amorphous zones in cellulose differ in their thermophysical properties. The amorphous zones have greater heat capacity and entropy owing to the greater mobility of the elementary linkages as compared with the crystalline zones. But since the supermolecular structure of cellulose is characterized lengthwise by a regularly alternating ordered and disordered zones, the same macromolecule can cross several zones with different thermophysical characteristics.

It is also known that cellulose has a negative coefficient of longitudinal thermal expansion [4]. In view of the entropy nature of the resilience of elastic polymers, the negative coefficient of thermal expansion can be regarded as a result of the transverse and at the same time longitudinal compression of zones due to an increase in the conformational mobility of interatomic linkages with an increase in temperature. It can be assumed that the longitudinal compression of the amorphous zones is the internal source of the resultant stresses. These stresses act on the glucoside linkages of the macromolecules passing through in the adjacent regions of the crystallites. The stresses weaken the glucoside bonds. This facilitates their fracture as a result of the simultaneous action of thermal fluctuations and coordination of the active centers in the macromolecules with the acidic reagents.

Local fractures of fibrils within a bundle of macromolecules can be considered to be submicroscopic cracks. These cracks are analogous to fractures in the macromolecules caused by external mechanical stresses. These defects do not yet give rise to macroscopic effects of the brittle destruction of the primary cellulose fibers which we have observed during our electron microscopic investigation of the samples (Fig. 1). On the analogy of the kinetic theory of mechanical destruction of solid bodies we can assume that the thermocatalytic destruction of the cellulose fibers is caused by the progressive accumulation of submicroscopic cracks until they reach a critical concentration. Following this the cracks merge into larger cracks which led to the fracturing of fibers along the traverse cracks [3].

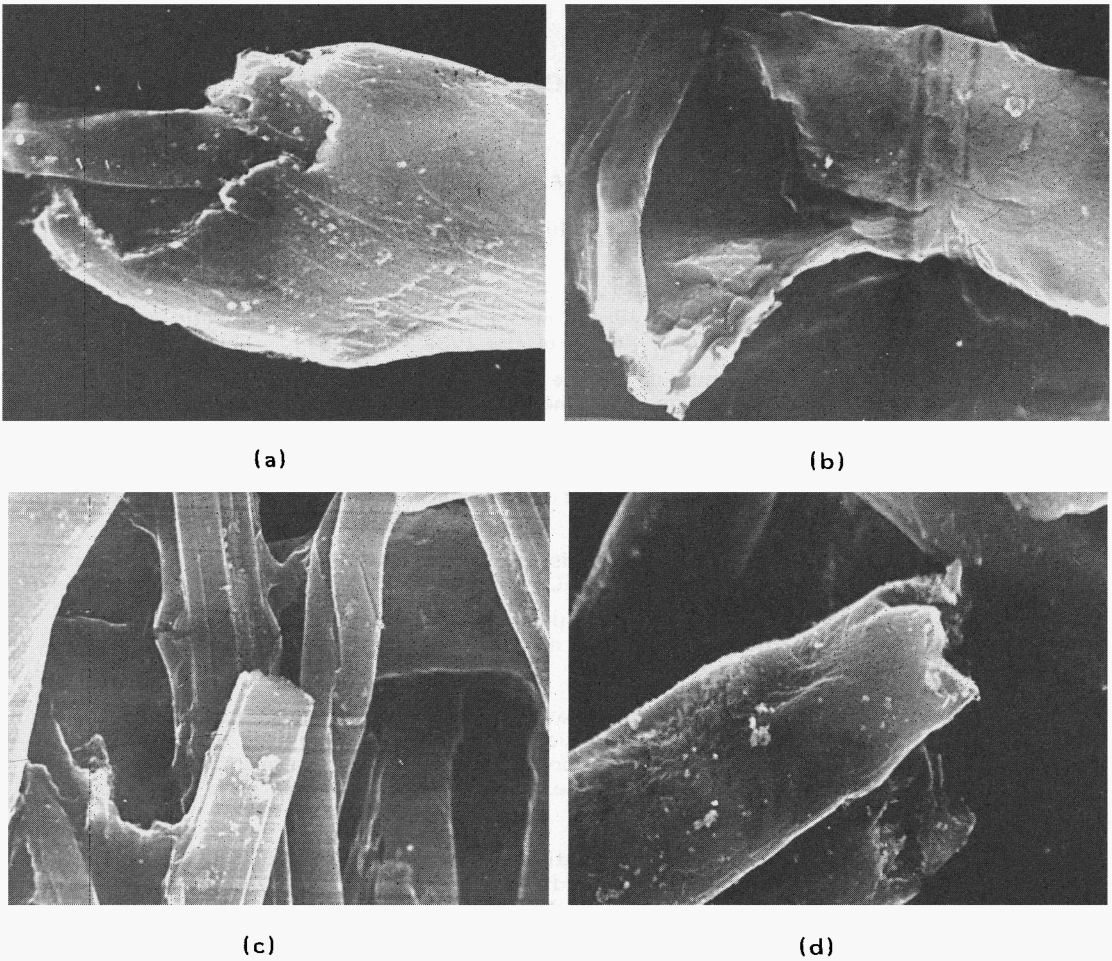
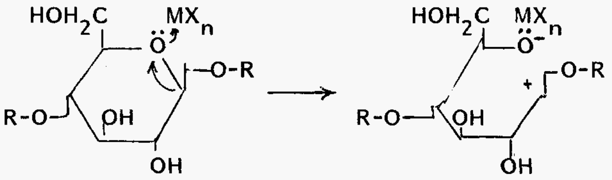


Fig. 1 Fractured fragments of fibers. Scanning electron microscope:
a - CP-$SbCl_5$ (x5230); c - CP-$TiCl_4$ (x2070)
b - CP - $AlCl_3$ (x4190) d - CP-$SnCl_4$ (x5230).

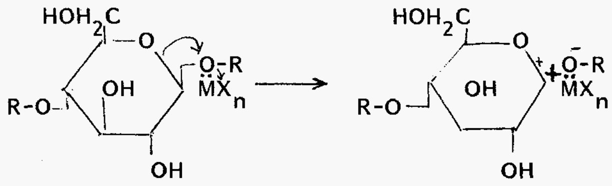
By examining the thermodestruction of cotton cellulose in the presence of $TiCl_4$ by the low-angle x-ray scattering method we have analyzed the accumulation dynamics of microcracks having dimensions of the order 90-100 Å. We have found that the concentration of the pores increases linearly with time. Our observations accord with the situation of the general destruction of polymers under external stresses.

The mechanism of the destructive reaction of cellulose macromolecules in the presence of Lewis acids can be described as the coordination of the central oxygen atom in the acid with the semi-acetal (cyclic or glucoside) oxygen atom. This results in the formation of donor-acceptor bonds owing to the vacant orbital in the central oxygen atom and unpaired electrons of the oxygen atoms. As a result the carbon-oxygen bond becomes weaker and the fracturing of the bond takes place:

I



II



In this, according to variant I of the reaction the first carbon atom changes into a carbonium ion, and according to variant II a fracturing of the glucoside bond takes place at the same time, leading to the destruction of the macromolecular chain.

The formation of the MX_n-cellulose complex is indirectly confirmed by a small increase in the original mass of the cellulose. This increase has been observed in all cases following the removal of an excess of the catalyst by washing the sample. If such cellulose is subjected to heat treatment at 80-100 °C, the magnitude of the average degree of polymerization (DP_{av}) of these samples decreases considerably as compared with the sample that has been dried at 20 °C; in other words, the sample undergoes destruction (cf., Table 1).

TABLE 1. Changes in DP_{av} caused by the drying temperature (the samples were kept for 5 min in 0.1% MX_n solution followed by washing off an excess of the catalyst)

T(°C)	The average degree of polymerization (DP_{av})		
	$SnCl_4$-C_6H_{14}	$AlCl_3$-CCl_4	$TiCl_4$-CCl_4
20	1800	1390	1040
105	200	320	240

This destruction can be attributed to the preliminary formation of a Lewis acid-cellulose complex. An infrared spectral analysis shows the appearance of absorption bands which can be attributed to the formation of oxygen-metal bonds. Thus, the infrared spectra of cellulose samples destroyed in the presence of $TiCl_4$ are found to contain absorption bands at 1100-1000 cm^{-1} due to the C-O-Ti bond.

As a result of such a treatment we obtain cellulose in the form of a powder whose characteristics are summarized in Table 2.

TABLE 2. Some properties of cellulose obtained by thermocatalytic destruction in the presence of different Lewis acids

Lewis acid	DP_{av}	Fraction with DP<200 (%)	Moisture content (%)	Ash content (%)	COOH-group (%)	CO-group (%)
$TiCl_4$	110	100	4.1	0.34	0.69	0.48
$SbCl_5$	120	100	5.2	0.32	0.65	0.45
$SnCl_4$	130	97	4.1	0.34	0.54	0.42
$BF_3 \cdot O(Et)_2$	130	100	4.4	0.04	0.18	0.38
$AlCl_3$	150	95	5.1	0.31	0.12	0.24

The degree of crystallinity of cellulose powder decreases somewhat in comparison with the starting material. It is considerably less than in cellulose powder obtained by the hydrolytic method (Table 3).

After using three different methods for determining the degree of crystallinity we can conclude that during the destruction of cellulose in the presence of Lewis acids there is a noticeable degree of amorphousness of the ordered regions in the cellulose. One of the causes of this phenomenon may be the diffusion of the complex-forming agent into the polymer crystallite and the cross-linking of macromolecules along the formed carbonium ions.

The partial change of the cellulose powder into an amorphous state due to the action of Lewis acids is also indicated by the change in the form of 002 reflex and a decrease in its intensity.

TABLE 3. Crystallinity of cellulose powder

Sample	Degree of crystallinity (%)		
	x-ray diffraction (%)	IR spectrum (D_{2900}/D_{1375})	absorption of iodine (%)
Original C	0.76	1.09	92
CP-$AlCl_3$	0.70	1.02	84
CP-$SbCl_5$	0.68	0.97	82
CP-$TiCl_4$	0.65	1.02	81
CP-$SnCl_4$	0.62	0.91	79

TABLE 4 **Some characteristics of cellulose powder according to x-ray diffraction analysis**

Sample	Crystallite dimensions (Å)	Pore size (Å)		Concn. of pores ($N \cdot 10^{13}$ cm^{-3})	
		large	small	large	small
CP-$SnCl_4$	71	191	77	57	3676
CP-$TiCl_4$	77	196	101	312	2541
CP-$AlCl_3$	67	221	97	163	1816
CP-$SbCl_5$	83	202	95	80	870
MC	56	197	100	60	558
Original C	90	186	90	21	265

The total concentration of the ordered portion of the fibers remains at the original level or somewhat below it (the Nelson-O'Connor index; cf., Table 3).

The obtained true dimensions of the crystallites (cf., Table 4) make it possible to conclude that in the presence of Lewis acids the reaction of cellulose along the glucoside bonds destroys the cellulose crystallites to a lesser degree as compared with hydrolysis in the presence of hydrochloric acid: the dimensions of the crystallites are only 3-14% smaller than the original ones; while for MC samples they are smaller by 22%. These results are also confirmed by the relatively small amount of water-soluble fraction formed (2-5%) versus the 10% weight loss in the case of hydrolytic destruction.

A comparison of the modified cellulose samples and MC samples by the low-angle x-ray diffraction method (Table 4) shows that the dimensions of the micro- and submicrofissures, capillaries and pores are practically identical. At the same time the concentration of the pores in CP samples is 2-6 times greater than the porosity of the MC samples. We believe that the difference in the degree of porosity of cellulose powders is due to the difference in the ability of Lewis acids to penetrate deep into the cellulose fibers. And consequently, the difference is due to the number of transverse cross links formed by the coordinational reaction between the central atoms of the Lewis acid and the oxygen atom in the polymer chain, as well as to the establishment of bonds with the carbonium ions formed in the course of destruction.

The disturbance of the crystal lattice, the formation of a developed system of micro- and submicro-capillaries, pores and fissures provide a high internal specific surface area of the cellulose powders produced. In Table 5 are summarized data on the specific surface area of samples which have been obtained by the gas-chromatographic method from the retention time of n-hexane vapors and by the adsorption of benzoic acid from heptane solutions. A MC sample served as the standard. It was found that under the conditions of an additional treatment [6] the surface of modified cellulose powders in some cases reaches >500 m^2/g.

TABLE 5. Specific surface area and the absorption ability of cellulose powder

Sample	Specific surface area (m^2/g)		
	x-ray diffraction	gas-chromatographic	sorption of benzoic acid
CP-TiCl$_4$	7.4	108	6.3
CP-SnCl$_4$	3.5	86	10.1
CP-SbCl$_5$	3.4	57	2.7
CP-AlCl$_3$	0.7	1.9	1.8
MC	1.5	1.8	1.0
Original C	0.6	1.7	-

The high porosity of modified cellulose powders results in their greater adsorption of the bromophenol blue as compared with the adsorption of the dye by the hydrolyzed cellulose.

A comparative study has been carried out of the separation capacity of thin layers of cellulose powders obtained by the destruction of cellulose in ethanol solutions of different Lewis acids and that of MC powders. The results show that the differences in the specific surface area of the cellulose powders practically have no effect on their separation capacity. All the sorbents with particles $\geqslant 0.1$ - $\leqslant 0.5$ mm in diameter provide a good separation of such amino acids mixtures as glycine-alanine-valine-leucine and alanine-phenylalanine-tyrosine-tryptophan. A good separation has been obtained also for the following mixtures: threonine-serine, glutamic acid-aminosuccinic acid, and arginine-lysine-histidine (the difference in R_f of these compounds is constant, being equal to approximately 0.09). Amino acids already on a single-run chromatographic separation appear as well-defined spots. The separation proceeds without the formation of the band-effect.

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