

STUDY OF LEATHER AND GELATIN SPECIMENS Original, and processed with traditional and new reagents

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Abstract

The change of properties of leather and gelatin after the treatment by poly(hexamethyleneguanidine) derivatives was studied. The study of thermal transformation was performed by means of derivatograph Q-1500-D (MOM, Hungary). The dehydration process, melting of crystal areas of anhydrous collagen, the destruction of poly(peptides) chains proceed one after another in the range from 20 to 250°C.

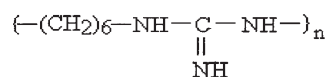
The computer program TA 1B for the non-isothermal kinetics (on the basis of the integer method) was used for data processing. The best kinetic description for the thermal dehydration in all cases was the equations of diffusion processes. We believe that this process can be considered as inner chemical diffusion: the hindrance for water molecules removal from the sample because of alternate breaking and forming of hydrogen bonds with aminoacids chains on the contact surface of pores.

Both the difference in water content, and the slight difference in values of kinetic parameters (E and A) are discussed; they are attributed to the structure difference between leather collagen and gelatin and processing effect.

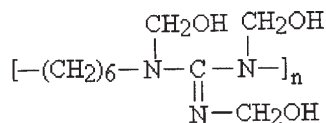
Keywords: dehydration, diffusion processes, gelatin, kinetics, leather, poly(hexamethyleneguanidine)

Introduction

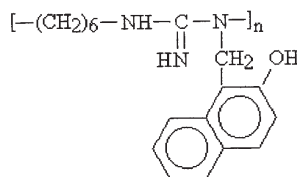
The basic goal of the work was the comparison of the different modes of treatment for leather-shoe specimens: the traditional chrome tanning and dyeing, or the treatment by new reagents, synthesized on the basis of poly(hexamethyleneguanidine):



The possible forms of the methylol derivative:



and α -naphthol derivative:



All changes of leather structure, taking place under leather processing by different reagents, are due to the interaction of these reagents with collagen, the main leather protein. A certain characteristic of collagen change in the engineering procedure is the thermal stability of leather. The edible gelatin is the product of partial hydrolysis and disaggregation of collagen; although both macrostructure, and microstructure are missing in it, general sequencing of aminoacids groups arrangement is maintained. The qualitative similarity in gelatin and collagen behavior under heating was disclosed earlier [1]. We considered that it makes sense to check, whether or not the edible gelatin is the appropriate model substance for the study of the collagen characteristics change after leather processing.

Experimental

The specimens of the leather and gelatin were studied (gelatin films were formed by drying of the 5% water solution on air). These specimens were treated by water solutions of poly(hexamethyleneguanidine) or its derivatives. Poly(hexamethyleneguanidine) derivatives are new reagents, proposed for leather processing [2]. Leather specimens, being subjected to traditional factory treatment (chrome tanning and dyeing) are studied for comparison. The storage conditions were identical, therefore it was possible to compare both the dehydration processes kinetics, and the quantity of bonded water.

The study of thermal decomposition was performed by means of derivatograph Q-1500-D (MOM, Hungary). Samples (mass 280 mg for kinetic studies and 560 mg for water determination) were cut into pieces (0.3×0.3×0.2 cm) and placed on plate-like sample holder; constant heating rate was 2.5 grad min⁻¹; atmosphere: static air.

The computer program TA 1B [3–4] for the non-isothermal kinetics (on the basis of the integer method) was used for data processing. TG curve was used as the kinetic curve. The selection of the best kinetic description between 13 different topochemical equations has been going on by the linearity of $\log g(\alpha)$ vs. $1/T$ separately for three areas of conversion degree: $0.05 \leq \alpha \leq 0.30$; $0.30 \leq \alpha \leq 0.80$; $0.80 \leq \alpha \leq 0.95$. During calculations these starting areas of conversion degree expand until the difference

in activation energies (calculated from one point to the other) goes for all calculated area (because of non-linearity of obtained $\log g(\alpha)$ function) beyond the predetermined deviation value ($\Delta E=5\%$ in this case). Certain areas of conversion degree and standard deviations for $\log g(\alpha)$ in the confidence regions (where the kinetic parameters E and A are calculated) are found for every equation. The selection of the best kinetic description is effected both on the standard deviations values, and on the extent of the conversion degree area.

Results and discussion

It is known that gelatin loses water at 20–184°C, the anhydrous sample melts at 200–220°C, and the destruction undergoes at 235°C [5, 6]. Our TG experimental data are in Fig. 1. The thermal properties are scarcely affected by processing of gelatin with the poly(hexamethyleneguanidine) derivatives, although the quantity of water contents decreased: mass losses are 13.1 in the processed sample and 14.8% in untreated gelatin.

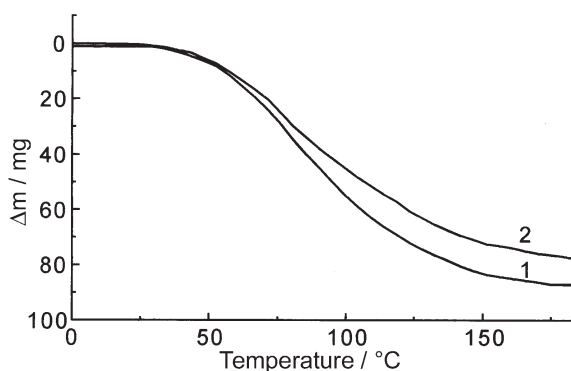


Fig. 1 Thermogravimetric curves for gelating samples (sample mass 555 mg); 1 – starting sample; 2 – treated by methylol derivative of poly(hexamethyleneguanidine)

The shape of DTA and TG curves of leather are more or less akin to these curves of gelatin samples, though the more complicated morphological structure of collagen changes the character of the thermal transformation: the endothermic effect at 200–220°C is stipulated by melting of the crystal zones of anhydrous collagen, and the next peak is connected with the break-up of the cross-cut bonds between the poly(peptide) chains in collagen and with the break-up of the chains itself [7]. The typical curves are in Fig. 2 (endothermic effects are not intensive because of plate-like holder type). The water mass loss is higher for the leather dehydration: it is close to 16% (13–15% for original and processed gelatin samples).

The best kinetic description for the thermal dehydration in all cases (for the initial part of the dehydration reaction) was equations of diffusion processes: such as Jander (D2), Ginstling–Brounstein (D4) and Zhuravlev–Lesokhin–Tempelman (D5) models. The difference both in standard deviation values, and in kinetic parameters

between them was rather small. We believe that such a transfer from one kinetic diffusion model to another one is not significant by itself, and can be assigned to the structure change: the leather collagen structure is more complicated than gelatin one.

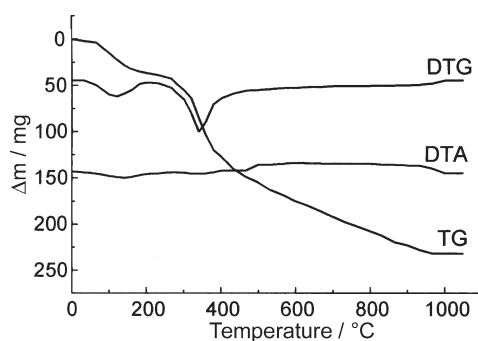


Fig. 2 Thermoanalytical curves for leather sample, treated by methylol derivative of poly(hexamethyleneguanidine)

In most cases Zhuravlev–Lesokhim–Tempelman model (D5) covered the dehydration process over a wider area of conversion degree α , and this equation was taken for generality of the description for all sample dehydration. Only single specimens of leather and gelatin were studied, so we could not calculate the random error. Standard deviations for the activation energy and pre-exponential factor do not usually go beyond 3–5% in studies of similar poorly reversible processes [8].

Table 1 Kinetic parameters of the dehydration processes for leather and gelatin specimens

Specimen	Treatment by reagents	$E/\text{kJ mol}^{-1}$	$\log A$	α
Gelatin	'as is'	114	12.8	$0.02 \leq \alpha \leq 0.34$
Gelatin	Methylol derivative of poly(hexamethyleneguanidine)	106	11.4	$0.07 \leq \alpha \leq 0.39$
Leather	Factory-made (being shaved, chrome-tanned)	116	13.1	$0.03 \leq \alpha \leq 0.37$
Leather	Methylol derivative of poly(hexamethyleneguanidine), without chrome tanning	116	13.0	$0.03 \leq \alpha \leq 0.46$
Leather	Aminophenyl derivative of poly(hexamethyleneguanidine), chrome tanned	117	13.3	$0.03 \leq \alpha \leq 0.42$

Kinetic parameters of dehydration processes (calculated from TG data) are presented in Table 1; it is worth noting, that full water mass loss ($0 \leq \alpha \leq 1.0$) occurs inside temperature interval 30–184°C for all specimens. We believe that this process can be considered as inner chemical diffusion: the hindrance for water molecules motion

(during their removal from the sample) because of alternate breaking and forming of several hydrogen bonds by every water molecule with aminoacids chains on the contact surface of pores. This is verified by rather big activation energy values of diffusion process.

Kinetic parameters of gelatin dehydration are changed slightly after the gelatin treatment by methylol derivative of poly(hexamethyleneguanidine), and the water content decreases. Kinetic parameters of leather dehydration remains constant, no matter what kind of treatment was used, although (as compared with standard factory-made specimens) processing with methylol and naphthol derivatives decreased the water content by several percents.

Kinetic parameter values of dehydration processes for all samples point at a negligible change in the collagen structure of both leather and gelatin if treated with varied reagents. The incorporation of poly(hexamethyleneguanidine) derivatives can result in cross-linking in the structure, so the observed decrease of the bonded water content after the treatment is most likely connected with the decrease of the amount of active centers, sorbing the water molecules with mentioned hydrogen bonds formation.

Conclusions

The thermoanalytical research confirms the identity of processes, being proceeded both in gelatin collagen, and leather collagen under heating. Such a conclusion allows to consider the gelatin as the workable model for studying leather properties. It is established that leather samples, treated with different reagents, are similar in behavior under heating. It was disclosed that the required leather quality (being estimated on water content and water containment) survived after treatment with a new kind of reagents, poly(hexamethyleneguanidine) derivatives, (when compared with traditional processing).

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