Thermal Degradation Kinetics of Sweat Soaked Cattlehide Collagen Fibers

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Abstract

In this paper, samples of untanned cattlehide collagen fibers, chrome tanned cattlehide collagen fibers, and glutaraldehyde tanned cattlehide collagen fibers are prepared and soaked in man-made sweat solutions. Studies of their thermal degradation behaviors are completed, and the factors affecting their thermal degradation behaviors are discussed. Two methods, Flynn-Wall-Ozawa and Satava-Sestak, are applied in the study of thermal degradation kinetics of these samples. The results indicate that, after being soaked in sweat for 15 days, the thermal degradation activation energies of all samples change in different degrees. Sweat-soaking process affects the thermal degradation activation energy of chrome tanned cattlehide collagen fibers the most obviously, and the chrome tanned sample is the worst in sweat resistance of the three samples studied here. The interaction between sweat and different modified cattlehide collagen fibers are discussed.

Abstracto

En esta presentación, muestras de fibras de colágeno de piel vacuna sin curtir, fibras de colágeno de piel vacuna curtida al cromo, y fibras de colágeno de piel vacuna curtida con glutaraldehido se preparan y se sumergen en solución de sudor artificial. Estudios de su comportamiento a la degradación térmica son completados, y se discuten los factores que afectan sus comportamientos de degradación térmica. Ambos métodos de Flynn-Wall-Ozawa y Satava-Sesták son aplicados en el estudio de cinética de degradación térmica de estas muestras. Los resultados indican que, después de estar remojados en sudor durante 15 días, la energía de activación de degradación térmica de todas las muestras cambia en formas diferentes. El proceso de remojo en solución de sudor afecta en mayor medida la energía de activación de degradación témica de las fibras de colágeno de pieles vacunas curtidas al cromo y esta misma es la peor encuanto resistencia al sudor de las tres muestras aquí estudiadas. Se discute la interacción entre el sudor y diferentes fibras de colágeno de pieles vacunas modificadas.

Introduction

Thermal stability is a very important property for leathers. The untanned skins or hides shrink markedly at about 60°C, and therefore behaves very poor in thermal stability. In order to increase the thermal stability of leathers, some modification must be done. It's well known that the main composition of hides and leathers is collagen, which is a natural macromolecular material. The leather-making process is essentially the modification of this macromolecular material. The modification methods include tanning, retanning, filling, fatliquoring and so on. Tanning is the most convenient and efficient way to increase the thermal stability of leathers. Different kinds of tanning agents used in leather-making may provide leathers with different properties and styles. There are many kinds of tanning agents, including chrome tanning agent, aluminum tanning agent, oil tanning agent, vegetable tanning agent, aldehyde tanning agent, synthetic tanning agent and so on. Among these tanning agents, chrome tanning agent can provide leathers with the most excellent thermal stability. Zhang[1] and his colleagues studied the thermal denaturation behaviors of pickled pelt and different tanned leathers. The results indicated that, in the process of tanning, tanning agent molecules dispersed among collagen fibers and destroyed the hydrogen bonds. Consequently, some of the crystal region in collagen fibers was turned into amorphous structure. On the other hand, molecules of tanning agents might react with collagen fibers and accessional cross-linking between collagen fibers were formed. Accordingly, the structure stability was increased and the thermal stability of collagen fibers was improved. V. V. Bondarev[2] thought that the numbers of linking bonds between collagen fibers and chrome tanning agent molecules affected the shrinkage temperature greatly.

When leathers are exposed at high temperature environment, the collagen in them may begin to be decomposed, and thermal degradation may take place as a result. In our previous studies[5-7], un-tanned cattlehide collagen fibers, chrome tanned cattlehide collagen fibers, and glutaraldehyde tanned cattlehide collagen fibers were prepared and their thermal degradation activation energies were obtained by both methods of Flynn-wall-Ozawa and Satava-Sestak. The thermal degradation activation energy of un-tanned cattlehide collagen fibers is 130-160 *kJ/mol*. After being chrome tanned, it is increased to 225-255*kJ/mol*. In the case of glutaraldehyde tanned cattlehide collagen fibers, the thermal degradation activation energy is only 120-163*kJ/mol*, which is close to that of un-tanned cattlehide collagen fibers. Chrome tanning process can increase the thermal degradation activation energy of collagen fibers, while glutaraldehyde tanning process has little influence on the thermal degradation activation energy of collagen fibers[13].

As an important clothing material, leathers may inevitably be penetrated and soaked by sweat when being used. Similar to other clothing materials, collagen in leathers may react with the matters in sweat and the physical properties of leathers may be decreased as a result. As to the influence of sweat soaking on the properties of leathers, Zhang Wenxiong and his colleagues[8] studied the changes in physical properties of leather samples with different sweat soaking durations. They found that, with the increase of sweat soaking durations, the chrome content and the denaturation temperature of leathers decreased, the tanning degree of leathers decreased, and the mechanical properties of leathers decreased too. In the case of influencing mechanisms of sweat soaking on the structure and behaviors of leathers, no investigation may be found at all.

In our previous researches, works of sweat soaking process on the pigskin garment leathers were done from viewpoints of water vapor permeability, chrome content and hydrothermal stability. The mechanisms of these changes were discussed. It was found that the chrome content in leathers decreases with the increase of sweat soaking duration, as well as the thermal shrinkage temperature. Which say that sweat soaking has a de-tanning effect on leathers[9-10].

In this paper, such samples as un-tanned cattlehide collagen fibers, chrome tanned cattlehide collagen fibers, and glutaraldehyde tanned collagen fibers are soaked in man-made sweat for 15 days, and their thermal degradation activation energies are studied by both methods of Flynn-Wall-Ozawa and Satava-Sestak. The influencing mechanism of sweat soaking on the thermal degradation behaviors of cattlehide collagen fibers is discussed preliminarily.

Experimental

Main Materials and Apparatus

Chrome tanning liquor reduced by glucose, basicity of 38%, was prepared in our laboratory. Glutaraldehyde (GTA), a water solution of 25% (w/w), was produced by Shanghai Chemical Reagents Co., Ltd. Sodium carbonate (analytical pure), Sodium chloride (analytically pure), and potassium chloride (chemically pure) were made by Shanghai Chemical Reagent Co.; Ltd. Urea, analytically pure, was made by Luoyang Chemical Plant. Glucose and lactic acid, chemically pure, were made by Zhengzhou Chemical Reagent Co., Ltd. The X4 thermal platform Microscope was made by Beijing No.3 Optical Instrument Factory in Beijing, China. THZ-82 water bath constant temperature oscillator was made by Fuhua Instruments Plant in Jiangsu province, China. TG209 thermal analyzer was made by NETZSCH, Germany.

Procedures

Preparation of the Un-tanned Cattlehide Collagen Fibers

After being soaked, degreased, limed, split, and delimed according to traditional leather making technology, a cattlehide pelt was acetone dehydrated. Un-tanned cattlehide collagen fibers were carefully removed from the center layer of the dehydrated pelt. And then, the un-tanned cattlehide collagen fibers were put in a desiccator with silica gel in it for more than two weeks until the weight of the samples did not change anymore.

Preparation of Chrome Tanned Cattlehide Collagen Fibers

0.5 grams of un-tanned cattlehide collagen fibers were processed in solution, which contained 4.8 grams of sodium chloride, 60 milliliter of distilled water and 10 grams of chrome tanning liquor reduced by glucose per liter (calculated as Cr_2O_3). At room temperature, the pH of the mixture was adjusted with 0.01 M of sodium hydroxide to 4.0 in one month. Sufficient shaking was needed occasionally. After being taken out and filtrated, the filtered cake (chrome tanned cattlehide collagen fibers) was washed with distilled water, until precipitation can not be observed when dropped a solution of 0.05 gram silver nitrate per liter into the washed water. The filtered sample obtained was put in a desiccator with silica gel in it for more than two weeks until its weight did not change anymore.

Preparation of Glutaraldehyde Tanned Cattlehide Collagen Fibers

The tanning reagent used here was a solution that contained 25 percent by weight of glutaraldehyde. 0.12 grams of un-tanned cattlehide collagen fibers were put into a solution with 3 grams of glutaraldehyde per liter and 30 milliliter of distilled water. In the room temperature, the mixture was let alone for 14 hours and sufficient shaking was provided. The pH was adjusted to 8.5 with 20 percent of sodium carbonate by weight within 2 hours while the mixture was stirred well. After being taken out and filtered, the cake (glutaraldehyde tanned cattlehide collagen fibers) was washed 10 times with 20 milliliter distilled water. The filtered cake was put in a desiccator with silica gel in it for more than two weeks until the weight of the sample didn't change anymore, and the glutaraldehyde tanned cattlehide collagen fibers were obtained.

Preparation of man-made sweat

Physiology statistics showed that sweat is a water solution, containing sodium chloride, potassium chloride, urea, glucose, lactic acid and so on. The man-made sweat was prepared with the components listed in Table I, according to reference.[11]

TABLE I
Components and their Content of Man-made Sweat

Sodium Chloride (g/L)	Potassium Chloride (g/L)	Urea (g/L)	Lactic Acid (g/L)	Glucose (g/L)
4.68	0.37	0.45	2.50	0.36

Process of the Cattlehide Collagen Fibers in Sweat

The samples prepared above were processed in man-made sweat for 15 days. The amount of man-made sweat is 20 times of the samples in weight. After being washed for 10 times with 20 milliliter of distilled water, the samples were put in a desiccator with silica gel in it for more than two weeks until the weight of the samples didn't change anymore.

Thermo-gravimetric (TG) Analysis

The TG analysis was carried out on a TG209 thermal analyzer made by NETZSCH, Germany. The amount of the samples used here was 3-4 milligrams. The samples were put into aluminum capsules. After all the experimental parameters of the apparatus were regulated, the temperature was raised. The heating rate procedures used here had been set up before the experiments, which were 5, 10, 15, 20 degrees Kelvin per minute, respectively. Pure nitrogen gas was introduced in the aluminum capsules while the experiments were conducted. The experiment information was input into a computer and the TG curves of all the samples were plot by computer automatically.[13]

Process of TG Data and Calculation of Thermal Degradation Activation Energy

Both methods of Flynn-wall-Ozawa and Satava-Sestak, which have been being widely used in the study of thermal degradation kinetics of synthetic polymers successfully, are being used in the process of the data obtained from TG analysis of the three samples at different temperature heating rates. And the thermal degradation activation energies of the samples were obtained. The two methods had been described in details and applied successfully in the thermal degradation kinetics of collagen fibers in our previous paper.[13]

RESULTS AND DISCUSSION

TG Curves of Collagen Fibers Being Sweat Soaked for 15 Days

The thermo-gravimetric (TG) curves of the un-tanned cattlehide collagen fibers, chrome tanned cattlehide collagen fibers, and glutaraldehyde tanned cattlehide collagen fibers after being sweat soaked for 15 days at different temperature heating rates are shown in Figure 1. From Figure 1, it can be seen that the TG curves move to higher temperature with increasing temperature heating rates in all the three samples studied. It is shown more clearly in Figure 2. Figure 2 shows the DTG curves of different samples after being sweat soaked for 15 days

Influence of Temperature Heating Rates (β) on Thermal Degradation Temperature

The relation between thermal degradation temperature and temperature heating rates of all the three samples are shown in Figure 3. It should be noted that, in the figure, T_o, T_f and T_p represent initial degradation temperature, terminal degradation temperature, and peak degradation temperature, respectively.

For the un-tanned sample after being sweat soaked for 15 days (Figure 3(a)), the relationship between β (temperature heating rates) and T_o, T_f and T_p in the figure can be obtained as shown in the following equations:

$$T_o = 256.4 + 1.45\beta$$
$$T_p = 289.8 + 2.73\beta$$
$$T_f = 347.3 + 1.84\beta$$

For chrome tanned sample after being sweat soaked for 15 days (Figure 3(b)), the following equations can be obtained:

$$T_o = 267.9 + 1.75\beta$$
$$T_p = 297.2 + 1.96\beta$$
$$T_f = 344.7 + 2.02\beta$$

And, for the glutaraldehyde tanned sample after being sweat soaked for 15 days (Figure 3(c)), the following equations can be obtained:

$$T_o = 256.7 + 1.64\beta$$
$$T_p = 301.2 + 2.35\beta$$
$$T_f = 351.2 + 1.95\beta$$

From Figue 3, we can find that, for all the samples, the thermal degradation temperatures increase with increasing of temperature heating rates. It is indicated that, the temperature heating rates obviously affect the thermal degradation temperatures of the samples studied here.

Thermal Degradation Activation Energy

In our previous researches on the thermal degradation kinetics of cattlehide collagen fibers without a sweat soaking history, both methods of Flynn-wall-Ozawa and Satava-Sestak were used to process the data from TG Analysis[13]. The two methods were also applied to analyze and process the TG data to obtain the thermal degradation activation energies of the sweat soaked samples studied here.

Un-tanned Cattlehide Collagen Fibers after Being Sweat Soaked for 15 Days

The Flynn-Wall-Ozawa method

The Flynn-Wall-Ozawa method is used to analyze and process the TG data of the un-tanned sample after being sweat soaked for 15 days obtained at different temperature heating rates as shown in Figure 1(a). The thermal degradation rates (β) and the corresponding absolute temperature (°K) are obtained then. The relation between $lg\beta$ and $1/T$ was got as shown in Figure 4(a). It can be observed that there is a linear correlation between $lg\beta$ and a)

b)

c)

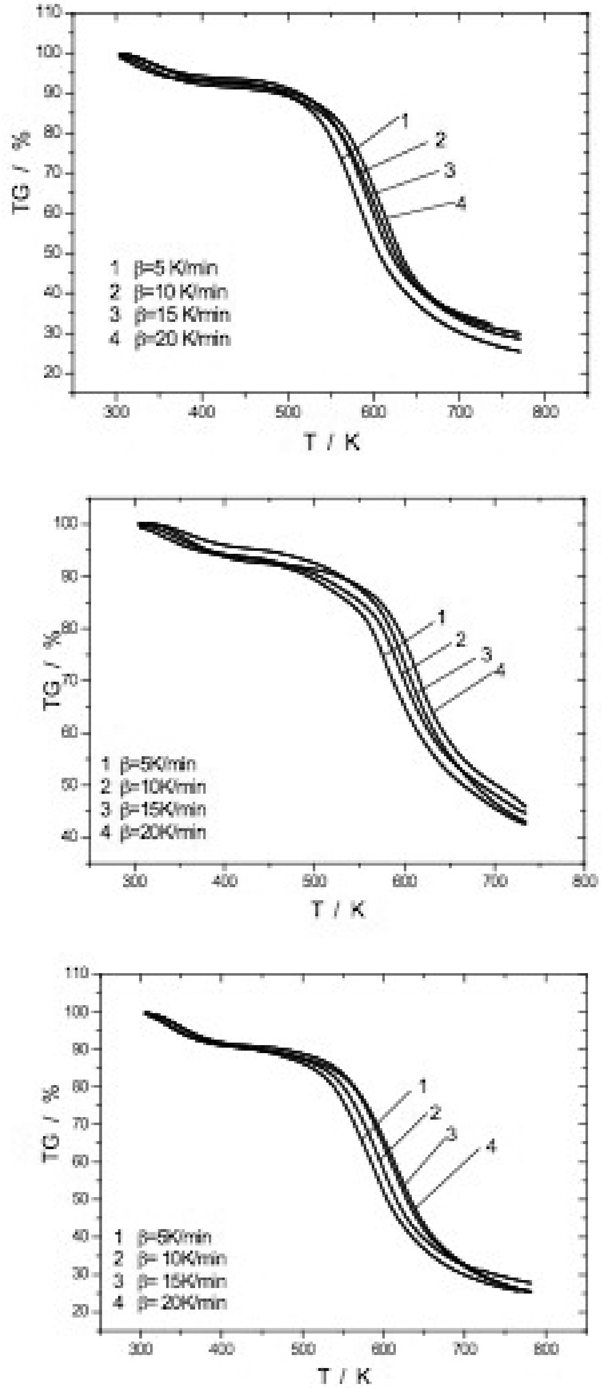

Figure1 TG thermographs of different samples after being sweat soaked for 15 days at different temperature heating rates

(a) Untanned cattlehide collagen fibers
(b) Chrome tanned cattlehide collagen fibers
(c) Glutaraldehyde tanned cattlehide collagen fibers

1/T. Thus, the thermal degradation activation energy $(E_0, \Delta E)$ of the un-tanned cattlehide collagen fibers after being sweat soaked for 15 days may be obtained from the slopes of the lines in Figure 4(a) and according to Equation 1 in our previous paper 13. The slopes of the fitted lines and the thermal activation degradation are shown in Table 2. The thermal degradation activation energy of un-tanned cattlehide collagen fibers after being sweat soaked for 15 days by Flynn-Wall-Ozawa method is between 153 *kJ/mol* and 163 *kJ/mol*.

a)

b)

c)

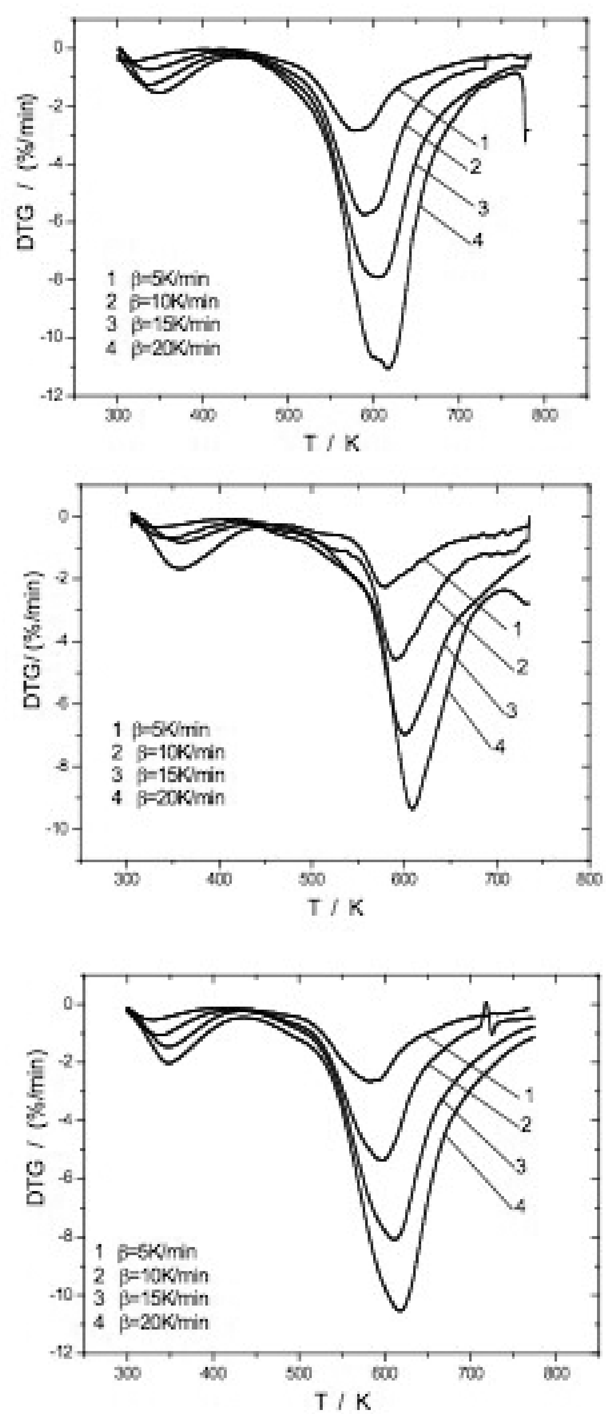

Figure 2 DTG curves of different samples after being sweat soaked for 15 days at different temperature heating rates

(a) Untanned cattlehide collagen fibers
(b) Chrome tanned cattlehide collagen fibers
(c) Glutaraldehyde tanned cattlehide collagen fibers

Satava-Sestak Method

The TG curves of un-tanned cattlehide collagen fibers as shown in Figure 1(a) had also been applied to Satava-Sestak Method. The data obtained is shown in Table 3.

By fitting and comparing, the function of $G(\alpha)= [-\ln(1-\alpha)]^3$ was selected in the subsequent study. The linear relations between $\lg(G(\alpha))$ and *1/T* are shown in Figure 5(a). The average value of the correlation coefficients of the fitting is

TABLE II
Thermal Degradation Activation Energy (ΔE) of Untanned Sample after Being Sweat Soaked for 15 Days by Flynn-Wall-Ozawa Method

C(%)*	20	25	30	35	40	45
Slope	-8.38	-8.72	-8.69	-8.93	-8.46	-8.63
ΔE(kJ/mol)	153	159	158	163	154	157

Where C is the degradation rate of the sample studied.

TABLE III
Original Data of the Thermo-gravimetric (TG) of Un-tanned Sample after Being Sweat Soaked for 15 Days

β (K/min)	Lgβ	$1/T\alpha_{-0.20}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.25}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.30}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.35}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.40}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.45}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.50}$ $x10^3(K^{-1})$
5	0.70	1.83	1.79	1.76	1.73	1.71	1.68	1.65
10	1.00	1.79	1.75	1.72	1.69	1.67	1.64	1.62
15	1.18	1.78	1.74	1.71	1.68	1.65	1.63	1.60
20	1.30	1.76	1.72	1.69	1.66	1.63	1.61	1.58

TABLE IV
Thermal Degradation Activation Energy of Untanned Sample after Being Sweat Soaked for 15 Days by Satava-Sestak Method

β (oK /min)	5	10	15	20
Slope	-8.49	-8.82	-8.12	-8.75
ΔE(kJ/mol)	155	161	148	160

TABLE V
Thermal Degradation Activation Energy (ΔE) of Chrome Tanned Sample after Being Sweat Soaked for 15 Days by Flynn-Wall-Ozawa Method

C(%)	15	20	25	30	35	40
Slope	-5.10	-6.95	-6.89	-7.61	-8.26	-8.75
ΔE(kJ/mol)	93	127	125	139	150	159

0.9991, which is rather close to 1. It shows a linear relations between *lg(G(α))* and *1/T*. The slopes of the fitted lines and the thermal degradation activation energy *(Es, ΔE)* of the un-tanned sample after being sweat soaked for 15 days are shown in Table 4. It can be seen that the thermal degradation activation energy of un-tanned cattlehide collagen fibers after being sweat soaked for 15 days is between 148 *kJ/mol* and 161 *kJ/mol* by Satava-Sesták method. Compared with the data by the Flynn-Wall-Ozawa method (Table 2), which is between 153 *kJ/mol* and 163 *kJ/mol*, it is thought that the thermal degradation activation energy *(ΔE)* of un-tanned cattlehide collagen fibers after being sweat soaked for 15 days should be between 148 *kJ/mol* and 163 *kJ/mol* then. Because of the complexity in structure and behaviors of collagen fibers, the thermal degradation activation energy of untanned cattlehide collagen fibers after being sweat soaked for 15 days varies within a range.

Chrome Tanned Cattlehide Collagen Fibers after Being Sweat Soaked for 15 Days

Flynn-Wall-Ozawa Method

Flynn-Wall-Ozawa method was also used in the study of chrome tanned cattlehide collagen fibers after being sweat soaked for 15 days. The relations between *lgβ* and *1/T* were obtained as shown in Figure 4 (b). The slopes of the fitted lines and the thermal degradation activation energy data (E_0, *ΔE*) obtained are shown in Table 5. It can be seen that the thermal degradation activation energy of the chrome tanned cattlehide collagen fibers after being sweat soaked for 15 days by Flynn-Wall-Ozawa method is between 93 *kJ/mol* and 159 *kJ/mo*l.

Satava-Sestak Method

The TG curves of chrome tanned cattlehide collagen fibers after being sweat soaked for 15 days as shown in Figure 1(b)

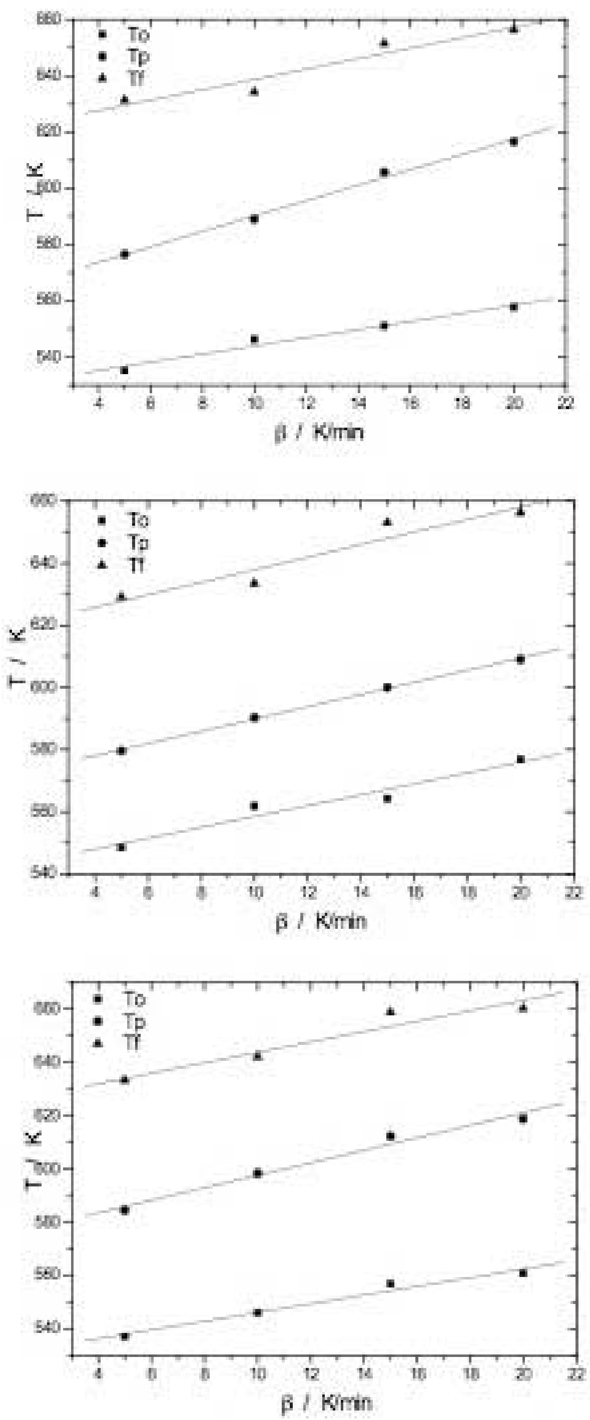

Figure 3 Relations between thermal degradation temperature and temperature heating rates of different samples after being sweat soaked for 15 days

(a) Untanned cattlehide collagen fibers

(b) Chrome tanned cattlehide collagen fibers

(c) Glutaraldehyde tanned cattlehide collagen fibers

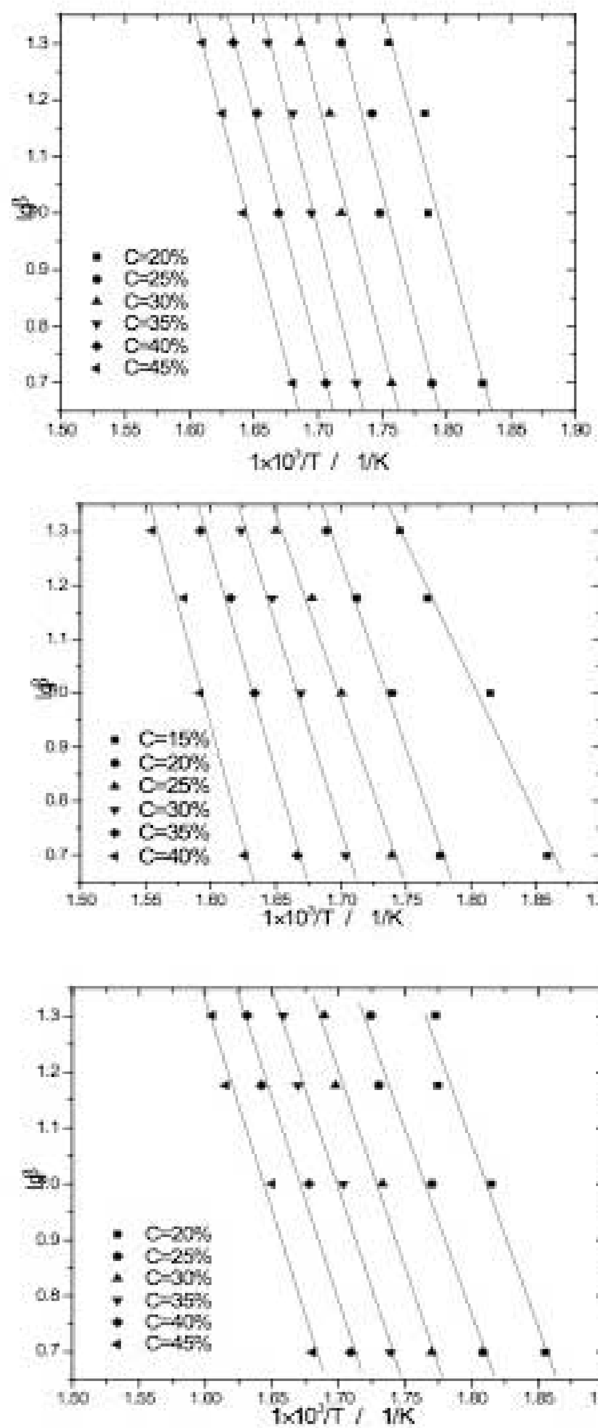

Figure 4 Relations between lgβ and 1/T

(a) Untanned cattlehide collagen fibers

(b) Chrome tanned cattlehide collagen fibers

(c) Glutaraldehyde tanned cattlehide collagen fibers

had also been applied to the Satava-Sesták method. The data obtained are shown in Table 6.

By fitting and comparing, the function of $G(\alpha)= [-ln(1-\alpha)]^{4}$ was selected in the subsequent study. The relations between *lg(G(α))* and *1/T* are shown in Figure 5(b). The average value of the correlation coefficients of fitting is 0.9925. It means that there are ideal linear relations between *lg(G(α))* and *1/T*. The slopes of the fitted lines and the thermal degradation activation energy *(Es, ΔE)* of the chrome tanned cattlehide collagen fibers after being sweat soaked for 15 days obtained by the method are shown in Table 7. It can be seen that the thermal degradation activation energy of chrome tanned cattlehide collagen a)

b)

c)

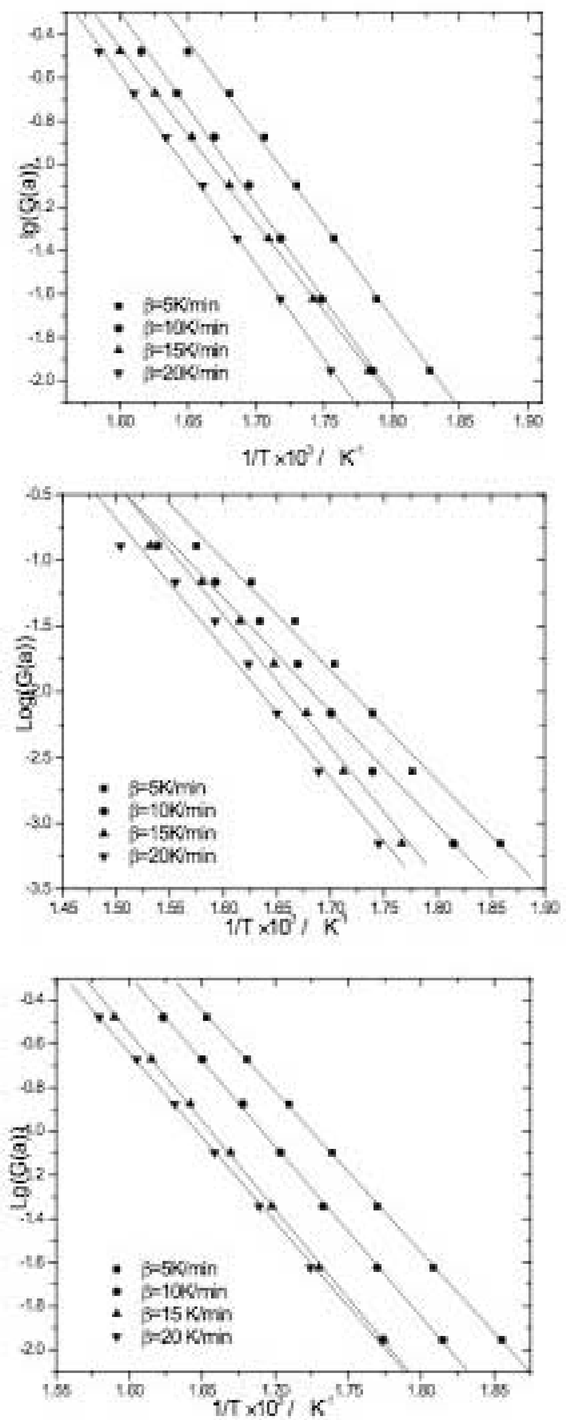

Figure 5 Relations between lg(G(a)) and 1/T
(a) Untanned cattlehide collagen fibers
(b) Chrome tanned cattlehide collagen fibers
(c) Glutaraldehyde tanned cattlehide collagen fibers

fibers after being sweat soaked for 15 days is between 153 *kJ/mol* and 182 *kJ/mol* by Satava-Sestak method. Compared with the data obtained by the Flynn-Wall-Ozawa method (Table 5), which is between 93 *kJ/mol* and 159 *kJ/mol*, it is thought that the thermal degradation activation energy (ΔE) of chrome tanned cattlehide collagen fibers after being sweat soaked for 15 days should be between 93 *kJ/mol* and 182 *kJ/mol*.

Glutaraldehyde Tanned Collagen Fibers after Being Sweat Soaked for15 Days

Flynn-Wall-Ozawa Method

Flynn-Wall-Ozawa method was also used in the study of glutaraldehyde tanned cattlehide collagen fibers after being sweat soaked for 15 days. The chart that shows the relations between $lg\beta$ and $1/T$ was obtained as shown in Figure 4(c). The slopes of the fitted lines and the thermal degradation activation energy (E_0, ΔE) obtained are shown in Table 8. From Table 8, it can be seen that, in the case of glutaraldehyde tanned cattlehide collagen fibers after being sweat soaked for 15 days, the thermal degradation activation energy by Flynn-Wall-Ozawa method is between 120 *kJ/mol* and 137 *kJ/mol*.

Satava-Sestak Method

The TG curves of glutaraldehyde tanned cattlehide collagen fibers after being sweat soaked for 15 days as shown in Figure 1(c) had also been applied to the method of Satava-Sestak. The data obtained are shown in Table 9.

By Fitting and contrasting, such function as $G(\alpha)= [-ln(1-\alpha)]^3$ was selected in the subsequent study. The relations between $lg(G(\alpha))$ and $1/T$ are shown in Figure 5(c). The average value of the correlation coefficients of the fitting is 0.9997. The linear relations between $lg(G(\alpha))$ and $1/T$ are shown clearly. The slopes of the fitted lines and the thermal degradation activation energy (ES, ΔE) of the glutaraldehyde tanned cattlehide collagen fibers after being sweat soaked for 15 days obtained by Satava-Sestak Method are shown in Table 10. Table 10 shows that, in the case of glutaraldehyde tanned cattlehide fibers after being sweat soaked for 15 days, the thermal degradation activation energy is between 134 *kJ/mol* and 148 *kJ/mol* by Satava-Sestak method. Compared with the data by the Flynn-Wall-Ozawa method (Table 8), which is between 120 *kJ/mol* and *137 kJ/mol*, it is thought that the thermal degradation activation energy (ΔE) of glutaraldehyde tanned cattlehide collagen fibers after being sweat soaked for 15 days should be between 120 *kJ/mol* and 148 *kJ/mol*.

Results from Both Methods of Flynn-Wall-Ozawa and Satava-Sesták

When the thermal degradation activation energies from both the methods of Flynn-Wall-Ozawa and Satava-Sestak were listed, Table 11 was obtained.

For untanned and glutaraldehyde tanned samples, the thermal degradation activation energy ranges of values are relatively close. For the chrome tanned sample, however, a difference occurred in the results by the two methods. The thermal degradation activation energy range of values is much smaller by the Flynn-Wall-Ozawa Method. It is even less than that of the untanned sample. This is to say, that the sample is weaker than the untanned one in thermal degradation resistance. When looking at the thermal degradation activation energy of chrome tanned sample by Satava-Sestak Method, one may found that the sample is stronger than the untanned sample in

TABLE VI
Original Data of the Thermo-gravimetric (TG) of Un-tanned Sample after Being Sweat Soaked for 15 Days

β (K/min)	Lgβ	$1/T\alpha_{-0.15}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.20}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.25}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.30}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.35}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.40}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.45}$ $x10^3(K^{-1})$
5	0.70	1.86	1.78	1.74	1.70	1.67	1.63	1.57
10	1.00	1.81	1.74	1.70	1.67	1.63	1.59	1.54
15	1.18	1.77	1.71	1.68	1.65	1.62	1.58	1.53
20	1.30	1.75	1.69	1.65	1.62	1.59	1.56	1.50

TABLE VII
Thermal Degradation Activation Energy of Chrome Tanned Sample after Being Sweat Soaked for 15 Days by Satava-Sestak Method

β(°K /min)	5	10	15	20
Slope	-8.41	-8.65	-9.99	-9.81
ΔE(kJ/mol)	153	157	182	179

TABLE VIII
Thermal Degradation Activation Energy (ΔE) of Glutaraldehyde Tanned Sample after Being Sweat Soaked for 15 Days by Flynn-Wall-Ozawa Method

C(%)	20	25	30	35	40	50
Slope	-6.57	-6.58	-7.02	-7.11	-7.26	-7.50
ΔE(kJ/mol)	120	120	128	129	132	137

TABLE IX
Original Data of the Thermo-gravimetric (TG) of Glutaraldehyde Tanned Sample after Being Sweat Soaked for 15 Days

β (K/min)	Lgβ	$1/T\alpha_{-0.25}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.25}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.30}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.35}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.40}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.45}$ $x10^3(K^{-1})$	$1/T\alpha_{-0.50}$ $x10^3(K^{-1})$
5	0.70	1.86	1.81	1.77	1.74	1.71	1.68	1.65
10	1.00	1.81	1.77	1.73	1.70	1.68	1.65	1.62
15	1.18	1.77	1.73	1.70	1.67	1.64	1.62	1.59
20	1.30	1.77	1.72	1.69	1.66	1.63	1.61	1.58

TABLE X
Thermal Degradation Activation Energy of Glutaraldehyde Tanned Sample after Being Sweat Soaked for 15 Days by Satava-Sestak Method

β(°K /min)	5	10	15	20
Slope	-7.37	-7.82	-8.11	-7.74
ΔE(kJ/mol)	153	157	182	179

thermal degradation resistance. So, in the study of thermal degradation activation energies of both samples of untanned and glutaraldehyde tanned cattlehide collagen fibers, the results are close. When the both methods were applied in the sweat soaked chrome tanned sample, however, there is a difference in results by the both method. Some unknown reactions must have taken place in the sweat soaking process of chrome tanned cattlehide collagen fibers, which resulted in the difference in the thermal degradation activation energies by the two methods. Further studies should be done on the applicability of the two methods in chrome tanned collagen fibers and some modifications should be done as well.

Influence of Sweat Soaking on the Thermal Degradation Activation Energies of Different Samples

With the thermal degradation activation energies of different

TABLE XI
Thermal Degradation Activation Energies of Different Samples with Different Methods (after Sweat Soaking)

Sample	Flynn-Wall-Ozawa Method		Satava-Sestak Method	
	Range(kJ/mol)	Averge(kJ/mol)	Range(kJ/mol)	Averge(kJ/mol)
Untanned	153-163	158	148-161	154.5
Glutaraldehyde tanned	120-137	128.5	134-148	141
Chrome tanned	93-159	126	153-182	167.5

TABLE XII
Thermal Degradation Activation Energy of the Three Samples before and after Being Sweat Soaked for 15 Days

Samples	Before being sweat soaked (kJ/mol)	Sweat soaked for 15 days(kJ/mol)	Average changes (kJ/mol)
Untanned Sample	130-160	148-163	+11
Chrome Tanned Sample	225-255	93-182	-120
Glutaraldehyde Tanned Sample	120-163	120-148	-8

samples obtained in our previous study before[13] being considered, the thermal degradation activation energies of the samples before and after being sweat soaked for 15 days are listed in Table 12.

In both cases of un-tanned and glutaraldehyde tanned samples, little differences may be found in thermal degradation activation energies of the samples before and after being sweat soaked for 15 days. The thermal degradation activation energy of un-tanned cattlehide collagen fibers is 130-160 kJ/mol. After being sweat soaked for 15 days, it is increased to 148-163 kJ/mol, only an increase of 11 kJ/mol in average. In the case of glutaraldehyde tanned cattlehide collagen fibers, the thermal degradation activation energy is 120-163 kJ/mol. After being sweat soaked for 15 days, it is decreased to 120-148 kJ/mol, only a decrease of 8 kJ/mol in average. As to chrome tanned cattlehide collagen fibers, however, there is a remarkable change in thermal degradation activation energy. It is 225-255 kJ/mol before sweat soaking process. After being sweat soaked for 15 days, it falls down to 93-182 kJ/mol, a decrease of 120 kJ/mol in average. It is indicated that sweat soaking may have little influence on the un-tanned cattlehide collagen fibers and glutaraldehyde tanned cattlehide collagen fibers in thermal degradation activation energies, compared with the obvious effect on that of chrome tanned cattlehide collagen fibers. After being sweat soaked, the chrome content in leathers is decreased[14]. In the sweat soaking process, some bonds formed by the combination of chromium complexes and collagen groups may have been destroyed, and a reaction of de-tanning may take place. The collagen structure in the sweat soaked sample is not as stable as that in the sample without a sweat soaked history. The thermal degradation may take place more easily, and the thermal degradation activation energy is decreased obviously as a result. In the process of being used, leathers might inevitably be penetrated and soaked by sweat. A de-tanning reaction may take place. This may be the reason why the physical properties of chrome tanned leathers decrease so much after a long period of wearing and sweat soakage.

In the case of un-tanned cattlehide collagen fibers and glutaraldehyde tanned cattlehide collagen fibers, however, little effect may be found in thermal degradation activation energies because of sweat soaking. It may be concluded that, after a long period of sweat soaking, chrome tanned cattlehide collagen fibers are the worst in sweat resistance from viewpoint of thermal degradation activation energy. The sweat resistance of the coordination bonds formed in chrome tanning is poorer than that of the covalent bonds formed in glutaraldehyde tanning. Much more studies should be done in the mechanism of sweat soaking on different collagen fibers to obtain leathers with good sweat resistance.

CONCLUSIONS

Untanned cattlehide collagen fibers, chrome tanned cattlehide collagen fibers, and glutaraldehyde tanned cattlehide collagen fibers are soaked in man-made sweat, and their thermal degradation activation energies are obtained by both methods of Flynn-wall-Ozawa and Satava-Sestak. After being sweat soaked, the thermal degradation activation energies of untanned cattlehide collagen fibers, chrome tanned cattlehide collagen fibers, and glutaraldehyde tanned cattlehide collagen fibers are 148-163kJ/mol, 93-182 kJ/mol and 120-148 kJ/mol, respectively. Compared with the data of the corresponding samples without sweat soaked histories, the changes in thermal degradation activation energies may be neglected in both cases of un-tanned sample and glutaraldehyde tanned sample. But sweat soaking process decreases the structure stability of chrome tanned collagen fibers greatly, and the thermal degradation activation energy is decreased remarkably as a result. From viewpoint of thermal degradation activation energy, chrome tanned sample is the worst in sweat resistance in the samples studied here.

ACKNOWLEDGEMENT

This investigation was supported by funds from both the National Nature Science Fund Commission (No: 50473021, 20174037) and the National "the Tenth years" Key Technological Research and Development Program (No. 2004BA320B). The authors are grateful to all the staffs in the Laboratory of Leather Chemistry and Engineering of Zhengzhou University.

REFERENCES

1. Zhang, X., Wei, D., Liu, Z., DSC Investigation of Tanned Leather Ultilized ART-1[J]. *Macromolecule Material Science and Engineering*, **11(1)**: 104-107, 1995
2. Wang, W., Ma, J., Yang, Z., Leather Tanning Agent and Tanning Mechanism [J]. *China Leather*, **263(8)**: 27-32, 1997
3. Hu, R., Shi,Q., Thermal Analysis Dynamics[M]. Science Press, Beijing, China, 2001
4. Chen, J., Li, C., Thermal Analysis and Its Applications[M]. Science Press, Beijing, China, 1985
5. Tang, K., Liu,J., Wang,F., etal, Dry Heat Resistance of Hide and Leather[J], *JALCA*, **98(5)**, 168-172, 2003
6. Tang, K., Liu, J., Wang, F., Studies on the Thermal Degradation Activation Energy of Cattlehide Collagen Fibers[J], *China Leather*, **33(7)**, 25, 2004
7. Tang, K., Rheology Behaviors of Nappa Leather from pigskin[D]. Doctor's degree papers of Sichuan University, 1998
8. Zhang, W., Tusnoda,Y., Okamara,H.. Study the Performance of Shoe Lining Leather from Its Application[J]. *China Leather*, **32(20)**, 138-141, 2003
9. Liu, J., Wang, F., Tu, L., etal, Influence of Sweat on the Performance of Leathers[J]. *China Leather*, **34(3)**: 8-12, 2005
10. Tang, K., Liu, J., Qin, S., Effect of Sweat on Dry Heat Resistance of Leathers[J]. *Journal of Shaanxi University of Science and Technology*, **22(3)**: 72-75, 2004
11. Yao,T., Physiology, Publishing Company of People Sanitation, Beijing, 271, 2001.
12. Tang, K., Liu, J., Factors Influencing the Dry Heat Shrinkage Behaviors of Leathers[J]. J*ournal of Shaanxi University of Science and Technology*, **22(3)**: 63-66, 2004
13. Tang K., Wang F., Liu J., etal, Preliminary Studies on the Thermal Degradation Kinetics of Cattlehide Collagen Fibers, *JALCA*, **99(10)**: 401-408, 2004
14. Tang K., Liu J., Wang F., etal, Influence of Sweat on Hide and Leather, XXVIII IULTCS Congress, Florence, Italian, March, 2005