Effect of chrome tanning on the thermal behavior of collagen fibers: A calorimetric and kinetic analysis

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Abstract
To further understand the effect of chrome tanning on the thermal stability of leather, the thermal shrinkage behaviors of native and chrome-tanned collagen fibers were studied by differential scanning calorimetry (DSC) using isoconversional and multivariate non-linear regression (Multivar-NLR) methods. The activation energies of the shrinkage processes were evaluated by both the differential (Friedman) and the integral (Ozawa-Flynn-Wall) isoconversional methods and the Multivar-NLR method was applied to fit the DSC data with several kinetic models. Moreover, the shrinkage behaviors of the chrome-tanned collagen fibers were simulated at different heating rates or temperatures based on the best of the estimated models and the corresponding kinetic parameters determined by Multivar-NLR. Results showed that the chrome-tanned samples had relatively higher shrinkage temperature, enthalpy and effective activation energy than the native ones under the same conditions. The activation energies decreased throughout the shrinkage process, which could be best described by a three-step model (a reversible step followed by an irreversible one); the three-state (native, unfolded and denatured states) shrinkage behaviors of collagen fibers could approximate to a two-state (native and denatured states) process at low heating rates or temperatures. This work might provide a theoretical basis for the design of chrome-free tanning agent from the perspective of the kinetic thermostability of collagen fibers.

Keywords: Chrome-tanned collagen fibers, thermal shrinkage, DSC, Kinetic analysis, Model.

1 – Introduction
In spite of the fact that the chrome discharge problem concerning chrome tanning has attracted an increasing attention and various chrome-free tanning systems have been developed to solve this problem, the conventional chrome tanning will be still the most popular tannage for a long time due to its convenient operations and the perfect properties of chrome-tanned leather (Cai et al. 2015; Komanowsky 1991). Among the excellent properties of leather conferred by chrome tanning, a high thermal stability is the most important, which is conventionally characterized as shrinkage temperature (Ts) determined by a Ts measuring equipment or by differential scanning calorimetry (DSC) (Covington 1998; Komanowsky 1992; Komanowsky 1991). However, the thermal shrinkage of collagen or leather is a kinetic process and thus a single value of Ts could not provide an accurate estimate for its thermal stability. While a number of literatures have been focusing on the thermostability of collagen, the knowledge of the thermal shrinkage of collagen fibers is far from enough to understand how the shrinkage intrinsically occurs, how the shrinkage process can be regulated with temperature and how the shrinkage behavior of chrome-tanned leather differs from that
of hide. The above questions are of great importance to the practical handlings (e.g., manufacture, storage and use) of leather and to the design of chrome-free tanning agent which can endow leather with the desired thermostability.

DSC has been widely used as one of the best techniques to study the thermal stability of collagen-based materials, although it might mask the information about several simultaneously occurring steps during the thermal shrinkage of collagen fibers due to its intrinsic deficiency for the complete isolation of elementary reactions (Liu et al. 2014; Liu and Li 2010; Vyazovkin and Sbirrazzuoli 2006). Furthermore, non-isothermal DSC measurement was highly recommended for the kinetic analysis of thermal degradation of polymers including collagen (Liu and Li 2010; Budyrbac 2005). Also, it should be noted that multi-heating-rate and isoconversional methods are very useful in exploring the kinetics and mechanisms of complex processes, according to the proposal of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Project (Brown et al. 2000). However, such methods have rarely been applied to the kinetic analysis of the thermal shrinkage of collagen fibers. In the present work, therefore, the thermal shrinkage behaviors of native and chrome-tanned collagen fibers were studied by non-isothermal DSC using two powerful kinetic approaches highlighted by the ICTAC Kinetics Project, i.e., isoconversional and multivariate non-linear regression (Multivar-NLR) methods. These technologies were applied in combination to determine the mechanism and kinetic parameters of the shrinkage process, and the shrinkage behaviors of chrome-tanned collagen fibers under different temperature conditions were simulated. The fundamental data are expected to further understand the effect of chrome tanning on the thermal stability of leather.

2 – Material and Methods

2.1. Materials

Native un-tanned collagen fibers were purchased from a local company. Chromium sulfate hexahydrate (50%), sodium chloride, sodium bicarbonate and sulphuric acid were of analytical grade. Chrome-tanned collagen fibers were prepared according to conventional chrome tanning procedures with a much lower dose of chrome. All the native and chrome-tanned collagen samples were equilibrated over saturated salt solutions for more than two weeks in a desiccator before calorimetry.

2.2. Calorimetry

DSC curves for the native and chrome-tanned collagen fibers were determined using DSC 200PC (Netzsch-Gerätebau GmbH, Wittelsbacherstrasse, Germany) at heating rates of 2, 5 and 10 K/min, respectively. All the samples (3.0 ± 0.1 mg) were sealed in 100 µL aluminium pans and an empty pan was used as the reference. The dependences of Ts and enthalpy on heating rate were investigated. All measurements were performed thrice and the DSC data were evaluated using Proteus® from Netzsch.

2.3. Kinetic analysis

Kinetic analyses of the DSC data were performed according to Liu et al. (2010) with some modifications. In brief, the differential (Friedman) and the integral (OFW) isoconversional methods were applied to estimate the dependence of the effective activation energy (E) on the degree of conversion (α) (a ratio of the heat released between the start of a reaction and the actual time to the total heat). It should be emphasized that a variation of E with α unambiguously indicates a multi-step process and the shape of Ea (the value of E corresponding to a given α) dependence could provide important insights into the mechanism of the process.

For Multivar-NLR, the following models were evaluated: the Lumry-Eyring model (defined as model ‘t:r,f’) containing three steps, all of which are of nth-order reaction (Fn: f(α) = (1-α)^n) type
where $k_1$, $k_2$ and $k_3$ stand for rate constants, and $N$, $U$ and $D$ are the native state, the partially unfolded state and the denatured state of collagen fibers, respectively. And the two-state irreversible model, defined as model ‘Fn’ or ‘F1’, respectively, according to the reaction type is Fn or first-order reaction (F1: $f(\alpha) = (1-\alpha)\alpha$)

$$N \xrightarrow{k_1} U \xrightarrow{k_2} D$$

where $k_{app}$ is the apparent rate constant of the step. The fit quality was characterized by the minimum sum of least squares (LSQ), the mean value of deviations (MD) and the correlation coefficient (Corr. coeff.). The differentiation of fit-quality among models was estimated using the experimental F-value ($F_{exp}$) and the critical F-value at the confidence level of 0.95 [$F_{crit}(0.95)$] by F-test. In addition, The changes in the fraction of the three states ($N$, $U$ and $D$) during the shrinkage behaviors of chrome-tanned collagen fibers were simulated at different heating rates, i.e., 0.001, 1, 2, 5, 10 and 1000 K/min, and at various isothermal temperatures including 78, 83, 88, 90, 92 and 100 °C, based on the best of the evaluated models and the corresponding kinetic parameters.

3 – Results and Discussion

Figure 1 shows the DSC curves for the thermal shrinkage of native and chrome-tanned collagen fibers. On the whole, the endothermal peaks for the native collagen fibers were wider (see the temperature interval) but lower (see the values of heat flow) than those for the chrome-tanned ones. When collagen fibers were chrome-tanned, the Ts and enthalpy changed from about 50 °C and 13 J/g to about 87-90 °C and 16 J/g, respectively. Note that Ts became much higher with the increase of heating rate for the chrome-tanned samples, while it was not the case for the native ones.
Figure 1. DSC curves of the thermal shrinkage of collagen fibers at different heating rates. (a) Native collagen fibers. (b) Chrome-tanned collagen fibers.

Figure 2 shows the $E\alpha$ dependences for the thermal shrinkage of native and chrome-tanned collagen fibers. As a whole, the $E\alpha$ dependences are decreasing and approximately have the concave and convex shapes at lower and higher conversion degree, respectively. And such a characteristic shape of the $E\alpha$ dependence might imply that the thermal shrinkage of collagen fibers conforms to a three-step process, in which a reversible reaction is followed by an irreversible one (see Eq. (1)). Moreover, for the same isoconversional method and a given $\alpha$, the $E\alpha$ values of chrome-tanned samples were higher than those of the native ones. It should be pointed out that, however, the estimated $E\alpha$ values might be incorrect under certain conditions, especially when a reverse reaction is present. So Multivar-NLR was essential to study the shrinkage mechanism of collagen fibers.
Figure 2. Dependences of the apparent activation energy on the conversion degree for the thermal shrinkage of native and chrome-tanned collagen fibers evaluated by the isoconversional methods according to Friedman and OFW, respectively.

Figure 3 shows the calculated DSC curves by Multivar-NLR for the thermal shrinkage of chrome-tanned collagen fibers based on the kinetic models F1, Fn and t,r,f. From the visual inspection, it is clear that model t,r,f was the best model compared with the other two models and model F1 was the worst one. In addition, the fit quality of these three models can be further differentiated from each other by mathematics (see Table 1). The kinetic parameters of the models evaluated for the thermal shrinkage of chrome-tanned collagen fibers are shown in Table 2.

Table 1. F-test and statistics on the fit quality of the kinetic models estimated for the thermal shrinkage of chrome-tanned collagen fibers.

<table>
<thead>
<tr>
<th>Model</th>
<th>$F_{exp}$</th>
<th>$F_{crit}(0.95)$</th>
<th>LSQ</th>
<th>MD</th>
<th>Corr. coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>t,r,f</td>
<td>1.00</td>
<td>1.27</td>
<td>15.8249</td>
<td>0.2516</td>
<td>0.9971</td>
</tr>
<tr>
<td>Fn</td>
<td>2.57</td>
<td>1.26</td>
<td>42.0748</td>
<td>0.4102</td>
<td>0.9882</td>
</tr>
<tr>
<td>F1</td>
<td>9.18</td>
<td>1.26</td>
<td>151.3143</td>
<td>0.7780</td>
<td>0.9591</td>
</tr>
</tbody>
</table>
Figure 3. Multivar-NLR kinetic analysis of the thermal shrinkage of chrome-tanned collagen fibers, showing the fits of the experimental data to (a) model F1, (b) model Fn, and (c) model t:r:f, respectively.

Figures 4 and 5 show the simulation results using model t:r:f and its kinetic parameters for the thermal shrinkage of chrome-tanned collagen fibers. Figure 4 displays the dependences of the fraction of the states ($N$, $U$, and $D$) on temperature at different heating rates. At low heating rates (e.g., 0.001 K/min) the fraction of $U$ is very low compared with the fractions of $N$ and $D$ (Figure 4a). It appears that the shrinkage process at low heating rates can be approximately described by a two-state model, i.e., Eq. (2). As the heating rate increases from 1 to 1000 K/min, there are increasing amounts of $U$ together
with \( N \) and \( D \), and the fractions of \( U \) reach their maximum nearly in the middle of the shrinkage processes (Figure 4b-f).

**Table 2.** Values of the parameters in the kinetic models estimated for the thermal shrinkage of chrome-tanned collagen fibers obtained from Multivar-NLR.

<table>
<thead>
<tr>
<th>Model</th>
<th>Kinetic parameters</th>
<th>Values</th>
</tr>
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<tbody>
<tr>
<td>t:r:f</td>
<td>( \lg A_1(s^{-1}) )</td>
<td>126.489</td>
</tr>
<tr>
<td></td>
<td>( E_1(kJ/mol) )</td>
<td>865.347</td>
</tr>
<tr>
<td></td>
<td>( n_1 )</td>
<td>1.882</td>
</tr>
<tr>
<td></td>
<td>( \lg A_2(s^{-1}) )</td>
<td>51.476</td>
</tr>
<tr>
<td></td>
<td>( E_2(kJ/mol) )</td>
<td>347.483</td>
</tr>
<tr>
<td></td>
<td>( n_2 )</td>
<td>0.696</td>
</tr>
<tr>
<td></td>
<td>( \lg A_3(s^{-1}) )</td>
<td>22.697</td>
</tr>
<tr>
<td></td>
<td>( E_3(kJ/mol) )</td>
<td>165.882</td>
</tr>
<tr>
<td></td>
<td>( n_3 )</td>
<td>0.751</td>
</tr>
<tr>
<td>Fn</td>
<td>( \lg A(s^{-1}) )</td>
<td>81.813</td>
</tr>
<tr>
<td></td>
<td>( E(kJ/mol) )</td>
<td>575.282</td>
</tr>
<tr>
<td></td>
<td>( n )</td>
<td>1.983</td>
</tr>
<tr>
<td>F1</td>
<td>( \lg A(s^{-1}) )</td>
<td>58.525</td>
</tr>
<tr>
<td></td>
<td>( E(kJ/mol) )</td>
<td>416.154</td>
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</table>

**Figure 4.** Fraction of collagen states *versus* temperature profiles for the thermal shrinkage of chrome-tanned collagen fibers simulated at various heating rates of (a) 0.001 K/min, (b) 1 K/min, (c) 2 K/min, (d) 5 K/min, (e) 10 K/min and (f) 1000 K/min.

Figure 5 displays the time dependence of the fraction of the states (\( N, U, \) and \( D \)) at different isothermal temperatures. At low temperatures (e.g., 78 °C), only \( N \) and \( D \) are significantly populated, while the fraction of \( U \) is very low (Figure 5a). Therefore, the isothermal thermal shrinkage of chrome-tanned collagen fibers at low temperatures can also be approximately described by Eq. (2). For the temperatures from 83 to 100 °C, \( U \) coexists with \( N \) and \( D \) (Figure 5b-f) but the changes of \( N \) and \( U \) appear to be in a different way compared with the simulation results shown in Figure 4b-f.
Figure 5. Fraction of collagen states versus time profiles for the thermal shrinkage of chrome-tanned collagen fibers simulated at various temperatures of (a) 78 °C, (b) 83 °C, (c) 88 °C, (d) 90 °C, (e) 92 °C and (f) 100 °C.

4 – Conclusion

Chrome tanning had a significant effect on the thermal shrinkage behaviors of collagen fibers, increasing $T_s$, enthalpy and apparent activation energy. The model $N\leftrightarrow U\rightarrow D$ was the most probable mechanism for the thermal shrinkage of chrome-tanned collagen fibers, determined by the isoconversional and Multivar-NLR methods. At low heating rates or temperatures, the shrinkage process of chrome-tanned collagen fibers could be approximately described by the model $N\rightarrow D$. Thermal kinetic analysis based on DSC was useful for understanding the thermal stability of leather.

5 – Acknowledgements

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6 – References