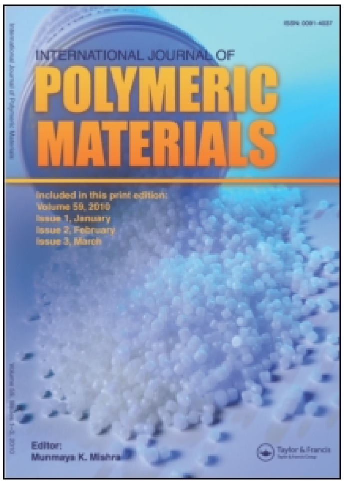

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The Study of Oxidation and Decay of Macroradicals in Cellulose Acetates

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This paper deals with a study of macroradical transformations after low-temperature radiolysis of cellulose acetate (CA).

KEY WORDS Oxidation, macroradicals, cellulose acetate

EXPERIMENTAL

The investigations were performed using glittering complex CA fibers with a linear density of 16.6 tex, with the oil washed out. The thermal fixation of the fibers was carried out in a laboratory chamber. The fibers were fixed without tension at 190°C during 60 s. The drying of the fibers was performed at a temperature of 100–105°C during 5 hours. The conditioning of the fibers was conducted in a desiccator with 65% RH at 20 ± 2°C over 24 hours. The fiber samples were placed in ampoules, evacuated at a pressure of ca. 1 Pa and sealed off. The ampoules with the samples intended for studying the macroradical reactions in the presence of air were sealed off without evacuation. The macroradicals in the samples were initiated by exposing the ampoules placed in liquid nitrogen to gamma irradiation up to a dose of 3×10^4 Gy. After the exposure, the macroradical concentration was ca. 10^{18} per gram. ESR spectra were registered at a cavity temperature of 85–90 K. To study macroradical transformations during the temperature increase, the samples were heated with a special thermostat at temperature intervals of 10°C. The heating duration was 10 minutes at each temperature.

RESULTS AND DISCUSSION

ESR spectra of gamma irradiated CA consist of six lines of SFS with a distance between the extreme peaks of about 6 mT. During the heating of the ampoules with CA fibers, in parallel with a radical concentration decrease, a change in the spectra takes place. At temperatures of -60 to $+60$°C, the spectrum of the dried CA samples turns to a triplet with a broad and intensive central component. On subsequent heating to 120–140°C, the spectrum represents an asymmetric singlet with a width of ca. 2 mT.

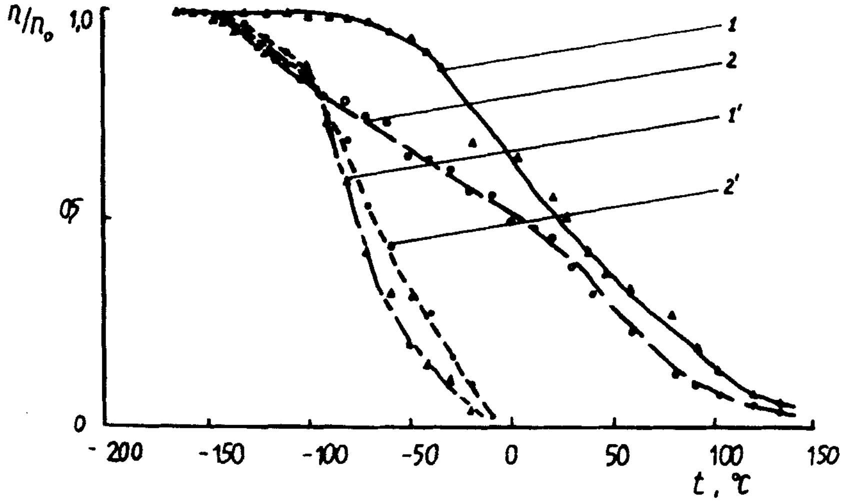

FIGURE 1 Macroradical decay curves in CA fibers prior to (1) and after (2) thermal fixation in free state: 1, 2-dried samples, 1', 2'-conditioned samples (65% RH, t = 20°C).

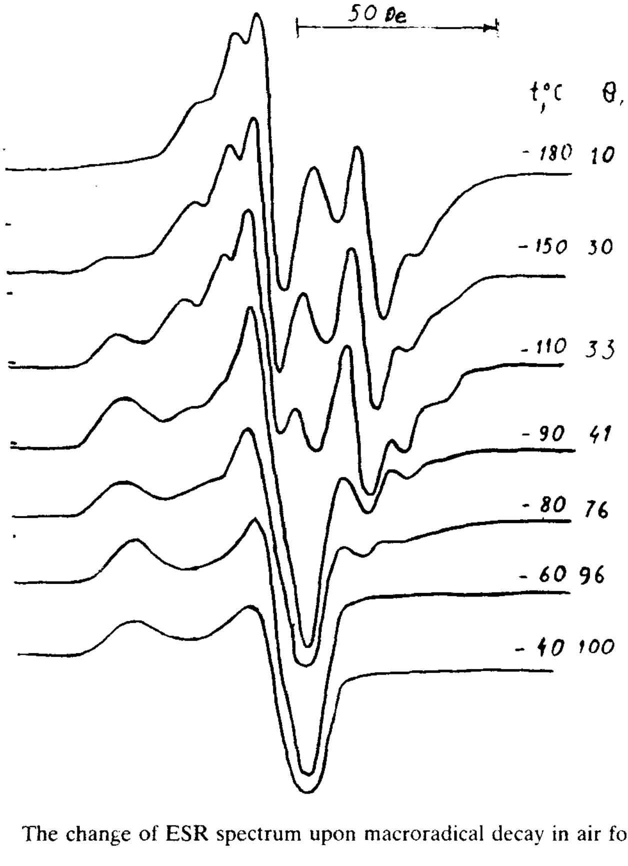

FIGURE 2 The change of ESR spectrum upon macroradical decay in air for dried CA fibers.

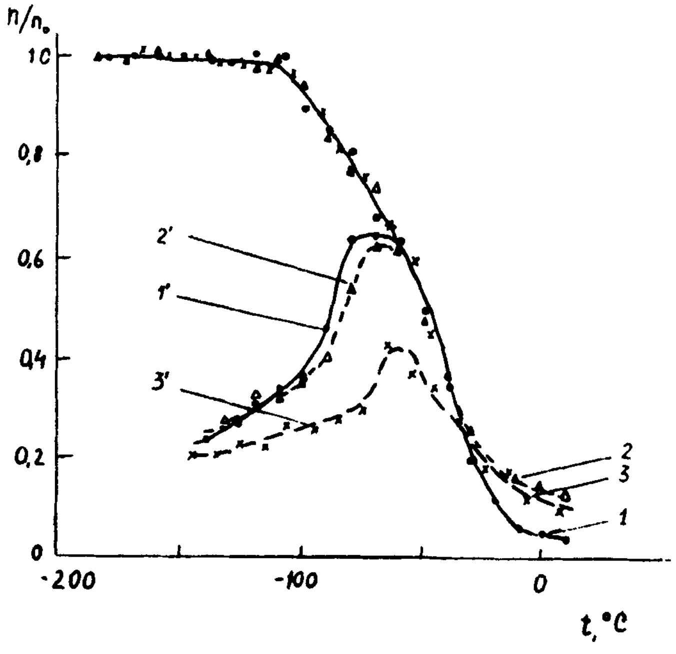

FIGURE 3 Decay (1, 2, 3) and oxidation (1', 2', 3') curves of macroradicals in dried acetate fibers: 1—initial, 2—0.1% of antioxidant, 3—0.5% of antioxidant.

It should be noted that the macroradical concentration in dried CA samples is almost unchanged up to −60°C (Figure 1, curve 1) but the spectrum shape changes indicating that only the structure of the macroradicals change over this temperature interval. On subsequent heating, the concentration of the radicals decreases. As can be seen from Figure 1, the thermal stability of macroradicals in dried fibers after thermal fixation without tension decreases sufficiently. Taking into account the fact that the macroradicals formed during low temperature radiolysis of CA have almost the same structure and molecular weight as the polymer macromolecules, one may conclude that the increase in the macroradical decay rate indicates molecular dynamics increase in the polymer. Hence, it may be assumed that thermal fixation without tension of the fibers leads to the amorphization of the CA structure.

The thermal stability of macroradicals decreases drastically in the presence of sorbed water. Hence, if at 0°C more than 50% of the macroradicals remain in the dried samples, than in conditioned samples, the macroradicals disappear completely. Moreover, in wet samples, thermal fixation almost does not affect the stability of macroradicals. Since ˙OH radicals formed during the radiolysis of water recombine completely at −140°C, and the transfer of the radical state through water molecules seems hardly probable, the decrease in the thermal stability of the CA macroradicals in the presence of water may be explained by the plasticizing action of water.[1]

When the air filled ampoules with CA fibers are heated, the ESR spectrum acquires the typical shape of a peroxide radical (Figure 2), which is indicative of

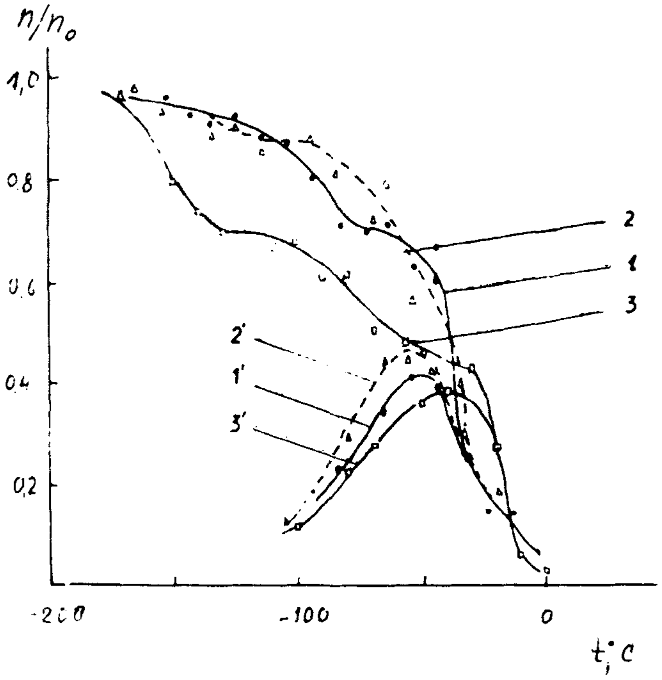

FIGURE 4 Decay (1, 2, 3) and oxidation (1', 2', 3') curves of macroradicals in conditioned CA fibers (65% RH, t = 20°C): 1—initial, 2—0.1% of antioxidant, 3—0.5% of antioxidant.

the macroradical's oxidation. As can be seen, for dried CA fibers, the complete oxidation of macroradicals is observed at −60°C.

In parallel with the control fibers, CA fibers containing 0.1 and 0.5% of an antioxidant have been studied. Figure 3 shows the curves of macroradical decay and oxidation in the samples.

As can be seen from Figure 3, the curves of macroradical decay for all the samples practically coincide but the degree of oxidation of the macroradicals decreases with an increase in the antioxidant concentration. Hence, the complete oxidation of macroradicals in the initial samples, for the fibers with 0.1% of the antioxidant and those with 0.5% of the antioxidant takes place at −60°C, −50°C and −10°C, respectively. This illustrates the mechanism of the antioxidant action, i.e., the termination of the macroradical oxidation kinetic chain.

Figure 4 shows macroradical decay curves of the samples containing sorbed moisture. In this case, the character of the curves differs significantly. The macroradical's thermal stability as well as the degree of their oxidation decrease noticeably. This is, apparently, accounted for by the increase in CA molecular mobility upon plasticization with water molecules. The change in the molecular-dynamic properties of the polymer result in an increase in the efficiency of stabilizer action, which is testified to by the decrease in the degree of macroradical oxidation, as well as the shift of the oxidation region to higher temperatures.

To determine the dependence of macroradical oxidation kinetics on the super-

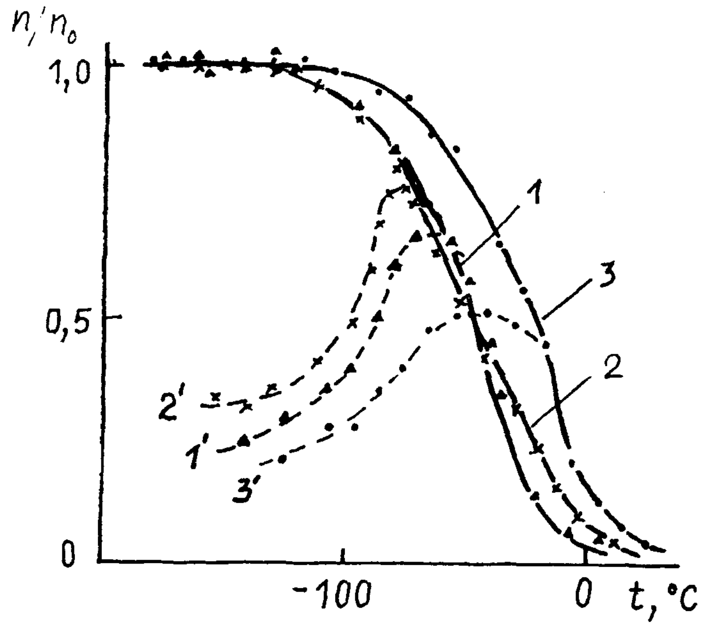

FIGURE 5 Decay (1, 2, 3) and oxidation (1', 2', 3') curves of macroradicals in initial (1), thermofixated (2) CA fibers and CA film (3).

molecular structure of the polymer, thermofixated CA fibers and 0.05 mm thick films obtained from the same batch of raw material have been investigated.

As can be seen from Figure 5, the degree of oxidation of the macroradicals increases. In the present work, it was shown earlier that upon thermofixation in the free state, the degree of order of the polymer structure decreases. Apparently, it promotes oxygen diffusion into the fibers. On the other hand, it can be seen that the degree of oxidation of macroradicals in the films is considerably lower, as compared with the fibers. The above examples illustrate the dependence of the diffusional path of oxygen molecules on the polymer structure.

As can be seen from the examples presented in this work, the study of the transformation of the macroradicals formed by low temperature radiolysis of cellulose acetate by ESR spectroscopy provides valuable information about the change in molecular mobility in CA after various actions. In addition, from the macroradical's oxidation rate, it is possible to estimate the depth of oxygen diffusion into the polymer, as well as the efficiency and mechanism of the action of various antioxidants and polymer stabilizers.

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