

PHYSICO-CHEMICAL STRUCTURE OF OXYCELLULOSE
AFTER ONE-MONTH AND ONE-YEAR STORING,
DETERMINED BY THE DERIVATOGRAPH

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(Received June 6, 1975)

The effects of ageing for periods of one month and one year upon chemically pre-oxidized and radiation-sterilized oxycellulose were investigated. Changes in chemical structure and energetic excitation of atomic groups of the oxycellulose skeleton were evaluated from qualitative and quantitative aspects. Use was made of numerical interpretation of activation energy quantities, weight losses, the quantitative energetic quantity EW, and thermal effects (areas of DTA curve peaks) of individual degradation reactions, when applying the oxidation pyrolysis method with a Derivatograph.

The physico-chemical structure of fresh oxycellulose prepared by nitrous pre-oxidation and radiation-sterilized with a dose of 100 kJ/kg was investigated in the preceding study [1]. The qualitative and quantitative interpretation of activation energies and weight losses made possible determination of chemical changes and energetic excitations of atomic groups. The present work deals with the evaluation of structural changes caused in nitrous oxycellulose during one-month and one-year storing. Structural changes of oxycellulose after two-year storing will be evaluated in the following study [2].

Methods

Samples of oxycellulose prepared by nitrous pre-oxidation and sterilized with a radiation dose of 100 kJ/kg (numbered 1 to 8 and differing in that the length of chemical pre-oxidation increased by a constant difference [3] were exposed to an ageing effect during storing in the dark in non-sealed polyethylene packages allowing approach of air at laboratory temperature for periods of one month (2nd series of samples) or one year (3rd series of samples).

The pyrolysis of samples was carried out with a derivatograph (MOM); the weight of powder samples was 50 mg, the heating rate was 5,5° min, and an air atmosphere was employed with constant exhaustion of pyrolysis products (80 ml/min).

For the interpretation of experimental results, an adapted method of determination of kinetic parameters was applied [4] after evaluating the expression E/n (activation energy, order of reaction), using experimental data [5] and graphical

construction of the tangent at the point of inflection, and employing a nomograph [6] and an approximative method [6] designed for the solution of more complicated overlapping pyrolytic reactions.

Results and discussion

Samples of fresh oxycellulose [1] and other exposed to one-month and one-year storing degrade during oxidation pyrolysis in four overlapping phases.

Interpretation of the oxidation pyrolysis of freshly-prepared radiation-sterilized oxycellulose has shown [1] that during the first phase of pyrolysis carbons C6 and C1 are degraded, while C5 and C2 are degraded during the second phase; during the third, divided into partial phases 3A and 3B, oxygenic atomic groups on C4 and C3 are degraded. Degraded during the fourth phase is the molecular part linked by a double bond between carbons in the molecular skeleton (C3 and C4).

The radiation-sterilization of oxycellulose is the main cause of changes occurring in the chemical structure and energetic excitation of atomic groups during storing.

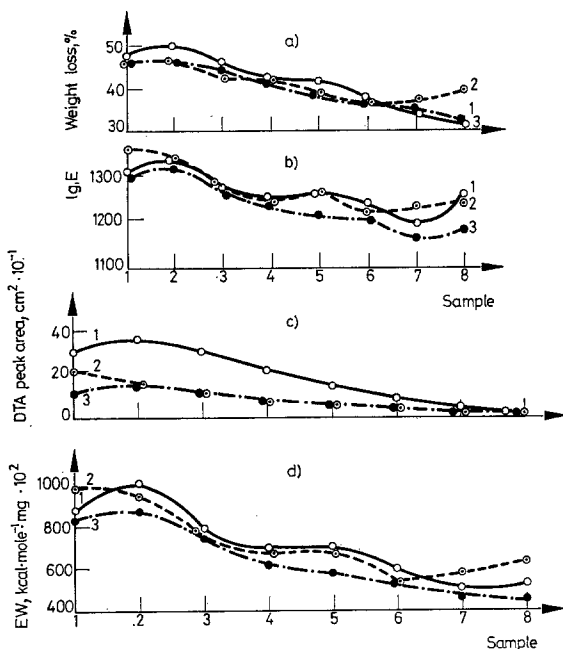


Fig. 1. Oxycellulose, first pyrolytic phase, samples 1 — fresh, 2 — one-month ageing, 3 — one-year ageing. a) Degraded weight portions. b) Logarithm of activation energy. c) Area of DTA peaks. d) Quantitative energetic quantity EW

The curves of weight losses and activation energy when atomic groups C6 and C1 [1] are degrading, have similar courses for both fresh samples and these stored during periods of one month or one year (Fig. 1a, b). Samples 7 and 8 form

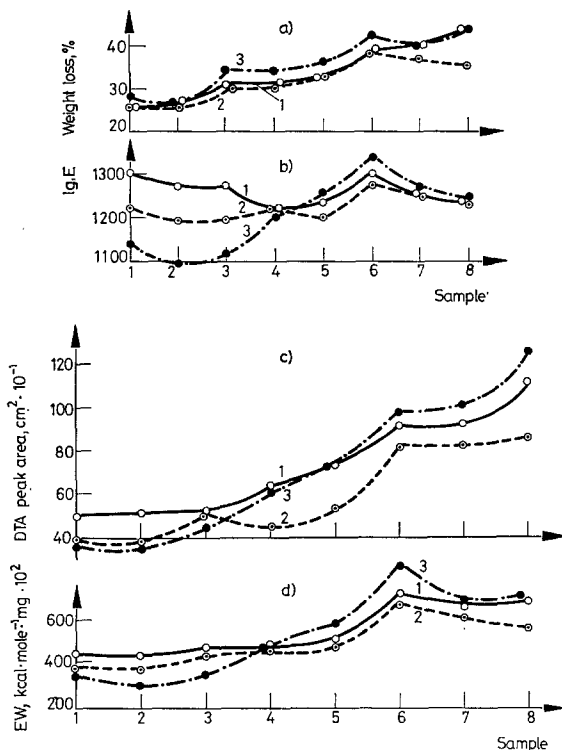


Fig. 2. Oxycellulose, second pyrolytic phase, samples 1 — fresh, 2 — one-month ageing, 3 — one-year ageing. a) Degraded weight portions. b) Logarithm of activation energy. c) Area of DTA peaks. d) Quantitative energetic quantity EW

an exception, in which a transitional elevation of weight occurs in the second series of samples. The weight curves for the third series of samples (one-year storing) are the most nearly linear. This indicates structural and chemical stability of groups C6 and C1 maximally oxidized up to the carboxyl stage.

The non-uniform activation energy curve (Fig. 1b, curve 2) and quantitative energetic quantity EW (Fig. 1d, curve 2) of the first pyrolytic phase for the second series of samples (one-month storing) demonstrate an energetically non-equilibrated unstable state, becoming equalized and stabilized at somewhat lower activation energy values (Fig. 1b, curve 3) in the third series of samples (one-year storing). The stabilization takes place through the equalizing of the free electron concentration on the terminal carbon groups (C6, C1), degrading during the first pyrolytic

phase. With the third series of samples groups C1 and C6 attain the most readily degradable oxidation stage, as is evident from the decrease in the quantitative energetic quantity EW (Fig. 1d, curve 3) and the DTA peak areas (Fig. 1c, curve 3).

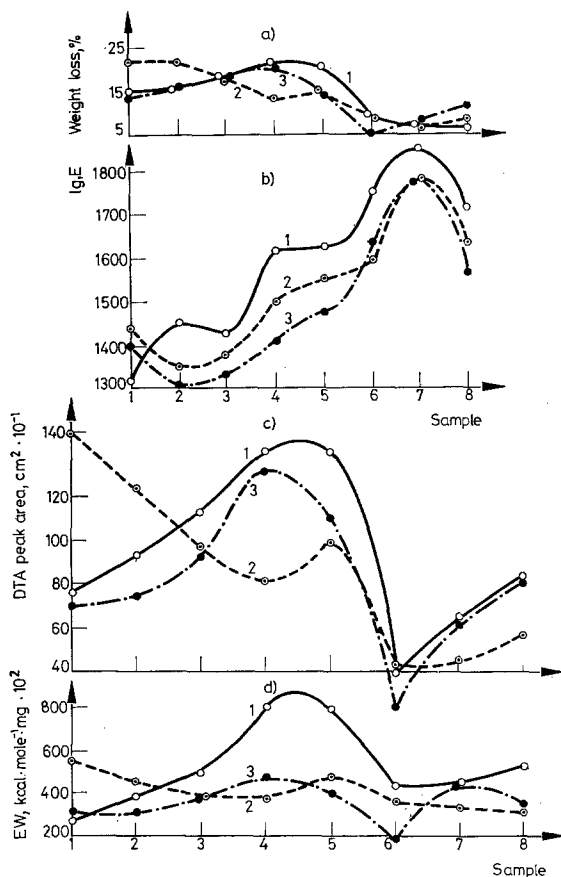


Fig. 3. Oxycellulose, pyrolytic phase 3A, samples 1 — fresh, 2 — one-month ageing, 3 — one-year ageing. a) Degraded weight portions. b) Logarithm of activation energy. c) Area of DTA peaks. d) Quantitative energetic quantity EW

The general structural instability of atomic groups C5 and C2 after opening of the pyran cycle is evident in samples stored for one month, in which the weight in the second pyrolytic phase (Fig. 2a, curve 2) does not change, or decreases (with samples 7 and 8) in favour of groups C1 or C6 (first pyrolytic phase). During the one-year storing the degradation of groups C5 and C2 slightly increases in samples 3–8 (Fig. 2a, curve 3) by an increase in the oxidation state of the oxygenic carbon group to the detriment of group C3 (pyrolytic phase 3B).

From the viewpoint of energetic excitation, group C5 has been in an unequalized state. During one-month storing it attracts free electrons, as shown by the decrease of the E curve in Fig. 2b, curve 2, for all samples 1–8. This causes facilitation of pyrolytic degradation, as shown by the decrease of DTA peak areas (Fig. 2c, curve 2), due to the decrease of the quantitative energy EW needed for pyrolysis with all samples of the second series (Fig. 2d, curve 2).

During one-year ageing the energetic excitation of groups C5 and C2 increases only for samples 1–3, while, in contrast, it otherwise decreases, with a maximum drop for sample 6, probably as a result of a higher oxidation degree of these atomic groups due to a longer period of chemical pre-oxidation, as shown by the corresponding courses of the E and EW curves and the DTA peak areas (Fig. 2b, 2d, 2c, curve 3).

The keto group formed by pre-oxidation on C4 (degrading during pyrolytic phase 3A) rearranges to a hydroxy group during the storing process, in favour of either a double bond between C4 and C3 (fourth pyrolytic phase) or further formation of a keto group on C3 (pyrolytic phase 3B).

After one-year storing the rearrangement of group C4 has stabilized it into a similar state as with freshly pre-oxidized samples. With samples 1–5 there is a tendency to reach an equal weight for group C4 during the storing, amounting to 22% (Fig. 3a, curve 3). With samples 6–8 a decreased weight is observed for group C4, which is less subjected to changes in chemical structure during storing. This is a consequence of the primary chemical pre-oxidation inducing formation of a keto group on C3 (fresh samples). This makes difficult the enol rearrangement producing formation of keto group on C4 (pyrolytic phase 3B in sample 6, Fig. 4a, curve 1).

The energetic excitation of group C4 increases during one-month and one-year storing for samples 2–8, but not for sample 1, as is shown by the course of energetic curve E (generally being lower) for samples subjected to the process of ageing (Fig. 3, curves 2 and 3). The decreasing tendency of group C4 to attach electrone depending on the length of pre-oxidation (samples 1–8) remains unchanged during ageing, as shown by the general increasing tendency of the activation energy curve for samples 2–7 (Fig. 3b, curves 2 and 3). The metastability induced during one-month storing in both chemical structure and energetic excitation of group C4 gives way to an equilibrium state after one-year storing, as shown by the unequal but successively equalized courses of the second and third curves of both EW and DTA peak areas in pyrolytic phase 3A (Figs 3d and 3c).

The atomic group C3 which, depending on the length of pre-oxidation behaves differently in fresh samples in pyrolytic phase 3B for samples 6–8 most pre-oxidized, becomes severed even after one-month ageing in the third and subsequent samples (Fig. 4a, curve 2). After one-year ageing the weight portion belonging to group C3 in samples 3–8 is reduced, probably due to a reversed rearrangement of the keto group in favour of group C4 (Fig. 4a, curve 3).

The energetic metastable state of group C3 after one-month storing gradually equalizes during one-year storing with almost all samples (pyrolytic phase 3B)

by yielding free electrons to other sites in the molecule, as is evident by the unequal and equal courses of the E curves for the second and third series of samples respectively (Fig. 4b).

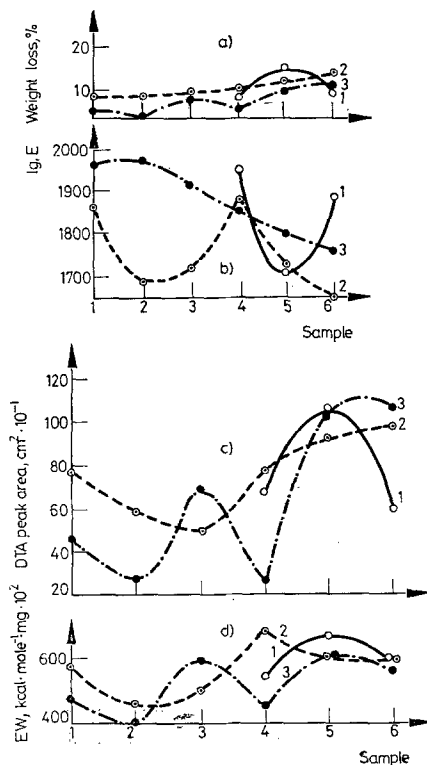


Fig. 4. Oxycellulose, pyrolytic phase 3B, samples 1 — fresh, 2 — one-month ageing, 3 — one-year ageing. a) Degraded weight portions. b) Logarithm of activation energy. c) Area of DTA peaks. d) Quantitative energetic quantity EW

The metastable chemical structure and energetic excitation of group C3, induced during one-month storing, is generally stabilized after one-year storing for samples 3–8, except for sample 5, as shown by the decreased and nearly corresponding course of the EW curves (Fig. 3d, curve 3) and the curves of DTA peak areas (Fig. 3c, curve 3) in pyrolytic phase 3B.

Weight changes in the fourth pyrolytic phase as a result of rearrangements of double bonds from the keto groups C4 and C3 (pyrolytic phase 3A and 3B) to the carbon-carbon bond cover only a fraction of the weight corresponding to a single carbon of the skeleton. During one-year ageing of samples the weight change in the fourth phase, (except for samples 1, 2 and 6) is stabilized by decrease to a minimum, while during one-month ageing a structurally unstable intermediate stage is formed (Fig. 5a, curves 2, 3).

The unstabilized energetic excitation of the carbon group with double bond in samples 1 and 2 is apparent from the elevated values of activation energy, the quantitative energetic quantity EW and the DTA peak areas in the fourth pyrolytic

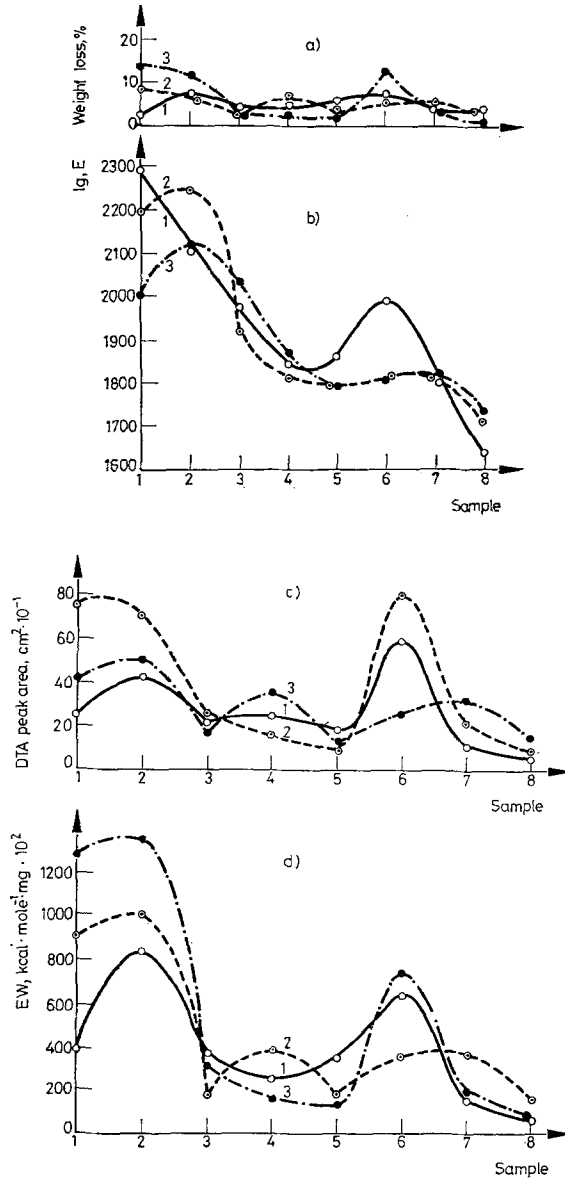


Fig. 5. Oxycellulose, fourth pyrolytic phase, samples 1 — fresh, 2 — one-month ageing, 3 — one-year ageing. a) Degraded weight portions. b) Logarithm of activation energy. c) Area of DTA peaks. d) Quantitative energetic quantity EW

phase for samples after one-month and one-year ageing (Figs 5b, 5c and 5d, curves 2 and 3). Successive equalizing of the activation energy values for samples 3 and 4, and the equalized course for samples 5–8 in both series of stored samples (Fig. 5b, curves 2 and 3), indicate that due to one-year ageing the atomic group linked by the double bond in the carbon skeleton attains energetic equilibrium. The electron excitation for all the samples pre-oxidized for a longer time (samples 4–8, Fig. 5b, curves 2 and 3) has approximately the same value. When changes in chemical structure and energetic excitation are evaluated simultaneously, it is apparent that the atomic group linked by the double bond is stabilized only in samples 3, 4, 5, 7 and 8 during one-year storing, while samples 1, 2, and 6 do not achieve the equilibrium state. This is shown for samples 1, 2 and 6 by increased, and for samples 3, 4, 5, 7 and 8 by decreased or equalized EW values and DTA peak areas in the fourth pyrolytic phase after one-year ageing (Figs 5d and 5c, curve 3).

Conclusions

The properties of oxycellulose exposed to ageing are characterized by:

- a) the structural chemical and energetic stability of atomic groups C6 and C1 during one-year ageing;
- b) the structural chemical and energetic instability of atomic groups C5 and C2, depending on the time of storing, in all samples;
- c) the successive stabilization of the chemical structure of group C4 in samples 1–5, partial instability in samples 6–8, and a decrease in energetic excitation in samples 2–7 on one-month and one-year ageing;
- d) the instability of the chemical structure and energetic excitation of group C3 in samples 3–8 on one-month ageing, and successive (uncompleted) stabilization during one-year ageing;
- e) the structurally unequalized formation of the C–C double bond after one-month storing and successive stabilization by decrease in the double-bond formation to a minimum on one-year ageing in all samples. The instability of energetic excitation of the group with double bond in samples 1–4 and successive attainment of stabilized excitation with samples 5–8 on one-month and one-year ageing.

References

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RÉSUMÉ — On a étudié l'effet d'un vieillissement d'un mois et d'une année sur l'oxy-cellulose préoxydée par voie chimique et stérilisée par irradiation. On a évalué d'un point de vue qualitatif et quantitatif les changements de la structure chimique et de l'excitation énergétique des groupes d'atomes du squelette de l'oxycellulose. En suivant la pyrolyse à l'aide d'un Derivatograph on a établi l'interprétation numérique des valeurs respectives de l'énergie d'activation, des pertes de poids, des quantités d'énergie EW et de l'effet thermique (surface des pics sur les courbes ATD) pour les réactions individuelles de dégradation.

ZUSAMMENFASSUNG — Die Wirkung der Alterung von einem Monat bzw. einem Jahr auf chemisch präoxidierte und durch Bestrahlung sterilisierte Oxycellulose wurde untersucht. Änderungen in der chemischen Struktur und der energetischen Aktivierung der Atomgruppen des Oxycellulose-Skeletts wurden qualitativ und quantitativ bewertet. Die numerische Interpretation der Aktivierungsenergien, die Gewichtsverluste, die quantitativen Energiemengen EW und die Werte des thermischen Effekts (die Fläche der DTA-Peaks) der einzelnen Abbaureaktionen wurden unter Einsatz der Oxidations-Pyrolysenmethode mit dem Derivatographen bestimmt.

Резюме — Было исследовано старение за период одного месяца и одного года предварительно химически окисленной и радиально стерилизованной оксицеллюлозы. Количественно и качественно выявлены изменения химической структуры и энергетического возбуждения атомных группировок скелета оксицеллюлозы. Была использована числовая интерпретация количества энергии активации, величин потери веса, количественная энергетическая величина EW и значения термического эффекта (площадь пиков кривых ДТА) индивидуальных деградационных реакций при использовании метода окислительного пиролиза с дериватографом.