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POLYCONJUGATED SYSTEMS FORMED DURING THERMAL TREATMENT OF CELLULOSE

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ABSTRACT

By applying TA (DTA, TG) and ESR-, and IR-spectroscopies, the formation of the systems of polyconjugated bonds in cellulose during its heat treatment (at 20-400°C) was studied. The results indicated that the amount of polyconjugated blocks and their dimensions are increased with the rising temperature of treatment. The influence of phosphoric acid as the dehydration agent on the formation of polyconjugated systems was also studied.

INTRODUCTION

Cellulose thermochemical transformations in low-temperature stage (below 250°C), in general, are due to the dehydrations, including intramolecular reactions. As the result, dehydrocellulose is formed with increasing amount of C=O groups and double bonds sequences. The formation of paramagnetic centers (PMC) in the preparation is fixed begining with 200-250°C. By ESR spectrum (narrow singlet placed at about free electron g-value), these PMC can be attributed to polyconjugated systems (ref.1). It is noted that the formation of such PMC is activated by the presence of phosphoric and boric acids (ref.2,3).

It seems important to concretize the influence of fire-retardants on the formation and the development of polyconjugated systems in cellulose.

MEASURING METHODS

Sulphate cellulose "Taircell" (α-cellulose 98%, index of crystallinity 0.65) was used for the study. 5% of phosphoric acid was introduced into the cellulose in the amount of preparation at room temperature.

Thermal analysis was performed using a derivatograph "MOM" within the temperature range of 20-500°C in the nitrogen flow at heating rate of 5°C per minute. The thermal treatment of prepara-

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tions was carried out at the same conditions.

ESR spectra were investigated using a RE-1306 spectrometer. A diphenylpicrylhydrazyl was applied as standard (N_{st}= 4.5x10^{17}). Spin concentrations were calculated by double integration of the detected spectra.

IR spectra were recorded from the samples in the form of KBr tablets by UR-20 Zeiss (Jena) spectrometer.

RESULTS AND DISCUSSION

The isolation of volatile products of cellulose degradation begins at 240°C, and thermally initiated reactions proceed up to 300°C with exothermic effect (see Fig. 1). This is due to the formation of condensed structures as the result of dehydration reactions.

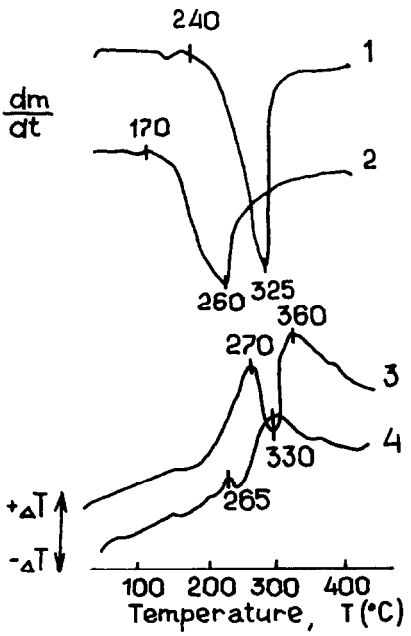

Fig. 1. DTG- (1,2) and DTA- (3,4) curves for the neat cellulose (1,3) and cellulose containing phosphoric acid (2,4).

By IR spectra of cellulose residues, the relative intensity of absorption band at 1630 cm^{-1} (conjugated C=C bonds) increased begining with the treatment temperature of 300°C (see Fig. 2a). However, the dimensions of conjugated regions at this stage are not enough for the stabilization of unpaired electrons: consider-

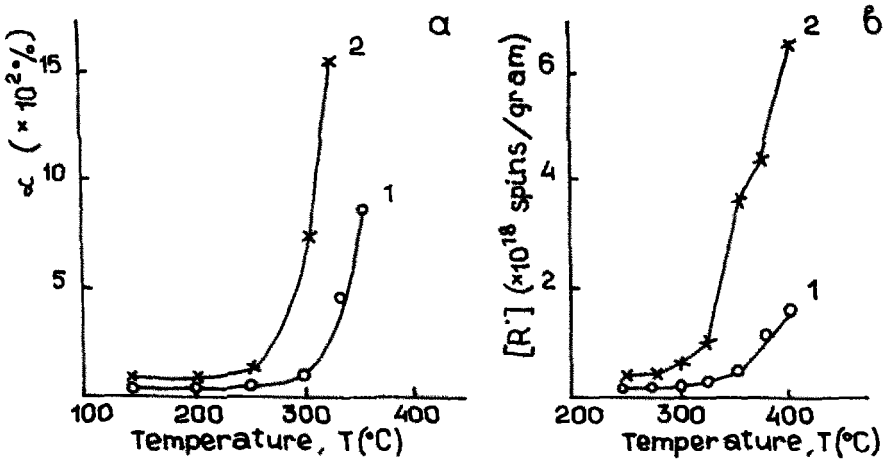

Fig. 2. A characteristic of cellulose residues after heat treatment. (a) The index α of relative intensity change for the absorption band at 1630 cm^{-1}. (b) Concentration [R'] of PMC. (1) Neat cellulose, (2) cellulose, containing phosphoric acid.

able increase of ESR signal intensity begins only at 350°C (see Fig. 2b), and, simultaneously, its line width decreases (see Table).

To characterize polyconjugated systems formed, the dimensions of the unpaired electron delocalization regions, i.e., "polyconjugated blocks", were estimated. The number of equivalent protons, n, interacted with unpaired electron can be defined as $n \geqslant 1 + (\Delta H_o / \Delta H_{ef})^2$,

where ΔH_{ef} = observed line width of ESR spectrum, and ΔH_o = the constant, corresponding to the interaction between p-electron and proton on the C-H fragment (~2.25 mT) (ref.4).

From the data obtained (see Table) it can be seen, that, up to 350°C, the delocalization region includes about 11 protons.

Within the temperature range of 350-400°C, condensation and aromatization reactions proceed. They are characterized by the exothermic effect (360°C) on DTA-curve (see Fig. 1). Up to 400°C, the polyconjugated block dimensions increase, about by 2 times, (see Table) with increasing PMC concentration by 20 times (see Fig. 2b), i.e., the formation of such PMC is more favourable at higher block dimensions (ref.3). Condensation and growth of aromatic clusters in the same temperature range are noted also in (ref.5).

Table
ESR spectra characteristics of cellulose residues

Sample	Treatment temperature (°C)	Line width (mT)	Number of CH groups in the polyconjugated block
Cellulose	250	0.7	11
	300	0.7	11
	350	0.7	11
	400	0.5	21
Cellulose + H_3PO_4	250	0.7	11
	300	0.65	13
	350	0.6	15
	400	0.55	18

The phosphoric acid accelerates cellulose dehydration and increases the intermediate structure thermostability. The degradation stage with the maximal rate of volatile products isolation shifts into the low-temperature range (see Fig. 1), when the yield of coke residue increases by 22%. The conjugated double bonds and paramagnetic polyconjugated blocks formation begins also at lower temperatures (see Fig. 2). However, up to 400°C, the polyconjugated block dimensions have the same values as those observed during neat cellulose treatment ($n \geqslant 18$ and $n \geqslant 21$). It may be attributed to the existence of an energetically stable configuration of polyconjugated block with dimensions restricted if compared to the length of cellulose macromolecule residue structure, as it was reported for synthetic polymers (ref.6).

REFERENCES

1 B. Milsch, W. Windsch, H. Heizelmann, Carbon 6 (1968) 807
2 T.N. Skripchenko, G.E. Domburg, V.V. Yurk"yan, in Wood-, Cellulose-, and Lignin-Based Carbon Materials. Abstracts of Barnaul Seminar, Barnaul 1983, 14
3 G.E. Domburg, G.A. Rossinskaya, G.V. Dobele, T.N. Skripchenko, V.V. Yurk"yan, R.V. Luksa, Khimiya drevesiny (to be published)
4 L.A. Blyumenfel'd, V.V. Voevodskii, A.G. Semenov, Application of Electronic Paramagnetic Resonance in Chemistry. Sibirskoe otdelenie AN SSSR, Novosibirsk 1962
5 F. Shafizadeh, I. Sekiguchi, Carbon 21 (1983) 511
6 G. Vansco, T.T. Nagy, B. Turcsanyi, T. Kelen, F. Tudos, Macromol. Chem. Rapid Commun. 3 (1982) 527