Effect of Urea Processing on the Thermal Degradation Kinetics of Cattlehide Collagen Fibers[#]

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Abstract: Both the Horowitz-Metzger method and Coats-Redferm method were employed to get the thermal degradation activation energy (TDAE) of the samples. With the changes in thermal degradation activation energy of the samples processed with urea solutions being considered, the influence and mechanism of urea processing on the aggregation structure of collagen fibers were discussed. It was found that, with the increase in urea concentration, the thermal degradation activation energy first decreases and then increases. After being processed in urea solutions, the samples were washed with distilled water to remove the urea, and the thermal degradation behaviour of the samples was also studied. It was found that the thermal degradation activation energy recovers to its original level, indicating that the urea function on collagen fibers is temporary and reversible. The mechanism of urea processing involves the destruction of hydrogen bonds between collagen chains. Upon water washing, the urea was removed from the samples, and the collagen structure returned to their original state.

Key words: collagen fibers; urea; hydrogen bonds; thermal degradation activation energy

1 Introduction

Collagen is widely used in food, medicine, bioengineering and the cosmetic industry for its unique structure, biochemistry and biological character¹. Leather is a natural collagen-based polymer composite from hides or skins through a series of physical and chemical processes².

Thermal stability is an important criterion for collagen materials, including leathers. The hydrothermal stability of leathers has been previously studied in detail ². However, the shrinkage and degradation mechanisms of collagen have not been thoroughly studied ³. In our previous study, the thermal degradation activation energy of differently tanned and sweat soaked collagen fibers were studied, and the influence of tanning and sweat soaking on the thermal degradation activation energy of collagen fibers was discussed ⁴⁻⁶.

In the liming process of leathermaking, urea is usually used. With regard to the influence of urea on structure, thermal degradation behaviours and aggregation state structure of collagen, however, no research has been reported. The interaction between urea and collagen is not clear, and there is no sufficient theoretical guidance for the use of urea in leathermaking. In the present paper, collagen fibers were soaked in various concentrations of urea solutions for a certain period of time, and then washed in distilled water. Thermalgravimetry (TG) and differential thermalgravimetric analysis (DTG) were employed to study the thermal degradation behaviour of the samples. The thermal degradation activation energy of the samples was calculated. The influence of urea treatment on the thermal degradation activation activation energy and aggregation state structure of the collagen fibers were analyzed and discussed.

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2 Experimental

2.1 Main materials and apparatus

Cattle hide collagen fibers, urea, and thermal analysis system.

2.2 Preparation of urea solutions

In 100 mL volumetric flasks, urea solutions were prepared with different concentrations.

2.3 Preparation of samples

Urea-processed samples: Cattlehide collagen fibers were immersed in the urea solutions with different concentrations for 7 days. After having been vacuum filtrated, the samples were air-dried and then place in a desiccator with silica gel in it for more than two weeks. The samples were then ready for Thermogravimetric (TG) analysis.

Water-washed samples: After being processed in 3.0 mol/L and 9.0 mol/L urea solutions for 7 days, the samples were repeatedly washed with distilled water to remove the urea contained in them. The filtrating and drying were the same as urea-processed samples

2.4 TG/DTG analysis and data processing

With nitrogen as a protective atmosphere, the samples were heated and TG and DTG curves were generated. The thermal degradation activation energies of all the samples were calculated by both methods of Horowitz-Metzger and Coats-Redferm.

3 Results and discussion

3.1 Thermal degradation behaviors of collagen fibers processed in urea solutions



Fig. 1 TG and DTG curves of samples

As can be seen from Fig. 1, when the samples were heated, two stages of weight loss were observed. The first one was completed before 100 °C, and it was most likely due to the evaporation of the water in the samples. The second stage appears in the temperature range from 250 °C to 450 °C. It is most likely the thermal degradation peak of the collagen fibers. The degradation of pure urea takes place between 130 °C and 250 °C. When the collagen fibers were processed in urea solutions, the degradation peak of urea appears in the TG and DTG curves of the samples. Upon increasing the concentration of the urea solutions, the peak continued growing, indicating the contribution of urea to the whole degradation of the samples.

The Horowitz-Metzger method ⁷⁻⁸: According to the Horowitz-Metzger method, the following equation is obtained:

$$\ln G(a) = \ln \frac{ART_s^2}{\beta E} - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2}$$
(1)

The thermal degradation activation energy (E) may be obtained from the slope of the plot of $\ln G(a)$ versus θ^{-7-8} .

By fitting and comparing, the function of $G(\alpha) = [-\ln(1-\alpha)]^4$ was found to present reasonable correction coefficients. The relation between $\ln G(\alpha)$ and θ was plotted to yield Fig. 2. The thermal degradation activation energy (TDAE) of the samples was calculated from the slopes of the lines as shown in Fig. 4(a).



Fig. 2 Relation between $InG(\alpha)$ and θ of samples processed in different urea solutions

The Coats-Redfern Method 7-8: According to the Coats-Redfern method, equation (2) is obtained.

$$\ln[G(a)/T^{2}] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT}$$
(2)

By fitting and comparing, the function of $G(\alpha) = [-\ln(1-\alpha)]^4$ was found to present reasonable correction coefficients. The relation between $\ln[G(\alpha)/T^2]$ and 1/T was plotted to yield Fig. 3. The thermal degradation activation energy (TDAE) of the different samples was obtained from the slopes of the lines as shown in Fig. 4(b).



Upon increasing the urea concentration, the thermal degradation activation energy (TDAE) of the samples first decreased and then increased. At a urea concentration of 2.0-3.0mol/L, the TDAE of the sample reached its minimum value. At a relatively low urea concentration, the hydrogen bonds between collagen peptides might be destroyed, and the interaction between collagen peptides were consequently weakened. As a result, the structure stability might be decreased. This results in a reduction of TDAE. A high urea concentration may cause serious damage to collagen fibers by destroying the inter-molecu lar and intra-molecu lar hydrogen bonds. The three-helical structure may even be partially damaged. When thermal shrinkage takes place in some regions, the collagen peptides may be closer to each other, and the interaction between peptide chains may be increased by the reaction between such groups as carboxyl, hydroxyl and amino on collagen fibers, resulting in a increase of thermal degradation activation energy. In the liming process of leathermaking, appropriate concentrations of urea should be used to obtain an excellent liming result.

3.2 Effect of washing on the thermal degradation of urea-processed collagen fibers



Fig. 5 TG and DTG curves of urea-processed samples before and after water washing

From these curves, it should be found that after washing, the maximum weight loss rate of the samples increased to near those of the samples without urea process. Before urea processing, two weight loss stages were observed in the TG/DTG curves of the samples. After urea processing, a new weight loss stage appeared in the temperature range of 130 °C to 250 °C, which was the degradation peak of urea contained in collagen fibers. When the samples had been FULLY washed, the urea degradation peak

disappeared, indicating that the urea in the collagen fibers was removed. The TG/DTG curves of the samples with urea process and washing history nearly overlap those of the samples without urea process. The effect of urea on collagen fibers is temporary and reversible, and no chemical reactions exist in the interaction between urea and collagen fibers. In the liming, the action of urea on collagen fibers is to open the possibility for other chemicals to penetrate into the pelts and react with collagen molecules. When everything is finished, the urea is washed from the hides. Urea, consequently, acts as an agent to assist in the liming process.

The Horowitz-Metzger Method: By fitting and comparing, the function of $G(\alpha) = [-\ln(1-\alpha)]^4$ was found to best fit the data. The correction coefficients of all the samples are reasonable. The relation of $lnG(\alpha)$ versus θ were plotted to yield Fig. 6. The TDAE was calculated from the slopes of the lines, as shown in Tab. 1.



Fig. 6. InG(a) vs. 0 for samples

Fig. 7. $\ln[G(a)/T^2]$ vs. 1/T for samples

The Coats-Redfern method: By fitting and comparing, $G(\alpha) = [-\ln(1-\alpha)]^4$ was found to present reasonable correction coefficients. The graph of $\ln G(\alpha)$ versus θ was plotted to yield Fig. 7. The TDAE was calculated from the slopes of the lines, as shown in Tab. 1.

Urea Concentration (mol/L)	0	3.0 *	3.0 **	9.0 *	9.0 **
E(kJ/mol) by Horowitz-Metzger	251.2	105.1	246.7	254.4	251.9
E(kJ/mol) by Coats-Redfern	232.5	82.8	228.4	239.2	233.5

Tab. 1. TDAE of the samples by Coats-Redfern method

* Before water washing. ** After water washing

From Tab. 1, it was found that no matter what concentration of urea solutions was used, the TDAE of collagen fibers will recover to the level of samples without a urea processing history, if the samples are fully washed in distilled water. Although the TDAE of the collagen fibers was decreased remarkably when processed in 3.0 mol/L urea solution, it will recover to the unprocessed level, if washing is performed to remove the urea. The action of urea processing on the TDAE is temporary and reversible. The effect of urea on collagen fibers is a physical action, which may interfere with the formation of hydrogen bonds between collagen molecules by forming hydrogen bonds between urea molecules and collagen molecules instead. The thermal stability of collagen fibers is decreased as a result.

4 Conclusions

Upon increasing the urea concentration, the thermal degradation activation energy of collagen fibers first decreases and then increases. At a urea concentration of 2-3mol/L, the thermal degradation activation energy of collagen fibers reaches the lowest level. At a urea concentration of more than 6.0mol/L, the thermal degradation activation energy of collagen fibers is close to that of unprocessed collagen fibers. 2. The influence of urea processing on the thermal degradation activation energy of collagen fibers is

temporary and reversible. When the urea-processed collagen fibers are fully washed in distilled water, the thermal degradation activation energy will recover to the level of unprocessed collagen fibers.

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