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POSITRON ANNIHILATION IN COTTON CELLULOSE

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The changes of the cotton fibre microstructure as a result of annealing at temperatures from 20°C to 300°C were investigated by positron lifetime spectroscopy and differential scanning calorimetry. The aim of the paper was to examine the cotton cellulose thermal degradation process.

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1. Introduction

Cellulose is one of the most abundant biopolymers. It is a linear homopolymer of D-glucose units with carbon 1 of the non-reducing end linked to carbon 4 of the glucose of the reducing end. The most common crystalline form of native cellulose is cellulose I, which can be converted into another, seldom made in nature, crystalline forms: cellulose II, III, and IV, which are generally the products of swelling and dissolution of cellulose I [1]. Different kinds of cellulose can be identified by its characteristic X-ray or electron diffraction pattern [2]. The cellulose polymers are packed parallel to each other in structures known as microfibrils composed less than 36 cellulose chains. The microfibrils are often associated in bundles or macrofibrils. Cellulose is not only a major structural component of both primary and secondary plant cell walls or extracellular matrix, but also very important technological material. Most of natural cellulose is found in: cotton fibres (92%), flax (71%), jute (71%), and wood (45%) [3]. The native cellulose contains ordered (crystalline) and disordered (amorphous) regions [4-6]. The cellulose polymers of different biological origin vary in degree of crystallinity from 40% in bacterial to 60% in cotton and 70% in Valonia cellulose.

The aim of this paper is to examine the cotton cellulose thermal degradation process. The microstructural information about cotton fibres under different temperature conditions was obtained using positron lifetime spectroscopy and differential scanning calorimetry.

2. Experimental methods

The investigations of the thermal cotton cellulose polymers degradation was performed on pressed (at the same pressure 11 MPa) native cotton fibres. Before differential scanning calorimetry measurements in order to eliminate free water and obtain dry mass, samples were dried in an oven during 48 hours at the temperature of 50°C. Calorimetric measurements were performed in the temperature range from 20°C up to 300°C using a Perkin–Elmer DSC-7 differential scanning calorimeter. The output signal (heat flow — dQ/dt), proportional to the difference between the power input to the sample and that to the reference, was recorded as a function of the sample temperature. For positron lifetime measurements the two parts of the examined sample were sandwiched with positron source ^{22}Na , enveloped in a polyethylene foil to prevent get moist, and located in a fast–fast positron lifetime spectrometer with NE 111 scintillators. The source activity was 0.2 mCi, time resolution (FWHM) 300 ps, a positron lifetime spectrum contained 10^6 counts. Before PAS experiments samples were heated during 48 hours in pre-determined temperature and next slowly cooled to the room temperature. This operation permitted us to eliminate thermal dynamics of the sample microstructure and examine only its permanent changes. Data were analysed using the computer program called LT [7]. In the analysis of the spectra the background and source corrections were taken into account.

3. Results and discussion

The calorimetric measurements were performed in air and in helium used as a purge gas, both for origin samples and after their cooling without removing samples from the calorimeter. The scanning rate was 30°C/min. The dependence of the heat flow absorbed by cotton fibres vs. temperature is presented in Fig. 1a, b. A very wide bump is seen on the thermogram in the temperature range of 20÷150°C for both origin samples. This gives evidence for the endothermic process taking place in the material. Integration of these anomalies (after subtraction of arbitrary chosen linear background) leads to the value of the absorbed heat which is estimated to be equal to *ca.* 120 J/g. The shapes of the anomalies allow us to suppose that the processes have an activation character, and can be associated with a change in the physical state which is probably cotton cellulose depolymerisation. This process does not depend on the oxygen concentration and occur in a similar way similar both in air and helium environments. The comparison of thermograms for origin samples (*o*) and after their cooling (*c*) indicates that depolymerisation of the samples is not reversible. From the literature [3] it is known that at temperatures higher than 160°C the dehydration and oxidation of cellulose molecules takes place and a lot of gaseous and liquid products are formed; it could be the pitch and various hydrocarbons (CO_2 , H_2O , C_2H_4 , $\text{CH}_3\text{—CO—CH}_3$, CH_3COOH , and others). The formation of new products depends probably on the oxygen concentration which could be deduced from the measurements in air and in helium flow. Figure 1a, b shows small differences in the high temperature tails of the thermograms. At temperatures higher than *ca.* 270°C some exothermic process starts

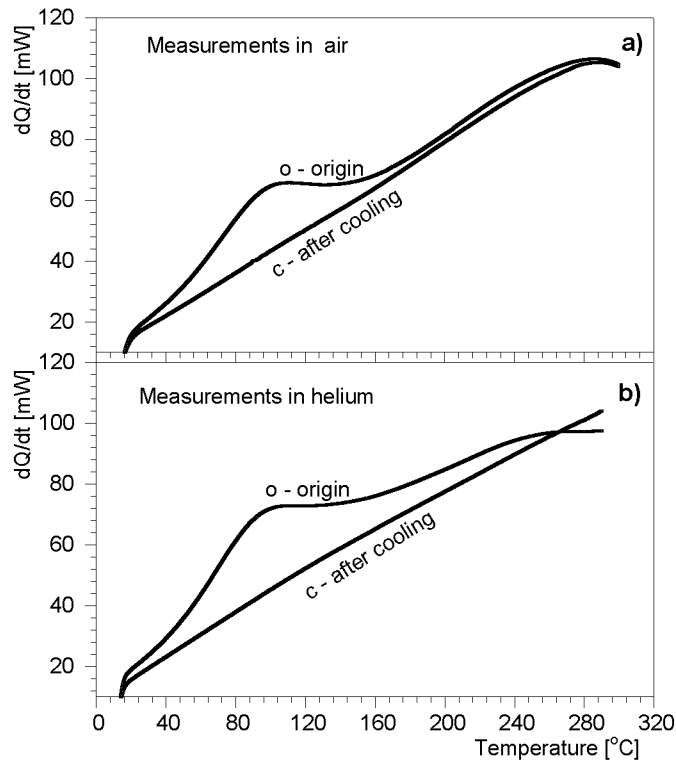


Fig. 1. Thermograms (dQ/dt vs. temperature) for cotton fibres: (a) measurements in air, (b) measurements in helium flow; *o* — thermogram for origin cotton fibres, *c* — thermogram for the same sample after cooling.

which manifests itself as a lowering of the thermograms. It is probably due to the beginning of the carbonisation of the cotton cellulose.

From the positron lifetime spectra measured for samples heated at different temperatures three lifetime components were extracted. The shortest one, τ_1 , was fixed at the value of 125 ps and related to the *para*-Ps decay. The component, τ_2 , ranging from 336 ps to 365 ps was due to the free positron annihilation in a singlet configuration with respect to orbital electrons. The longest one, τ_3 , was attributed to the *ortho*-Ps decay in the pick-off process with electrons in the free volume. Figure 2a, b presents the dependences of τ_3 and the intensity of this component, I_3 , on annealing temperature. Based on Tao's spherical model [8] the free volume radius can be evaluated, see Fig. 3. At the temperatures in the range of 20–270°C the average free volume radius decreases from 0.23 nm to 0.19 nm and next strongly increases to *ca.* 0.27 nm. The intensity of the longest lifetime component slightly increases from 13.4% to 17.1% at temperatures in the range of 20–200°C and next strongly decreases to 10.2% at the temperature of 270°C. At the temperatures in the range of 270–300°C the next increase in I_3 takes place. Cao et al. observed the correlation of the *o*-Ps intensity with crystallinity for the cellulose powders

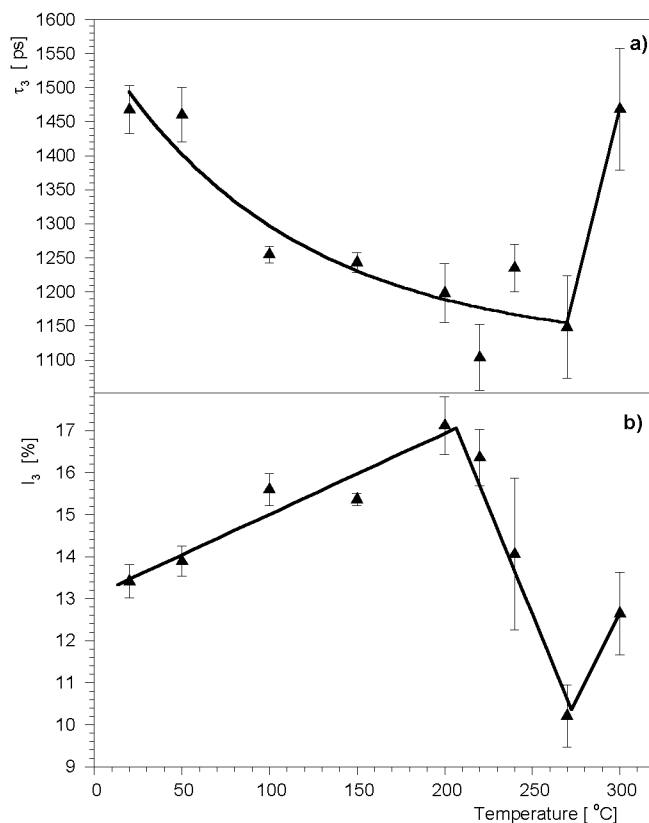


Fig. 2. Dependences of the longest lifetime component τ_3 (a) and its intensity (b) on annealing temperature.

depending on the milling time [9]. *o*-Ps intensity decreased as the degree of crystallinity increased. It seems that the initial increase in I_3 (Fig. 2b) agrees well with the depolymerisation process which decreases the crystallinity of the sample. The behaviour of I_3 at higher temperatures reflects the chemical changes of the cellulose molecules. Based on Figs. 2 and 3 it seems that at temperatures in the range from *ca.* 200°C to 270°C some new free volumes may be formed, some may be filled up or divided into parts by oxidation products. The strong increase in all the characteristics of *o*-Ps at temperatures higher than 270°C is caused probably by carbonisation of the cotton cellulose polymer, where its structure is destroyed.

The cotton fibre under high temperature conditions changes its microstructure. This phenomenon could be well correlated with chemical processes occurred in cotton fibres during their heating. The depolymerisation, oxidation, and hydration of the cotton cellulose, which take place at higher temperatures, cause a decrease in free volume dimensions. At temperatures higher than 270°C the strong increase in the radius of free volumes could be seen, which is caused by the fast carbonisation of cotton cellulose.

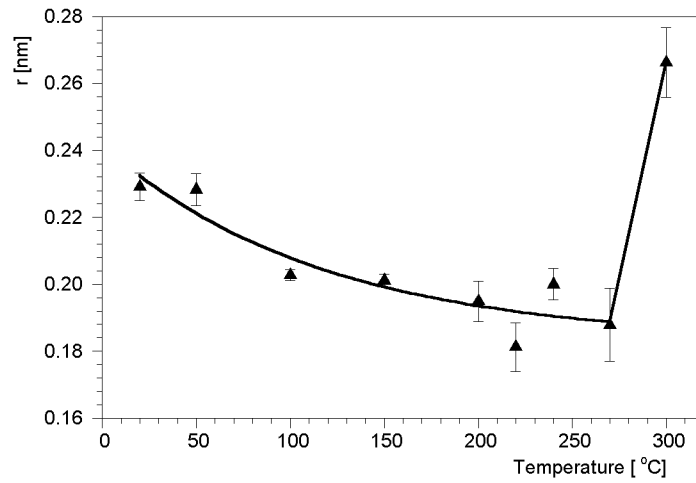


Fig. 3. Free volume radius vs. annealing temperature.

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