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INVESTIGATION OF THE PHYSICO-CHEMICAL STRUCTURE OF OXYCELLULOSE AFTER STORAGE FOR TWO YEARS AND DETERMINED BY DERIVATOGRAPH

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The effect of ageing for a period of two years upon chemically pre-oxidized and irradiated cellulose was investigated. Changes in the chemical structure and energy excitation of atomic groups of oxycellulose skeleton were evaluated from the qualitative and quantitative points of view. The numerical interpretation and complex comparison of the quantities (activation energy, energy quantity EW, values of the thermal effect (areas of DTA peaks) and weight losses) of four degradation phases of pyrolysis were employed, when applying the oxidation pyrolysis method with derivatograph.

The structural characterization of oxycellulose by thermal analysis has been reported and compared of pyrolytic degradations in air with that in nitrogen [1]. However, this method does not permit the characterization of oxycellulose from the aspect of chemical structure. The chemical methods used for determination of the functional groups (e.g. three various acidic [2], or six various aldehyde groups [3]) do not allow the determination of the chemical structure of oxycellulose from a complex point of view.

The physico-chemical structure has been determined by pyrolysis with a derivatograph on freshly-prepared, radiation-sterilized oxycellulose [4] and oxycellulose exposed to ageing for one month and one year [5]. Qualitative and quantitative interpretations of the activation energies and weight losses made possible the determination of the chemical changes and excitation energies of the functional groups. The present work deals with an evaluation of the structural changes in oxycellulose after storage for two years, as a continuation of a previous paper [6].

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Experimental

Material

Samples of oxycellulose (numbered 1 to 8 and differing in the duration of oxidizing treatment: 24–38 hours with a constant difference of 2 hours) were prepared by nitrous pre-oxidation (cotton gauze was oxidized by immersion in an oxidizing solution) and irradiation (involving radiation sterilization) with a radiation dose of 100 kGy, using a Van de Graaff electron accelerator (dose rate 1.17 $kGy \cdot s^{-1}$) [7, 8]. They were then aged by storage for two years in dark at laboratory temperature, in non-sealed polyethylene packages in the presence of air.

Methods

Pyrolysis of the samples was carried out with a derivatograph (MOM); sample size: 50 mg (powdered), heating rate: 5.5 deg/min; air atmosphere by removing the pyrolysis products in a gas flow of 80 ml/min.

For the interpretation of the experimental results, a previously reported method [9] was used for the determination of kinetic parameters. After the evaluation of the expression E/n (activation energy, order of reaction), using experimental data [10] and graphical construction of the tangent at the point of inflection, and employing a nomograph [11] and an approximative method [11] designed for the solution of more complicated overlapping pyrolytic reactions.

Results and discussion

Pure cellulose degrades pyrolytically in two steps, at 325° and 460°, but after chemical pre-oxidation and irradiation it degrades in four steps (phases) at about 220°, 290°, 420° and 540–600°. The third phase may sometimes be divided into two sub-phases. The adjacent phases of oxidation pyrolysis of oxycellulose partly overlap one another.

The results of the oxidation pyrolysis of freshly-prepared and radiation-sterilized oxycellulose [4], of oxycellulose exposed to ageing for one month and one year [5], and of irradiated and non-irradiated lactose [12], can be interpreted, that during the first phase of pyrolysis carbons C6 and C1 are degraded, while C5 and C2 (hydroxyl group) are degraded during the second phase; during the third phase (divided into partial phases 3A and 3B) oxygenic groups on C4 and the keto group on C3 (adjoining to hydroxyl group on C2)—phase 3A, and the hydroxyl group on C3—phase 3B, are degraded, and in the fourth phase of pyrolysis the molecular species

associated with the double bond between skeleton carbons (especially between C2 and C3) are degraded. In addition, during the first phase also the keto group on C2 and the keto group on C3 (adjoining the keto group on C2) are degraded.

The interpretation of the structural changes in the studied material is based on the assumption that structural changes in functional groups have been brought

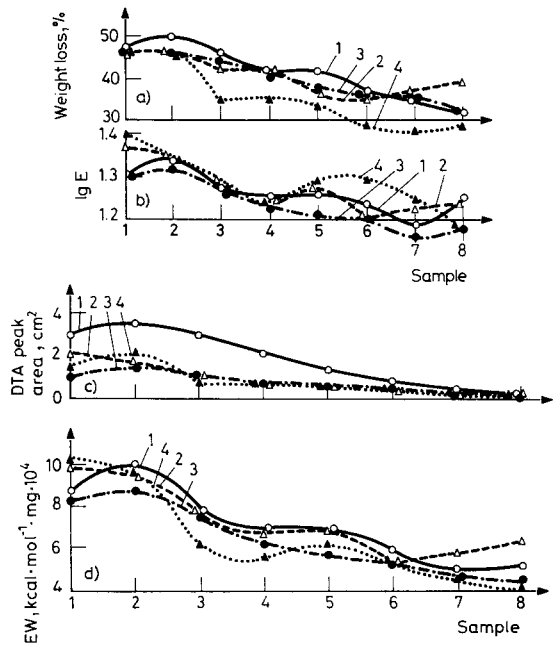

Fig. 1 Oxycellulose, first pyrolytic phase, samples 1 — fresh, 2 — one-month ageing, 3 — one-year ageing, 4 — two-year ageing. a) Degraded weight portions. b) Logarithm of activation energy. c) Area of DTA peaks. d) Quantitative energetic quantity *EW*

about during storing. The excitation by energy of the various groups makes possible to shifting of free electrons (free radicals) and the rearrangement of oxygenic functional groups during the period of storage (e.g. keto groups to double bonds between carbons and then to another adjacent carbon group; the double bond protects the carbon groups with steric accessibility from pyrolytic degradation.)

The chemical and energetic structural changes induced in oxycellulose samples by storage for two years (the fourth series of samples) are compared with those of the samples formed during one-year storage (the third series of samples) in the following evaluation.

Changes in the weight losses due to the first phase of pyrolysis after storage for two years are a result of keto group rearrangement on C2(C3) to hydroxyl on C2(C3), or carboxyl group on C6 to keto group on C5.

With sample 3, a rearrangement of the keto groups on C2 and C3 to hydroxyl groups on C2 and C3 occurs (a decrease in the weight loss in the first phase and an

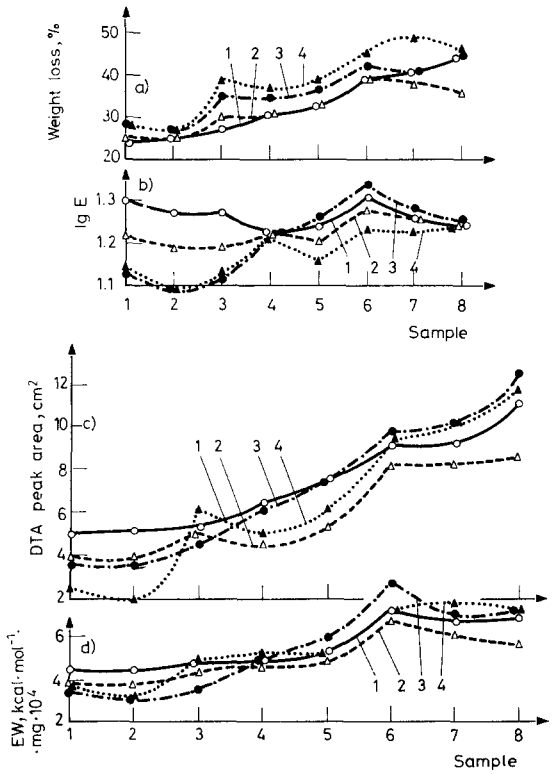

Fig. 2 Oxycellulose, second pyrolytic phase, samples 1 — fresh, 2 — one-month ageing, 3 — one-year ageing, 4 — two-year ageing. a) Degraded weight portions. b) Logarithm of activation energy. c) Area of DTA peaks. d) Quantitative energetic quantity *EW*

increase of the same in the second and the 3B phases, Figs 1a, 2a and 4a, curve 4); with sample 4, an additional rearrangement occurs, and a double bond is formed between C2 and C1, as it is seen in decrease in the weight loss in the first phase (Fig. 1a, curve 4) in favour of the fourth phase (Fig. 5a, curve 4). With sample 5, carboxyl groups on C6 rearrange into the keto groups on C5, and simultaneously rearranges the keto group on C2 in favour of C3 (decrease in weight loss of the first and 3B phases—Figs 1a and 4a, curve 4-in favour of the 3A and the second phases—Figs 3a

and 2a, curve 4); with sample 6, the keto groups on C2 rearrange partially into C1 (phase 1 in favour of phase 2, Figs 1a and 2a, curve 4) and in the same extent the keto groups on C3 (primarily degraded together with the keto groups on C2 within phase 1) rearrange into C4 while on C3 hydroxyl groups remain (increase in the

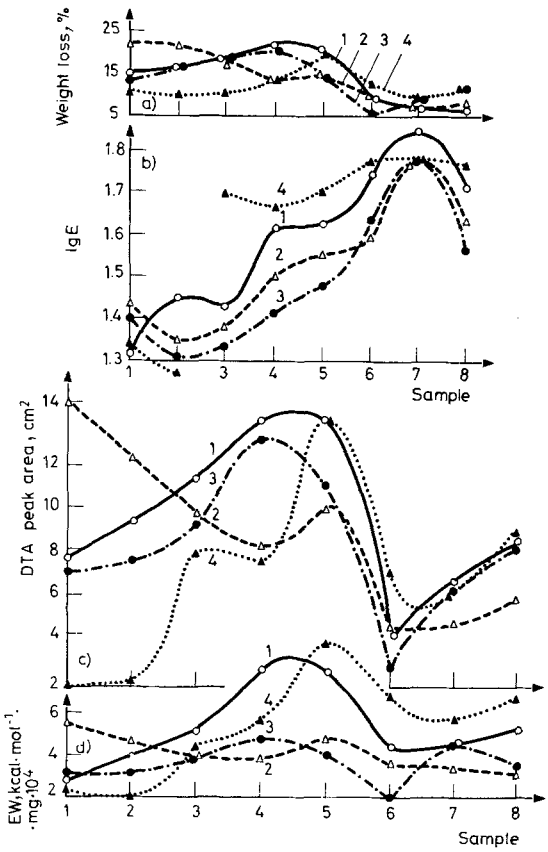

Fig. 3 Oxycellulose, pyrolytic phase 3A, samples 1 — fresh, 2 — one-month ageing, 3 — one-year ageing, 4 — two-year ageing. a) Degraded weight portions. b) Logarithm of activation energy. c) Area of DTA peaks. d) Quantitative energetic quantity *EW*

share of phase 3B also at the expense of phase 1, Figs 4a and 1a, curve 4); with sample 7, the keto groups on C2 (adjacent to hydroxyl groups on C3) rearrange in a considerable extent into C1 (phase 1 in favour of phase 2, Figs 1a and 2a, curve 4); and with sample 8, the keto groups on C2 (adjacent to hydroxyl groups on C3) rearrange to a smaller extent to C1 (phase 1 in favour of phase 2, Figs 1a and 2a, curve 4).

Activation energy of the first phase after two-year ageing is increased for sample 1,2 and 5–7, while it does not alter for samples 3, 4 and 8 (Fig. 1b, curve 4). Increase in the activation energy values of the first phase with samples 1 and 2 occurs owing to a loss of electron excitation of groups C1 and C6 in favour of C4 (decrease in

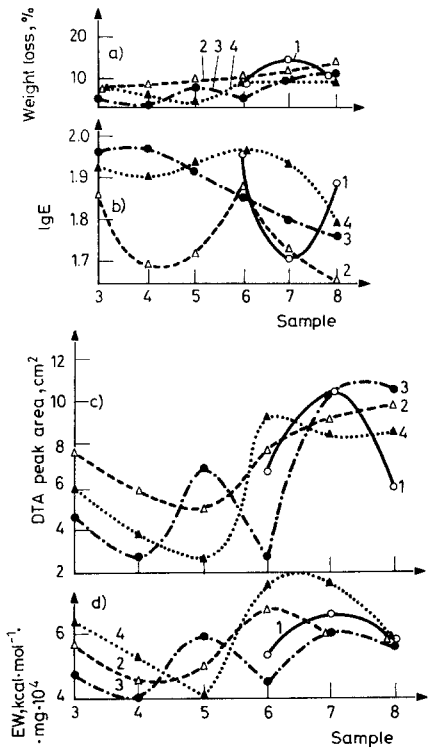

Fig. 4 Oxycellulose, pyrolytic phase 3B, samples 1 — fresh, 2 — one-month ageing, 3 — one-year ageing, 4 — two-year ageing. a) Degraded weight portions. b) Logarithm of activation energy. c) Area of DTA peaks. d) Quantitative energetic quantity *EW*

activation energy of phase 3A—Fig. 3b, curve 4), with samples 5–7 in favour of C2 or C5 (decrease in activation energy of phase 2, Fig. 2b, curve 4).

The combined effect of structural chemical (weight losses) and energetic (activation energy) changes is expressed in the quantitative energetic quantity *EW* (kcal · mg · mol^{-1}) [11]$^+$. The *EW* quantity represents the total quantitative energy necessary for pyrolysis proportional to the value of thermal effect of pyrolytic

$^+$ The units for energetic quantity *EW* are expressed in kcals. It was not considered practical to use SI-units as the previous papers [4–6] were issued before the SI-units have been established.

reaction expressed by the DTA peak area [11]. The *EW* quantity was used as a general complementary criterion of oxycellulose atomic groups stability. Only those groups can be regarded as stable that do not change simultaneously both from the energetic and chemical points of view.

With groups C1 and C6 it is possible to expect general energetic and weight equations for samples 6–8 and a non-equation for samples 1–5 as shown by the equable and unequable courses of *EW* curve for the fourth series of samples compared with the third series of samples (Fig. 1d, curves 4 and 3). This is indicated also by the course of the curve of DTA-peak areas expressing the unequalization only with samples 1–3, further differences are inconspicuous (Fig. 1c, curve 4).

Group C2 (the second phase of pyrolysis) enlarges the share of bound hydroxy groups (samples 3–8) always through rearrangements from keto groups on C2 as shown by the same or increased weight loss portions of the second phase and the corresponding decreased weight loss portion of the first phase for the fourth series of samples compared with the third one (Figs 2a and 1a, curve 4).

From the viewpoint of stability of analysed oxycellulose samples for further storing the rearrangements of the chemical groups can be taken as equalized after two-year ageing. Weight portions of carbon groups degraded during the first two pyrolytic phases (C1, C2, C5 and C6) form always the sum of about 75% of a total weight degraded during pyrolysis for each sample. The weight portion of the first pyrolytic phase makes a mirror image of the weight portion degraded during the second pyrolytic phase for samples 1–8 (Fig. 6, curves 1 and 2). Also the sum of the weight losses during the phases 3A (oxygenic groups C4, keto group on C3 adjacent to the C2 hydroxy group), 3B (hydroxy group on C3) and 4 (double bond on carbon skeleton) also makes always approximately 25% of the total weight for each sample (Fig. 6, curves 3A, 3B and 4). This structural equalization does not occur either with samples of freshly pre-oxidated oxycellulose [4] or with samples stored for a period of one month and of one year [5].

Decrease in activation energy with the second pyrolytic phase, samples 5–7 (Fig. 2b, curve 4) indicate an enlarged excitation by energy of C2 (C5) hydroxy group (decrease in activation energy, Fig. 2b, curve 4). The energy difference is compensated by the proportional part of decrease in excitation with the first phase of pyrolysis (groups C1 or C6) showing a considerable elevated value of activation energy with these samples (Fig. 1b, curve 4).

The general structural stability of groups C2 and C5 during the process of ageing (when comparing storage periods of two and one year), showing an equality with samples 1, 2, 4 and 8 according to values of the *EW* quantity (Fig. 2d, curve 4), is not actually achieved (Fig. 2c, curve 4) because of changes in value of the thermal effect (area of DTA peaks). Hydroxy groups on C2 and C5 in all analysed samples are not

completely structurally (as to changes in energy and weight losses) equalized during the process of ageing in the period of one to two years.

After two-year ageing the weight portions degrading during the pyrolytic phase 3A, 3B and 4 are predominantly results of rearrangements between the oxygenic groups on C4 or keto group on C3 (adjacent to hydroxy group on C2)—phase 3A,

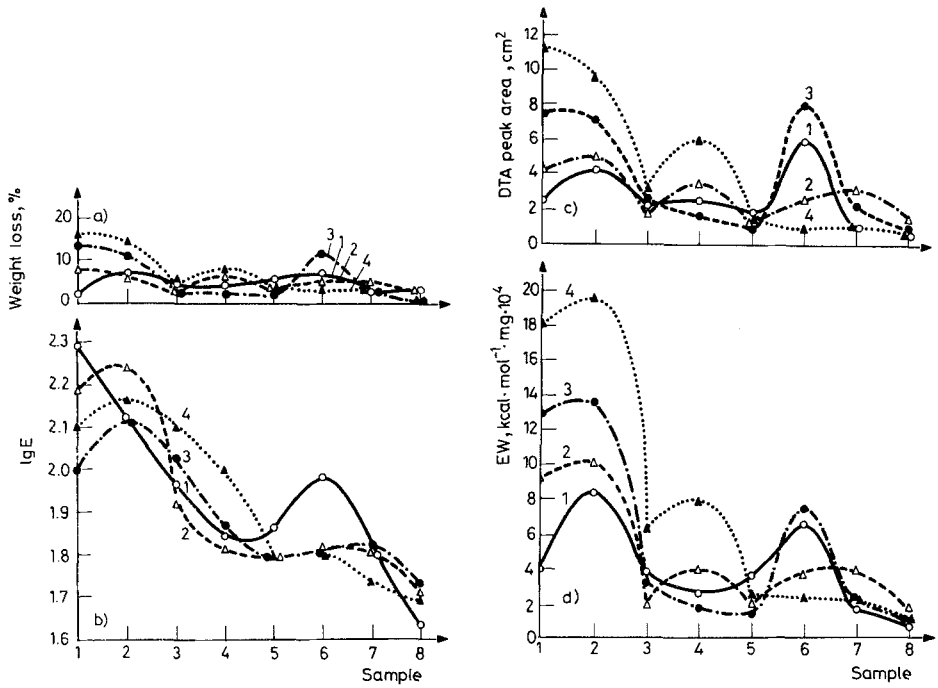

Fig. 5 Oxycellulose, fourth pyrolytic phase, samples 1 — fresh, 2 — one-month ageing, 3 — one-year ageing, 4 — two-year ageing. a) Degraded weight portions. b) Logarithm of activation energy. c) Area of DTA peaks. d) Quantitative energetic quantity *EW*

hydroxy group on C3—phase 3B, and double bond on the carbon skeleton—phase 4, compared with the third series of samples.

With samples 1 and 2 the rearrangement of keto groups occur from C3 (adjacent to hydroxy groups on C2) to the form of double bonds on C2 and C3 (decrease in weight loss of phase 3A in favour of phase 4, Figs 3a and 5a, curve 4); with samples 3 and 4 the rearrangement of the keto groups on C3 (adjacent to hydroxy groups on C2) occurs partially again to the double bonds between C2 and C3 (increase in the share of phase 4, decrease for phase 3A, Figs 5a and 3a, curve 4) and partially to the subsequent formation of the double bonds between C2 and C1 (increase in the share

of phase 4 and 3B, decrease in the share of phase 1, Figs 5a, 4a and 1a, curve 4) forming hydroxy groups on C3 partly linked with double bonds and partly without the double bonds on the carbon skeleton (between C2 and C3); on the contrary, with sample 5, the number of keto groups on C3 (adjacent to hydroxy groups on C2) increases due to rearrangements from keto groups on C2 (increase in weight loss of phase 3A and 2, decrease for phase 3B and 1, Figs 3a, 2a, 4a and 1a, curve 4); with sample 6, the number of keto groups on C3 (adjacent to hydroxy groups on C2) increases by rearrangement from the double bonds between C3 and C2 (increase in weight loss of phase 3A—Fig. 3a, curve 4—at the expense of phase 4—Fig. 5a, curve 4), while no evident weight changes occur with samples 7 and 8.

The greatest decrease in weight loss during ageing for a period from one to two years in keto groups on C3 (adjacent to hydroxy group on C2—Fig. 3a, curve 4) occurs with sample 3. This is induced by a low stability of group C3 caused by the primary chemical pre-oxidation enabling a spontaneous increase of phase 3B with sample 3 already during one-month ageing (Fig. 4a, curve 2). With samples 1–8, it can be explained by successively deepened degree of chemical pre-oxidation that the number of keto groups on C3 (adjacent to hydroxy group on C2) increases reversely due to two-year ageing with samples 5 and 6 (increase in weight loss of phase 3A—Fig. 3a, curve 4), namely successively to the detriment of hydroxy groups on C3 at first (decrease in weight loss of phase 3B—Fig. 4a, curve 4, sample 5), afterwards to the detriment of the double bond between C3 and C2 (decrease in weight loss of phase 4—Fig. 5a, curve 4, sample 6) as far as it reaches an equation with the most pre-oxidated samples 7 and 8 (equalizing of phase 3A, 3B and 4—Figs 3a, 4a and 5a, curve 4).

An increase of energy excitation of group C4 and keto groups on C3 (adjacent to hydroxy groups on C2) as shown by the decrease in activation energy with samples 1 and 2 (Fig. 3b, curve 4), is induced partly by a partial rearrangement of keto groups on C3 into double bonds between C2 and C3 (decrease in weight loss of phase 3A in favour of phase 4—Figs 3a and 5a, curve 4), partly by a decrease in energy excitation of C1 or C6 (increase in activation energy of phase 1—Fig. 1b, curve 4).

A great decrease in energy excitation of C4 and C3 (keto groups—adjacent to hydroxyl groups on C2) with samples 3 and 4 (increase in activation energy of phase 3A—Fig. 3b, curve 4) suggests the existence of free electrons on the hydroxyl groups on C3 and C2 or C5 (increase in weight loss of the second and 3B phases—Figs 2a and 4a, curve 4—is accompanied with the steadiness and a decrease in activation energy with these phases—Figs 2b and 4b, curve 4). With samples 5 and 6, decrease in energy excitation of C4 and C3 (keto group—adjacent to hydroxyl group on C2) occurs partly due to the increased yielding of free electrons to C2 or C5 group (increase in weight loss of the second phase, in addition it is accompanied with a

decrease in activation energy—Figs 2a and 2b, curve 4), partly as a result of an increase in the share of keto groups on C3 (increase in weight loss of phase 3A—Fig. 3a, curve 4). The energy excitation of C4 and C3 (keto group—adjacent to hydroxyl group on C2) with samples 6–8 reaches the same value indicating an equation in energy excitation of C4 and C3 (keto group—adjacent to hydroxyl group on C2)—samples influenced maximally by the primary chemical pre-oxidation.

The size and course of quantitative energetic quantity *EW* of phase 3A for the fourth series of samples (two-year storing, Fig. 3d, curve 4) complements the size and course of *EW* quantities with phases 3B and 4 (Figs 4d and 5d, curve 4) with regard to the duration of chemical pre-oxidation (samples 1–8) disregarding the differences in the third series of samples (one year of storage) as it is specified in the following section.

With samples 1 and 2, the low starting section of the curve indicating the energy requirement for pyrolysis of groups C4 and C3 (keto group—adjacent to hydroxy group on C2) relates to the increased course of the curve for groups of skeleton carbons linked by the double bond (a minimal and a maximal *EW* value for phases 3A and 4, respectively, Figs 3d and 5d, curve 4). Increase in required pyrolytic energy of grups C4 and C3 (keto group—adjacent to hydroxy group on C2) for samples 3–5 with a maximum for sample 5 (*EW* quantity, Fig. 3d, curve 4) is a consequence of decrease in this energy for groups with double bonds on skeleton carbons (*EW* quantity, Fig. 5d, curve 4) and a consequence of the gradual decrease in the energy share of hydroxyl groups on C3 with a minimum for sample 5 (*EW* quantity, Fig. 4d, curve 4). The consecutive decrease in required pyrolytic energy of groups C4 and C3 (keto groups—adjacent to hydroxyl groups on C2) for samples 6 and 7 (*EW* quantity, Fig. 3d, curve 4) is accompanied with an increase of energy share on C3 with hydroxyl groups (*EW* quantity, Fig. 4d, curve 4) and with an unchanged quantitative energy effect with the double bonds on the carbon skeleton (*EW* quantity, Fig. 5d, curve 4). Increase in pyrolytic energy of groups C4 and C3 (keto groups—adjacent to hydroxyl groups on C2) with sample 8 relates to subsequent decrease in value of this energy pertaining to hydroxyl groups on C3 (*EW* quantity, Figs 3d and 4d, curve 4).

The same dependences are valid in case we consider instead of quantitative energetic quantity *EW* required for pyrolysis of phases 3A, 3B and 4 the value of thermal effect accompanying the pyrolysis of those phases expressed by DTA peak areas (Figs 3c, 4c and 5c, curve 4).

After two-year storage the atomic groups C4, C3 do not become stable neither do the groups with double bond on the carbon skeleton as it is evident from the course of *EW* curves (Figs 3d, 4d and 5d, curve 4) and curves of DTA peak areas (Figs 3c, 4c and 5c, curve 4) for the pyrolytic phases 3A, 3B and 4.

The share of hydroxyl groups on C3 with samples 3, 4, 6–8 (Fig. 4a, curve 4), and oxygenic groups on C4 and keto groups on C3 (adjacent to hydroxyl groups on C2) with samples 1–3 and 6–8 (Fig. 3a, curve 4) approaches 10% of total weight of the sample after two-year ageing. An exception is sample 5 with a smaller weight portion for C3 (hydroxyl group)—Fig. 4a, curve 4—and proportionally greater weight portion for C4 and C3 (keto group adjacent to hydroxyl group on C2)—Fig. 3a, curve 4. This is apparently due to a mutual rearrangement of corresponding keto group on C2 to hydroxyl groups on C3 and an instability of this group after two-year storing with sample 5.

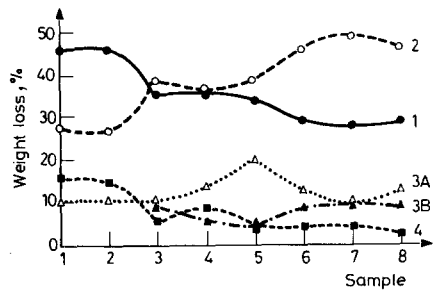

Fig. 6 Oxycellulose after two-year ageing (4th series of samples). Degraded weight portions during pyrolytic phases 1, 2, 3A, 3B and 4

The energy excitation of hydroxyl groups C3 with samples 3 and 4 slightly increases due to the two-year storing (decrease in activation energy of phase 3B, Fig. 4b, curve 4) with simultaneous increase in weight portion of this group on C3 (Fig. 4a, curve 4) at the expense of energy excitation of C4 and C3 (keto group—adjacent to hydroxyl group on C2)—increase in activation energy and simultaneous decrease in weight loss of phase 3A, Figs 3b and 3a, curve 4. On the contrary, with samples 6 and 7 the energy excitation of hydroxyl group on C3 decreases with the lowest for sample 7 (Fig. 4b, curve 4) in favour of C2 or C5 (decrease in activation energy—Fig. 2b, curve 4 and increase in weight portion, with a maximum for sample 7—Fig. 2a, curve 4—for the second phase of pyrolysis).

The share of double bonds formed on the carbon skeleton after two-year storing depends on the period of chemical pre-oxidation. As for samples 1–4 (a shorter period of pre-oxidation), the share of double bonds varies after two-year storing and depends on the rearrangement of C3 keto groups (Fig. 5a, curve 4). As for samples 5–8 (a longer period of pre-oxidation), the share of double bonds in the cause of the weight loss is stabilized in a minimal value 3% of weight (Fig. 5a, curve 4).

Significantly dependent on the period of chemical pre-oxidation is also the energy excitation of carbons linked by double bond. Samples 1–4 after two-year ageing are characterized by decreased energy excitation (elevated value of activation energy, Fig. 5b, curve 4), samples 5–8 have an equalized value of energy excitation with a slight lowering of activation energy for samples 7 and 8 (Fig. 5b, curve 4). The decreased energy excitation with samples 1–4 is connected with an increase in weight portion of carbons linked by double bond (Fig. 5a, curve 4). Slightly elevated energy excitation for samples 7 and 8 (decrease in activation energy, Fig. 5b, curve 4) is connected with a gradual decrease in energy excitation of hydroxyl groups on C3 with these samples (elevated value of activation energy of pyrolytic phase 3B, Fig. 4b, curve 4).

The general structural (chemical and energy) instability of carbon groups linked by double bonds on the carbon skeleton after two-year ageing is shown by samples 1–4 with a maximum for samples 1 and 2 (elevated values both of *EW* quantity and DTA peak areas, Figs 5d and 5c, curve 4), samples 5–8 are generally stabilized as for energy and chemical equilibrium with a decreased share of double bonds between skeleton carbons (equalized and lowered curve courses both of *EW* and DTA peak areas, Figs 5d and 5c, curve 4).

Conclusions

The influence of two-year ageing compared with one-year ageing upon the structural properties of oxycellulose can be summarized as follows:

— C2 and C3 groups simultaneously oxidized to keto-form are structurally chemically instable, in case of samples oxidized for 28 to 38 hours. Progressive oxidation (28 to 38 hours) rearranges the keto groups on C2 and C3 successively in favour of groups C1 and C4, double bonds between C2 and C1, group C5 (rearrangement of carboxyl group on C6), C1 and C4, C1, and C1, respectively. The energy excitation of groups C1 and C6 decreases in favour of groups C4 with samples oxidized for 24 to 26 hours, respectively, while with samples oxidized for 32 to 36 hours in favour of groups C5 or C2.

— The unoxidized groups C2 and C5 are stable regarding their structure and energy level for samples oxidized up to 26 hours while for samples oxidized for longer periods the weight loss in this range shows a maximum in the case of samples oxidized for 28 and 36 hours always at the expense of groups C1 and C6. The energy excitation of samples oxidized for 24–30 hours does not change, while with samples oxidized for 32–36 hours it increases mostly to the detriment of groups C1 and C6.

— Except for samples oxidized for 30–32 hours the keto group on C3 (adjacent to the hydroxyl group on C2) is stabilized together with the oxygenic group at C4 at a minimal value of a weight loss of 10% with samples oxidized for 30 hours at most in favour of the double bond on carbon skeleton, and in the sample oxidized for 28 hours in favour of the hydroxyl group on C3 also. The weight loss attributable to keto group on C3 (adjacent to hydroxyl group on C2) gradually increases up to the detriment of keto group on C2 and the double bond between C2 and C3 with samples oxidized for 32 and 34 hours. The chemical structure of the keto group on C3 (adjacent to hydroxyl group on C2) is stabilized for samples oxidized for longer periods.

— The energy excitation of group C4 and the keto group on C3 (adjacent to the hydroxyl group on C2) increases successively to the detriment of C1(C6), and C3 (hydroxyl group) or C2(C5) for samples oxidized up to 26 hours and for 28 hours, while as the oxidation time is increased it decreases in favour of C2 and C5. Samples oxidized for 36 hours are energetically stable.

— Hydroxyl group on C3 is stabilized at a value of 10% weight loss except for samples oxidized for 30 and 32 hours, which shows successively a decreased weight portion in favour of the double bond on the carbon skeleton and the keto group on C3 (adjacent to the hydroxyl group on C2). Except for the longest oxidation period of 38 hours the energy excitation of the hydroxyl groups on C3 is uniform and decreased. For samples oxidized for 34 and 36 hours decrease in the energetic excitation occurs in favour of groups C2 and C5.

— The portion of double bond between skeleton carbons increases non-uniformly with respect to the weight loss for samples oxidized up to 30 hours, while a uniform weight decrease of about 3% is recorded for samples oxidized for longer periods. The increase in share of double bonds between skeleton carbons for samples oxidized up to 30 hours occurs successively to the detriment of the keto group on C3 (adjacent to the hydroxyl group on C2). A decrease in the share of double bonds for the sample oxidized for 34 hours occurs reversely to the favour of the keto group on C3 (adjacent to the hydroxyl group on C2).

— The energy excitation of skeleton carbons linked by double bonds is unequal and decreases for samples oxidized up to 30 hours due to the increasing share of double bonds, while it is equalized for samples oxidized for longer periods except for a light increase for samples oxidized for 36 and 38 hours.

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Zusammenfassung — Die Wirkung einer zweijährigen Alterung von chemisch voroxydierter und bestrahlter Zellulose wurde untersucht. Veränderungen der chemischen Struktur und die energetische Anregung von Atomgruppen des Oxyzellulosegerüsts wurden unter qualitativen und quantitativen Gesichtspunkten studiert. Eine numerische Interpretation und ein komplexer Vergleich der Größen (Aktivierungsenergie, Energiemenge *EW*, Werte der thermischen Effekte — DTA-Peakflächen, Gewichtsverluste) von 4 pyrolytischen Abbauphasen wurden vorgenommen, wobei für die oxydative Pyrolyse ein Derivatograph verwendet wurde.

Резюме — Для исследования влыяния двухлетнего периода старения целлюлозы, предварительно химически окисленной и затем облученной, был использован метод окислительного пиролиза с дериватографом. Проведена качественная и количественная оценка изменений химической структуры и энергий возбуждения атомных группировок оксицеллюлозы. Для четырех стадий пиролиза приведена количественная интерпретация и дано сопоставление таких параметров, как энергия активации, количество энергии *EW*, величины термических эффектов (площади ДТА-пиков) и потери веса.