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THE EFFECT OF THE HYDRATION DEGREE ON THE HYDROTHERMAL AND THERMO-OXIDATIVE STABILITY OF SOME COLLAGENEOUS MATRICES

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Abstract

The methods of the thermal analysis (TG, DTG and DTA) were used in order to investigate the effect of the hydration degree on the thermal behaviour of some collageneous matrices. It was pointed out that the degradation of hydrated collagen in the temperature range 20–400°C occurs through two successive processes accompanied by mass losses. The first process, consisting in the collagen dehydration, is endothermic and takes place in the temperature range ≈25 – ≈125°C. The second process is exothermic and consists in the decomposition and/or thermo-oxidation of dry collagen. The thermal parameters of both processes depend on the hydration degree of collagen. The observed dependencies show that the hydrothermal and thermo-oxidative stability of collagen are strongly correlated with its water content.

Keywords: collageneous matrices, hydrothermal stability, thermo-oxidative stability

Introduction

The protein collagen is the most predominant and most important protein of the skin and, therefore, the results obtained in the investigation of collagen properties would be obtained in a large part for skin itself. The numerous utilization of collagen, especially in some pharmaceutical recipes, determined the research of its physical, chemical and biological properties.

The thermal analysis methods (TG, DTG, DTA, DSC) were used [1–7] for investigation of the following processes that occur at the heating of collagen and some collagen based materials (natural skins, processed leathers, parchments, etc.) in different environmental conditions (air, free oxygen atmosphere, water): *a*) the denaturation that consists in transition of collagen from the triple helix to a randomly coiled form; *b*) the dehydration; *c*) the thermal degradation; *d*) the thermo-oxidative degradation. It was pointed out that the thermal properties of collagen and collagen based materials depend on the procedure used for obtaining the collagen, the operating conditions of tanning, the water content and the deterioration resulted by natural or artificial aging.

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In this paper, the results obtained by thermal analysis methods (TG, DTG and DTA) at the investigation of the effect of the hydration degree of a collagen sort on the parameters that characterize the processes which occur at its progressive heating are presented.

Experimental

Materials

Collageneous matrices were obtained by hydrophilization of type I collagen gels, extracted from bovine hides according to a technology elaborated by Leather and Footwear Research Institute. The chemical and enzymatic processes of this technology allow extracting more than 90% of structural fragments of native conformation collagen molecules or their polymerizates. The collagen matrices used has a sponge-like structure with highly polydispersed micro- and macro-pores ($\approx 8 \cdot 10^9$ pores/cm^2). The physico-chemical and biological characteristics of this sort of collagen are: 23% humidity, 80% protein matter, 0.8% minerals, 30 days 'in vivo' resorption (tested by subcutaneous implant). The accuracy of the humidity evaluation was ±1.5%.

The hydration of collagen matrices was accomplished with saturated water vapors, at 20°C, varying the hydration time from 17 to 262 h. The humidity changes during the time followed in order to establish the maximum hydration capacity and the time needed to reach the hydration equilibrium are shown in Fig. 1. A matrix of 115% humidity has become lightly wet and the microporous structure has lost its elasticity. At 126% humidity, the matrices can be considered as a solid-liquid. For the thermal characterization of the hydrated matrices, samples of 21.74; 31.12; 60.30 and 80.03% humidity were selected.

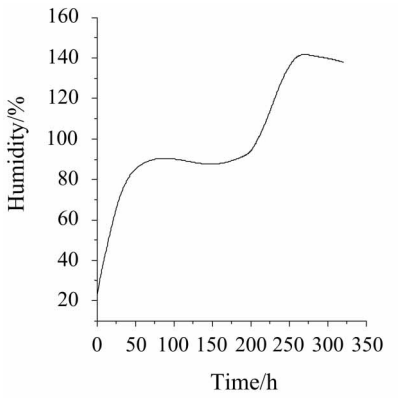

Fig. 1 The time dependence of the humidity of the collageneous matrices

Thermal analysis

The heating curves (TG, DTG and DTA) of samples were recorded with a Q-1500 D Derivatograph (MOM, Hungary), in static air atmosphere, in the temperature range 20–500°C, at a heating rate of 2.5 K min^{-1}. The masses of the analyzed samples were in

the range 18.9–20.8 mg. The heating of the sample was performed in a cylinder shape platinum crucible and α-Al_2O_3 was used as reference material. The standard deviations of measurements were: ±1.5% for the mass loss and ±0.5°C for the temperature.

Results and discussions

Figure 2 shows the TG, DTG and DTA curves for the sample *U*=21.74% (humidity). Similar curves have been obtained for all analyzed samples. These curves are similar with those reported previously for collagen [2, 5] and leather [4].

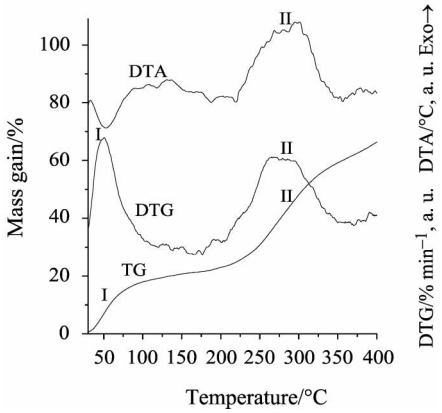

Fig. 2 Thermoanalytical curves of *U*=21.74%

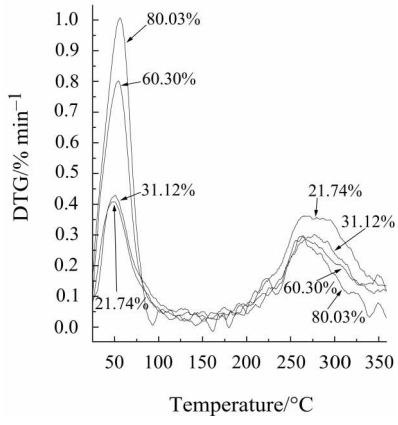

Fig. 3 DTG curves corresponding to the hydrated collagen samples

The thermal degradation of hydrated collagen in the temperature range 20–400°C occurs through two successive processes accompanied by mass losses. The first process (denoted by I) is an endothermic one and takes place in the temperature range 25 to 125°C. This process was attributed [2, 5] to the collagen dehydration. The second process (denoted by II) is an exothermic one and consists in the decomposition and/or thermo-

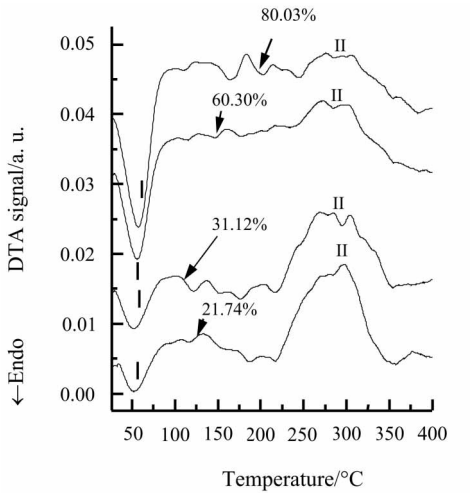

Fig. 4 DTA curves corresponding to the hydrated collagen samples

oxidation of dry collagen. Some volatile products with low molecular mass are released during this process.

Figures 3 and 4 depict comparatively the DTG and DTA curves corresponding to the analyzed samples. The main parameters of the processes I and II are listed in Table 1.

Table 1 The parameters of non-isothermal degradation of the hydrated collagen samples

Sample/ %	Δm_{125}/ %	Δm^{u}_{125}/ %	T^{I}_{max}(DTG)/ °C	T^{I}_{min}(DTA)/ °C	T^{II}_{max}(DTG)/ °C	Δm^{u}_{350}/ %	Δm^{u}_{400}/ %
21.74	19.30	23.94	48	47	≈277	49.37	58.22
31.12	18.52	22.73	50	50	≈273	39.06	46.53
60.30	33.02	47.11	53	53	≈266	44.21	53.30
80.03	38.05	61.42	56	56	≈263	39.99	43.61

Δm_{125}=the relative mass loss in process I (until 125°C), in respect with sample mass (%)

$\Delta m^{u}_{125} = \frac{\Delta m_{125}}{100-\Delta m_{125}} 100$ = teh relative mass loss in process I (until 125°C), in respect with dry collagen (%)

T^{I}_{max}(DTG)=the temperature corresponding to the DTG maximum characteristic for the process I

T^{I}_{min}(DTA)=the temperature corresponding to the DTA minimum characteristic for the process I

$\Delta m^{u}_{350} = \frac{\Delta m_{350}-\Delta m_{125}}{100-\Delta m_{125}} 100$; $\Delta m^{u}_{400} = \frac{\Delta m_{400}-\Delta m_{125}}{100-\Delta m_{125}} 100$; where Δm_{350} and Δm_{400} are the mass losses (%) at 350 and 400°C, respectively

The inspection of Table 1 and Figs 3 and 4 shows that the parameters of both processes II and I depend on the hydration degree of collagen.

For the dehydration process (process I), the following statements can be noted:

a) For samples *U*=21.74% and *U*=31.12%, the desorbed water masses are practically equal.

b) For the samples U=31.12%, U=60.3% and U=80.03%, the desorbed water loss increases progressively with the hydration degree.

c) For a given sample, the temperature corresponding to DTG maximum is practically equal with that corresponding to DTA minimum. This temperature increases with the hydration degree.

d)The rate of dehydration process increases with the hydration degree. It results that the amount of weak bonded water increase with the hydration degree.

For thermo-oxidative degradation process (process II), the following statements can be noted:

a)The mass loss, reported to the dry collagen mass, depends on the hydration degree. The maximum value was obtained for sample U=21.74%.

b)The sample U=21.74% exhibits the maximum rate of degradation.

c) For $T \geq 270$°C, the degradation rate increases with the hydration degree.

d)The DTG and DTA curves are roughly. It results that the materials resulted by dehydration have a heterogeneous structure.

e)The temperature of the main DTG maximum decreases weakly with the hydration degree.

f) The area of the DTA curves which is proportional with the evolved heat, as well as the height of this curve, which is proportional with the degradation rate, depends on the hydration degree. A good correlation between the results obtained by DTA method and those obtained by DTG method can be noted.

Conclusions

By using of thermal analysis methods (TG, DTG and DTA), it was shown that the following processes occur successively at the progressive heating of hydrated collagen: the dehydration and the thermo-oxidative degradation. The non-isothermal parameters of these processes were determined and the dependencies of these parameters on the hydration degree were put in evidence. It results that the hydrated collagen, as well as the dry collagen exhibit structures that depend on the initial hydration degree. The future works will report on the results obtained by other analytical techniques, which will be correlated with the results presented in this paper.

References

1 P. E. McClain and E. R. Wiley, J. Biol. Chem., 247 (1972) 692.
2 J. J. Lim and M. H. Shannos, Biopolymers, 13 (1974) 1791.
3 M. Komanowsky and J. A. Leather, Chemist. Assoc., 86 (1991) 209.
4 G. de Simone, B. Naviglio, M. Tomaselli, L. Bianchi, D. Sannino and P. Ciambelli, XXIII IULTCS Congress, Friedrichshafen, May 15–20, 1995, Part I, p. 21.
5 A. Kaminska and A. Sionkowska, Polym. Degrad. Stab., 51 (1996) 15.
6 C. Chahine, Thermochim. Acta, 365 (2000) 101.
7 V. Logvinenko, O. Kosheleva and E. Popova, J. Therm. Anal. Cal., 66 (2001) 567.