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Note

STUDY OF THE INFLUENCE OF AMMONIUM SALTS ON THE REGENERATED CELLULOSE THERMODESTRUCTION

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A mechanism of the influence of different inorganic additions on the thermal destruction of polymers is undoubtedly of interest for solving various problems in science and technology. However, the literature provides limited and often contradicting data on the above subject for cellulose materials [1–4].

Therefore, the aim of the present paper was to reveal the peculiarities and mechanism of the RC thermodestruction process in the presence of different ammonium salts on the basis of TA data and by comparison with the results obtained by other methods.

EXPERIMENTAL

For our studies we used viscose fibre samples impregnated with NH_4Cl, $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ water solutions and containing 1.0–7.5% nitrogen. Preparation conditions of the fibre and its composition were given earlier [4]. The runs were conducted in argon and in air under static and dynamic conditions at temperatures up to 400°C. TA curves were recorded by means of a Q-Derivatograph (Hungary). IR spectra were registered by a Specord 75 IR (G.D.R.) in the range 4000–500 cm^{-1}, and X-ray diffractograms were made using a DRON-2 diffractometer ($CuK\alpha$ radiation).

RESULTS AND DISCUSSION

Typical TA curves of the fibre samples are given in Figs. 1 and 2. One can see that for the studied systems the form, number and intensity of peaks and their position in the temperature scale depend on the nature of the inorganic addition, its quantity in RC, and on the thermal treatment atmosphere (when other conditions are identical). For example, in the case of the

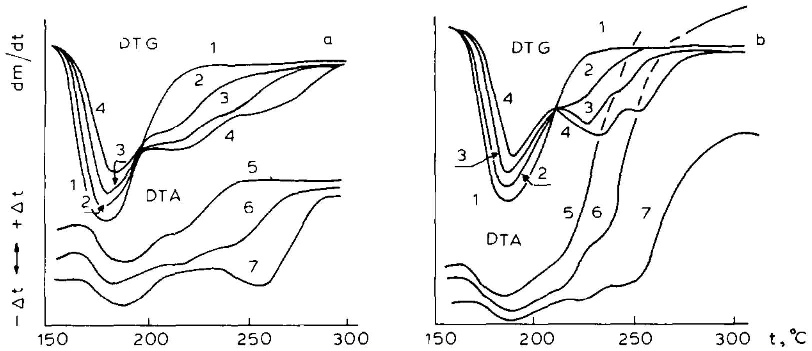

Fig. 1. TA curves in argon (a) and in air (b) for samples of the RC–NH_4Cl system with nitrogen contents (%): 1.0 (1); 2.6 (2), (5); 3.7 (3), (6); 6.8 (4), (7).

RC–NH_4Cl system an increase in the salt content in samples leads to an increase in the number of endothermic peaks from one (at 180°C) to three (at 180, 230 and 250–260°C) (Fig. 1). For the RC–$(NH_4)_2SO_4$ system (Fig. 2) a number of peaks on the TA curves do not depend on the salt content in the samples, but its increase shifts the third peak to higher temperatures (275°C at 1.5% N in the sample and 340°C at 6.3% N). The introduction of $(NH_4)_2HPO_4$ into RC, however, leads to an essential change in the shape of the TA curves in comparison with that of the initial RC, but within the limits studied the quantity of the salt introduced does not influence the number of,peaks and only slightly changes the general appearance of the TA curves. It should be noted that for all systems studied one can observe a sufficiently clear correlation between the DTG and DTA curves.

The transition from argon to air (Figs. 1 and 2) at temperatures above 230°C is accompanied by a specific and sufficiently sharp deviation of the

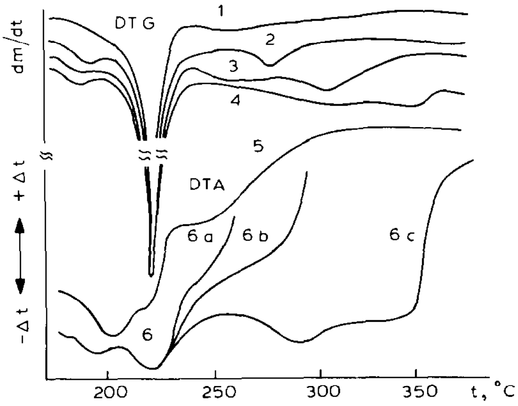

Fig. 2. TA curves in air for samples of the RC–$(NH_4)_2HPO_4$ (1), (5) and RC–$(NH_4)_2SO_4$ (2)–(4), (6) systems with nitrogen contents (%): 0.9 (1), 1.5 (2); 3.4 (5); 4.5 (6a); 5.1 (3), (6b); 6.3 (4), (6c).

TABLE 1

Data for the thermal treatment of the RC–NH_4Cl system in argon for 1 h (in equivalents per RC elemental units in initial sample)

t (°C)	NH_4Cl in initial sample	NH_4Cl "active" [a]	HCl gaseous	NH_4Cl "inactive"
250	0.340	0.324	0.308	0.035
250	0.535	0.425	0.410	0.135
250	0.754	0.524	0.532	0.230
250	0.989	0.568	0.551	0.422
250	1.176	0.624	0.632	0.550
270	0.672	0.503	0.475	0.195
270	0.892	0.543	0.527	0.365
270	1.184	0.640	0.632	0.551
300	0.616	0.389	0.405	0.219
300	0.884	0.527	0.511	0.365
300	1.167	0.608	0.601	0.568

[a] This value was calculated on the nitrogen analyses data basis (accuracy ±5%) and equivalent to its quantity in RCSR.

TA curves from the baseline in an exothermic direction, essentially dependent on the salt content in RC. If the temperature of the start of the deviation of the curve is increased with increasing salt content, the intensity of the deviation (Δt) from the baseline is decreased.

In order to discover the nature of processes observed at 180–350°C, we analyzed solid and some gaseous products using several methods. The results of chemical analysis (Table 1) show that the main process determining the behaviour of the components of the system during heating is their thermostimulated interaction. This process results in nitrogen binding by RCSD and the evolution of an equivalent quantity of free acid (Table 1), the subsequent behaviour of which, under the experimental conditions, is determined by its nature. The above process, under linear heating (2.5–5.0° min^{-1}), proceeds within the range 180–230°C and is accompanied by an essential loss of the introduced salt (up to 60–90%) and substantially less RC mass loss (not exceeding 10%). In our opinion this is determined by the fact that in this case the initial stage of RC thermal destruction, in which the group at the C_6-atom is transformed into an aldehyde group, takes place. For exactly this reason in the IR spectra of the corresponding samples the intensity of the absorption band at 1430, 1190 and 900 cm^{-1} is decreased compared to that of the initial RC, and a new band at 1700 cm^{-1}, belonging to $\nu(C{=}O)$ of the aldehyde group, is formed. Such a transformation plays a particular role in controlling the polymerization degree of the pyrolysis products, since it prevents the formation of different low-molecular weight products, and thus it determines the nature of the products being formed. One can suppose that the aldehyde group formed takes part in the subsequent secondary condensation processes by means of chemical interaction with ammonia, resulting in the above nitrogen binding by RCSR and complete amorphization of solid products (X-ray data). Note that not all of the nitrogen of the introduced salt is bound by RCSR, but only the part of it which is "active" (3.0–3.5% recalculated for nitrogen). The "inactive" form of salts do not influence the RC thermal destruction and proceed at temperatures close to those of their decomposition in the absence of RC.

Thus, the data obtained show that under RC thermal treatment in the presence of nitrogen-containing inorganic salts, primary and secondary processes take place. The former are stipulated by physicochemical properties of RC and additions, and the latter are due to the interactions of the system's components, in which products formed in the first stage take part. All these processes determine the shape of TA curves and their dependency on the nature of the inorganic additions.

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