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THERMOOXIDATIVE DEGRADATION OF WATER-SOLUBLE ACETYLCELLULOSE AND ITS CARBOXY-CONTAINING DERIVATIVES

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The thermooxidative degradation of water-soluble acetylcellulose and some of its carboxy-containing derivatives has been studied by the methods of thermal analysis. A relationship has been established between the thermostability of the aceto-mixed derivatives and the nature of the substituting group.

During synthesis and processing, cellulose derivatives undergo various thermal actions. The study of their thermostability and the determination of the laws characterizing the influence of the functional groups present in mixed acetic esters of cellulose under the action of heat is therefore very important.

We have investigated the thermooxidative degradation of water-soluble acetocellulose (WSAC) and its water-soluble carboxy-containing derivatives, such as the acetomaleate (WAMC) and the acetophthalate (WAPC) and also acetocarboxymethylcellulose (WACMC) by thermogravimetry (TG), differential thermogravimetry (DTG), and differential thermal analysis (DTA).

WSAC with a degree of substitution by acetyl groups of $\gamma = 55$ was obtained by the homogeneous hydrolysis of highly substituted cellulose acetate [1]. WACMC was obtained by the acetylation of partially substituted carboxymethylcellulose with a degree of substitution of $\gamma = 5$, followed by hydrolysis to the water-soluble state [2]. WAMC containing 25% of bound acetic acid ($\gamma = 85$) and 5.0% of maleate groups ($\gamma = 15$) and WAPC containing 24% of bound acetic acid ($\gamma = 70$) and 9.5% of phthaloyl groups ($\gamma = 29$) were obtained by esterifying secondary acetylcellulose with the appropriate dibasic acid anhydrides followed by hydrolysis of the mixed esters, again to the water-soluble state [3].

When the WSAC was heated even at 40°C, a loss in mass began at the rate of about 1%/minute. As a result, the weight of the sample fell by 9—10%. The process was accompanied by a small endothermic effect (Fig 1, *a*). It is likely that the volatilization of sorbed moisture and low-molecular-mass products took place in this temperature interval.

In the temperature interval from 100 to 240°C there was a section of relative thermostability (SRT) of the sample, where there was no loss in weight and no heat effects.

At 240°C and above, a gradually accelerating second process of loss in weight began, at first accompanied by a small absorption of heat (up to 320°C the loss in weight in this section was 6%), and then exothermic degradation reactions superposed on one another with a maximum at 370°C. As a result of this process a loss in weight of the sample of the order of 55-60% took place at an overall rate of 6%/min. According to the available literature information, the degradation of cellulose in this temperature interval proceeds with the evolution of a number of liquid and gaseous products, of which the most frequently mentioned are levoglucosan and its derivatives, and various ethers and esters and also the products of their oxidation as far as CO, CO_2, and water.

The final combustion of the residue (about 20—30%) is characterized by a considerable decrease in the rate of loss in weight and by a considerable total exothermic effect with a maximum at 520°C. As a rule, this third process is a gradual oxidation of the coke residue of cellulose and its derivatives with the evolution of, mainly, CO and CO_2.

The thermograms obtained for the other acetylcellulose derivatives were compared with the thermograms of the WSAC.

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An investigation of WAMC showed that the first process was distinguished by a fall in the loss of weight to 6% at a rate of about 0.5%/min and ended at 120°C (Fig. 1, *b*), while, in contrast to WSAC, a slight loss in weight was observed over the whole SRT.

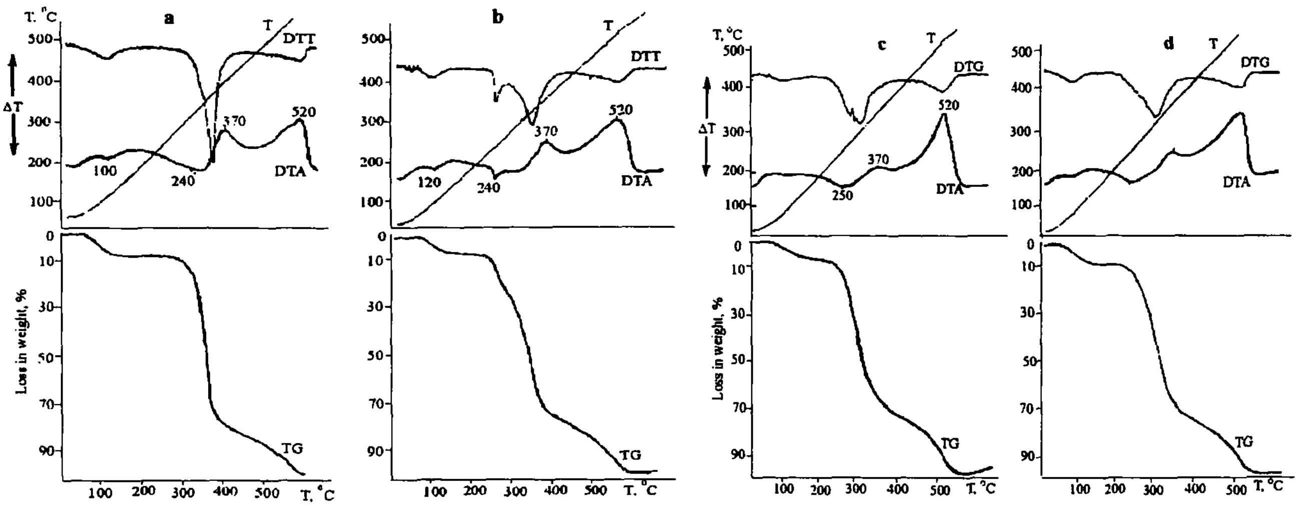

Fig. 1. Thermal analysis curves for WSAC (*a*), WAMC (*b*), WAPC (*c*), and WACMC (*d*).

The second process began at the same temperature, but, in contrast to the WSAC, there was a sharp boundary between the SRT and the second process, which began immediately with a sharp fall in weight (about 10%), accompanied by a considerable endothermic effect with a maximum at 250°C. After this effect (the sample continued to degrade) the rate of loss in weight decreased, which it was easy to see both in the exothermic stage of the second process and also in the third process, which, in general, were similar to these processes for WSAC but with some shift of their temperature characteristics towards higher temperatures. The observed differences can be explained by the influence of the unsaturated carboxy groups, which can take part in the cross-linking of the samples at elevated temperatures and thereby retard degradation. The formation of cross-linked structures was confirmed by the insolubility in water of the products of heat treatment. The endo-effect at 250°C could be caused by the dehydration or decarboxylation of the introduced carboxy groups.

In WAPC, as compared with WSAC, all the exo-effects were smoothed out and the passages from one process to another had no clear boundaries (Fig. 1, *c*). Thus, the first process passed smoothly into the second with almost no SRT. The endothermic effects accompanying the first and second (beginning) processes were extended in time, although their maxima coincided with those for WSAMC. The exothermic effect had decreased considerably (clear influence of phthalic acid as a consequence of thermooxidative stabilization) at the end of the second process. Because of this, the amount of carbonaceous residue and the exothermic effect of its combustion both rose. So far as concerns the WACMC, its temperature characteristics were almost identical with those of the WSAC (Fig. 1*d*).

Small differences were observed in a contraction of the temperature interval of the SRT to 200°C, the presence of an endothermic effect at the beginning of the second process, and the lower rate of loss in weight during the second process. These differences are probably a consequence of a slight additional cross-linking through carboxy groups, as noted above.

Thus, the thermooxidative stability of water-soluble cellulose derivatives depends on the nature of the introduced functional group. The smallest exothermic effect in the derivatives studied was observed when phthaloyl groups were present in the WSAC macromolecule.

EXPERIMENTAL

The thermal analysis of the samples investigated was conducted with a Paulik—Paulik—Erdey derivatographic system. The derivatograms were treated by a known procedure [4].

REFERENCES

1. G. A. Petropavlovskii and G. R. Rakhmanberdiev, Zh. Prikl. Khim., **39**, No. 1, 237 (1966).
2. G. R. Rakhmanberdiev, A. S. Sidikov, R. D. Yusupov, and Sh. S. Arslanov, Khim. Prir. Soedin., 102 (1977).
3. Sh. S. Arslanov, G. R. Rakhmanberdiev, A. S. Sidikov, and M. T. Mirkamilov, Uzbekistan Patent No. 9600158.1 (1996).
4. A. V. Obolenskaya, Z. P. El'nitskaya, and A. A. Leonovich, Laboratory Work in the Chemistry of Wood and Cellulose [in Russian], Ékologiya, Moscow (1991), p. 31.