

Fabrication, Characterization and Tanning Performances Investigation of a Novel Epoxide

by

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Abstract

A novel epoxide (IEGA) is synthesized using isophorone diamine (IPDA) and epichlorohydrin (ECH) as starting materials. The structure of IEGA is characterized by Fourier transform infrared (FT-IR) and ¹H nuclear magnetic resonance (¹H NMR). The tanning performance of IEGA is tested in ethanol from the aspects of the IEGA dosage, tanning temperature, pH value, and tanning time on shrinkage temperature (Ts) of sheep skin. It is found that under the optimized conditions with IEGA, the Ts of sheep skin tanned with IEGA is about 86°C, which is higher than normal epoxide tanned leather. Furthermore, SEM showed that IEGA tanned leather obtained better opened-up fiber structure than glycerol triglycidyl ether (GTE) tanned leather. Tanning mechanism investigation suggested that the cross-linking process should be predominately taking place among the -NH₂ groups of collagen fibers by the epoxy groups of IEGA.

Introduction

Chromium has been used as tanning agent in leather industry for more than 100 years. The well-known advantages of chrome-tanned leather include high shrinkage temperature (Ts), excellent handle feeling, good abrasion resistance, and storage stability, etc. However, chromium salts have been recognized as potential chemical hazards. The sludge and leather solid waste containing chromium have been listed on the hazardous wastes catalog in China since 2006. U.S. environmental protection agency also issued strict regulations for managing chromium-contained leather wastes under federal laws called the Resource Conservation and Recovery Act (RCRA). The disposition of these wastes is bringing a huge problem for tanning industries. Therefore, it is highly desirable to develop chromium free tanning, especially organic tanning, as alternative technology for the future leather manufacturing.¹⁻⁶

Since the first use in the tanning process in 1950s, epoxide has been regarded as one of the promising candidate for chromium free tanning agent.⁷ It is well known that epoxy group can react with -NH₂, -OH and -COOH groups under different conditions. Whereas, according to the literatures, the shrinkage temperature (Ts) of tanned leather using water soluble epoxide is typically limited to 74°C, showing relatively weak tanning effects.⁸⁻¹⁰ Currently, it was found that the collagen or hide powder exhibits better hydrothermal stability after cross-linking using epoxide with rigid ring and multi-epoxy groups. Polyepoxide triglycidyl isocyanurate (TGIC) has been shown good Ts of 85°C for cross-linking hide powder, in which multi-epoxy groups and heterocycle contained.¹¹ Although the aromatic epoxides with multi-epoxy groups could provide excellent tanned effect,¹² but the obtained leather was easily yellowing. Hence, a novel epoxide need to be investigated which contains not only multi-epoxy groups for high performance of tanning effects, but also rigid ring without use of aromatic ring.

In the process of leather manufacturing, water serves as a common transporting medium due to its transferring ability to drive the chemicals into three-dimensional matrix of leather. But the pollution problem is caused due to lower absorption of chemicals in water medium and lower recycling rate of waste water. Therefore, exploration of a green solvent to replace water is highly desirable. Ethanol, regarded as a non-toxic, biodegradable and recyclable medium, is currently used to replace water in the processes such as dry cleaning, textiles and paints.¹³ Moreover, it has been confirmed that ethanol has no negative effect on collagen.¹⁴ Additionally, owing to the hydrolysis stability of epoxy group and faster penetration rate of epoxide in ethanol medium at lower temperature, ethanol might be a good tanning medium for epoxide tanning system. It is true that ethanol is flammable, but the risk of explosion is controllable. As we known, ethanol is a common solvent used in many industries and its safety problems are well solved.

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In this work, a novel epoxide (IEGA) tanning agent with rigid ring was synthesized using isophorone diamine (IPDA) and epichlorohydrin (ECH) as starting materials, and the chemical structure of IEGA was characterized by FT-IR and ^1H NMR. Moreover, the tanning performances and tanning mechanism of IEGA in ethanol medium were also investigated.

Experimental

Materials

Isophorone diamine (IPDA) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Epichlorohydrin (ECH) and sodium hydroxide were supplied by Sinopharm Chemical Reagent Co. Ltd. Glycerol triglycidyl ether (GTE) was provided by Anhui Hengyuan Chemical Co. Ltd, and its molecular structure is presented in Figure 1. Monopotassium phosphate and acetic acid were supplied by Beijing Chemical Industry Plant. Hide powder was prepared using cattle hide according to our previous work.¹⁵ In brief, the cattle hide was prepared by soaking, degreasing, liming, splitting and deliming processes. Then the pelt was washed and adjusted pH value to 4.8~5.0 and dried in a vacuum. After grinding and sieving, 10 ~ 20 mesh hide powder (collagen fiber) with moisture $\leq 12\%$, ash content $\leq 0.3\%$, and pH value 5.0 was obtained.

Synthesis of IEGA

The synthesis process was carried out in a 500 mL glass reactor equipped with stirrer and reflux condenser in a temperature controller with water heating bath. In an optimal manner,

IPDA (1 mol) was added into the reactor, stirring and heating were started. Excess amounts of ECH (4.5 mol) was then dropwise added in slowly and kept at temperature of 35°C for 2 h under stirring. Then increased the temperature to 60°C and kept the reaction for 4 h. After that the resulting mixture was cooled down to 35°C and kept for another 1.5 h followed by dropwise addition of 40 wt.% sodium hydroxide solution (amount of sodium hydroxide was 4.5 mol). The mixture was neutralized using the solution of monopotassium phosphate (20 wt.%) and acetic acid. The organic phase was separated and then washed three times with distilled water to remove NaCl. Finally, the organic phase was distilled by vacuum rotary evaporation at 45°C to remove the un-reacted ECH and finally the IEGA was obtained. The synthesis process of IEGA is illustrated in Figure 1.

Tanning Process

The sheep skin after liming and fleshing was selected to test the tanning performances of IEGA, and GTE was used for comparison at same tanning process as IEGA. The chemicals dosage is based on the weight of limed skin. The process conditions of deliming, bating and tanning are summarized in Table I.

Investigation of Tanning Mechanism

Cross-linking of Hide Powder with IEGA

5.00 g hide powder was suspended in 100 ml ethanol (95 wt.%) and 12.0 g NaCl was added, and then the mixture was shaken at 180 rpm in a water bath oscillator under 35°C for 2 h. Then the Na_2CO_3 solution (30 wt.%) was added into the mixture to adjust pH value to 8.0.⁶ After that 2.5 g IEGA was added and the

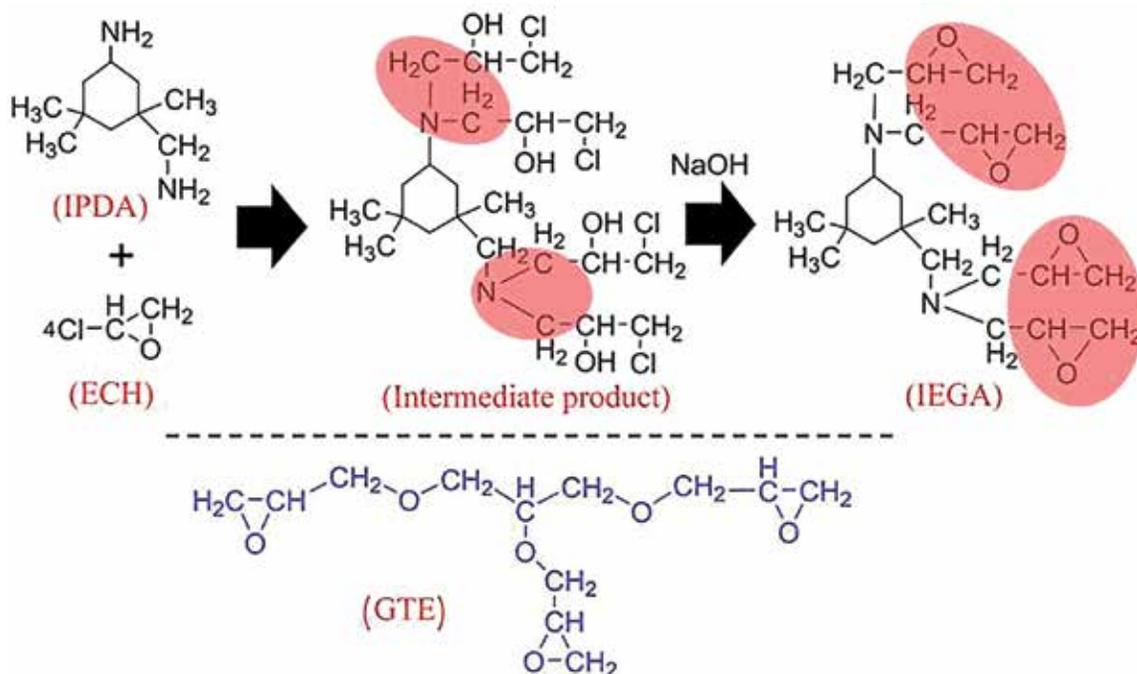


Figure 1. Schematic illustration of synthesis process of IEGA and molecular structure of GTE.

mixture was shaken another 18 h under 35°C. The cross-linking hide powder was collected by suction filtration, rinsed with 200 mL ethanol for three times and lyophilized. Finally, the cross-linking hide powder was characterized by FT-IR and DSC.

Chemical Modification of Sheep Hide ¹⁶

In order to insight understand the tanning mechanism of as prepared epoxide (IEGA), the -COOH and -NH₂ groups of collagens of sheep skin were blocked using esterification and deamination approaches.

Experiments were carried out on 4 pieces bated sheep skins (15×60 mm) which were cut from the sheepskin both along and across backbone line symmetrically. The chemicals dosage based on the weight of bated skin. The pH value of bated skins were adjusted to 6.0 ~ 7.0.

Preparation of esterified sheep skin: 2 pieces of bated skins of 25 g were placed in the 1000 ml erlenmeyer flask and kept in the constant temperature bath oscillator at 20°C. At the beginning,

Table I
Process conditions of deliming, bating and tanning.

Process	Chemicals	Dosage (%)	Tem. (°C)	Time (min)	Final pH	Remarks
Deliming	water	100	35	60		
	deliming agent	1.0			8.0	Drain
Washing	water	200	35	10		Double times and drain
Bating	water	100	40	60	8.0	
	Trypsin compound	0.5				
	Degreasing agent	2	40	30		Drain
Washing	Water	200	25	10×3		Drain
Tanning	Ethanol	80				the concentration of ethanol is 95 wt. %
	IEGA	a	b	c	d	a, b, c, d will be optimized
Washing	Water	200		10×2		Drain

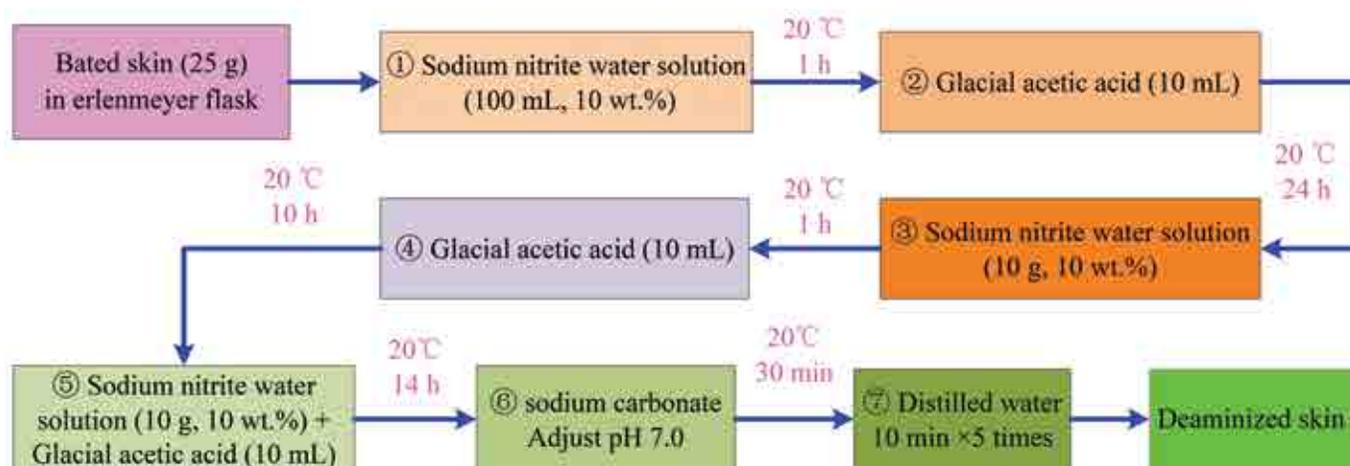


Figure 2. Preparation process of deaminized sheep skin.

500 ml methanol (2 mol/L) water solution and 3.75 ml 12 mol/L HCl were added and shaken in the intermittent manner for 48 h. After that the sodium carbonate was added to adjust pH value to 7.0 and shaken another 30 min. Finally, the samples were washed 5 times using the distilled water for 10 min every time.

Preparation of deaminized sheep skin: 2 pieces of bated skins were placed in the 1000 ml erlenmeyer flask and kept in the constant temperature bath oscillator at 20°C, and then prepared the deaminized skin as Figure 2.

The esterified and deaminized skins will be tanned as the tanning process in Table I. The tanned leathers were fully washed 10 min for 3 times using distilled water, acetone water solution (1:1, wt.) and 0.5 wt.% sodium carbonate, respectively. The Ts of samples before and after washing treatment were tested.

Characterization

FT-IR Analysis

FT-IR spectra were tested by a Bruker Tensor 27, using a Bruker/Pike MIRacle ATR Accessory (A529-P). The samples were scanned from 4000 to 600 cm^{-1} .

^1H NMR Analysis

^1H NMR (600MHZ) spectra were recorded by the superconducting pulse fourier transform nuclear magnetic resonance spectrometer (AV II type, Bruker in Switzerland). The chemical shifts relative to that of deuterated chloroform ($\delta=7.26$) were recorded.

Test for Ts of samples

The Ts of the samples was measured according to the standard method.¹⁷

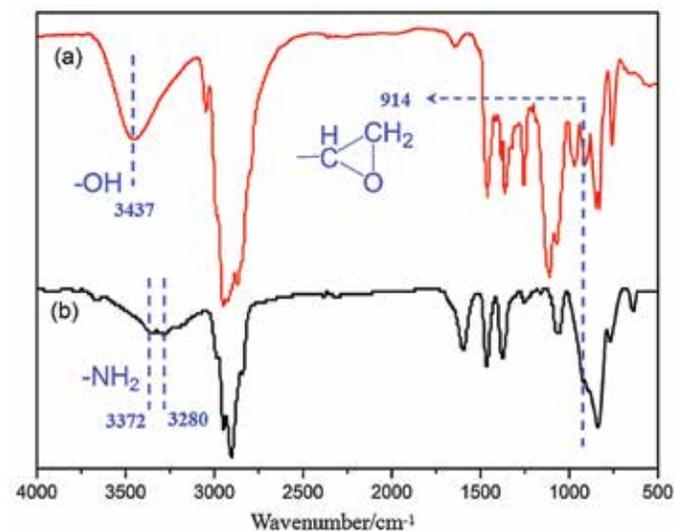


Figure 3. FT-IR Spectrums of (a) IEGA and (b) IPDA .

DSC Determination

Hide powder before and after reacted with IEGA were conditioned at 20°C, 65% RH (relative humidity) for 48 h. Then 3~5 mg sample was put into a standard aluminum pan and sealed, and an empty aluminum pan was used as reference. The thermal stability of the sample was measured using DSC (Netzsch DSC 204 F1, Germany) in dynamic mode from 20°C to 120°C at a heating rate of 10 K/min under N_2 atmosphere.

SEM Observation

The dried tanned leather was cut in cross section. The scanning electron microscopic analysis was carried out on a scanning electron microscope (JSM-7500F, JEOL Ltd.).

Results and Discussion

Synthesis of IEGA

The synthesis of IEGA involved two steps. First, amine group in IPDA was reacted with epoxy group in ECH. Then, under the alkaline condition, ring closing reaction was proceeded and epoxy groups were formed (Figure 1). Because the multi-epoxy groups of IEGA can react with amine groups of collagen fibers at alkali condition, the steady multi-dimensional network structure among the collagen fibers can be formed with the cross-linking effect of IEGA, and then provide an excellent hydrothermal stability for leather. Moreover, IEGA can be blended with ethanol in any proportion at normal temperature with little hydrolysis. Therefore, ethanol medium is suitable for the IEGA tanning system.

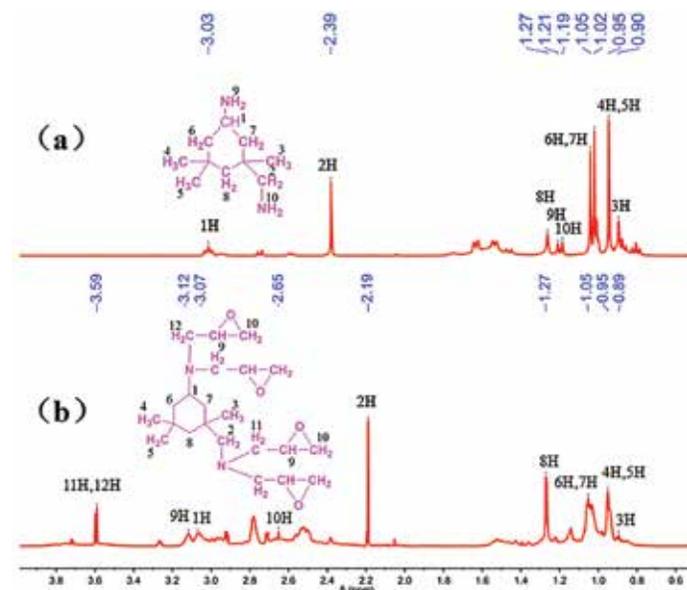


Figure 4. ^1H NMR of (a) IPDA and (b) IEGA .

Characteristics of IEGA

The FTIR spectra of IEGA and IPDA were presented in Figure 3. The absorption peak at 914 cm^{-1} illustrated the direct evidence for epoxy group in IEGA (Figure 3a).¹⁸⁻²⁰ The characteristic absorption band at 3447 cm^{-1} corresponded to the O-H stretching

vibration of hydroxyl group which is possible from the hydrolysis reaction of IEGA.²¹ The absorption peak at 3280 cm^{-1} and 3370 cm^{-1} were attributed to N-H stretching vibrations of primary amine in IPDA (Figure 3b),^{22,23} which are disappeared in IEGA.

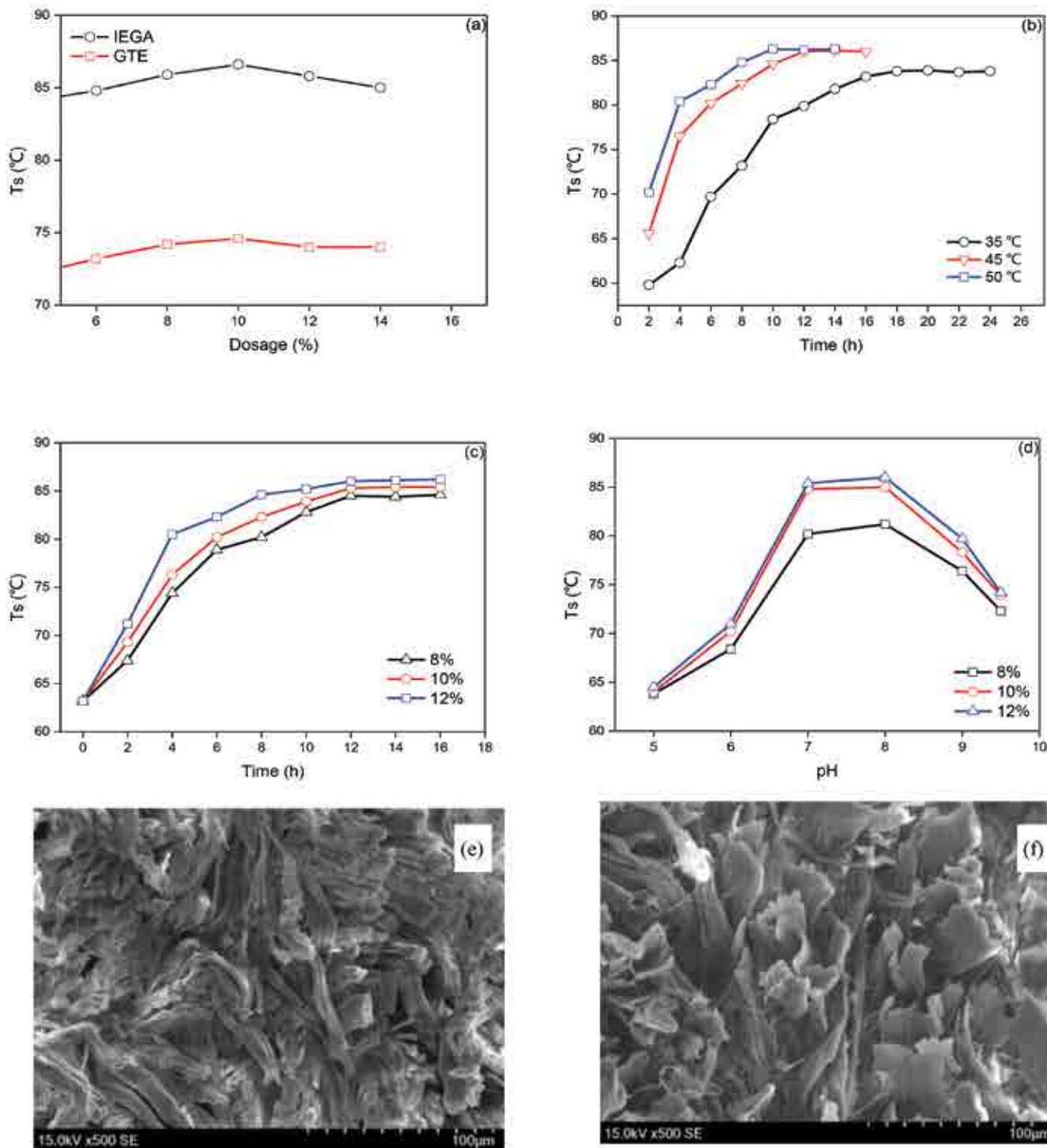


Figure 5. Effect of tanning conditions on Ts (a) the effect of dosage on Ts with IEGA and GTE (45°C, pH 8.0); (b) the effect of temperature on Ts with IEGA (10% dosage, pH 8.0); (c) the change of Ts with tanning time by different dosage of IEGA (45°C, pH 8.0); (d) the effect of pH on Ts with different dosage of IEGA (45°C, 12 h); (e) SEM image of leather tanned by IEGA; (f) SEM image of leather tanned by GTE.

Figure 4 was the ^1H NMR spectrum of IPDA and IEGA. The locations of all H of IPDA were identified, as shown in Figure 4a. According to the reference,²² the peaks of 1.0 ppm and 1.3 ppm should be attributed to the H of amine group (9H and 10H). By contrast, these two peaks were disappeared in the corresponding locations of IEGA, as shown in Figure 4b. However, in Figure 4b, the new characteristic peaks of 2.71 ppm (9H) and 3.12 ppm (10H) confirm the presence of H in epoxy groups of the as prepared IEGA.^{24, 25} In addition, more peaks should be related with H of ECH were also presented in Figure 4b because the residual of ECH. Combined with FTIR analysis, it can be concluded that IPDA was successfully reacted with ECH, and a new epoxide with desired structure was obtained.

Tanning Performances of IEGA

In general, the T_s indicates the cross-linking ability of tanning agent to collagen molecules. In order to evaluate the tanning performances of IEGA to sheep skin in ethanol bath, the effect of IEGA dosage, tanning temperature and bath pH value on T_s of leather were investigated.

As shown in Figure 5a, IEGA exhibited obvious tanning effect to sheep skin. Compared with commercial GTE, sheep leather tanned with IEGA has significant higher T_s of 86°C. As shown in Figure 5e and Figure 5f, SEM images indicated that the leather tanned by IEGA presents the higher fibers' dispersion and clear spacing among collagen fibers, while for that of GTE exhibited quite compact pattern. It can be well explained using the theory of tanning chemistry that well cross-linking effect will be beneficial to higher opening-up and fixing degree for collagen fibers, which leads to an increase in porosity of the fiber matrix.²⁶⁻²⁷ Meanwhile, as pointed by Covington and Chen,²⁸⁻²⁹ it is necessary to introduce steric hindrance into the tanning agent molecular structure in order to increase the stability of collagen. Hence, owing to the rigid hexatomic ring contained in the IEGA and its well cross-linking effect to the collagen fibers, the tanned leather shows excellent hydrothermal stability. As a result, the T_s of sheep leather obtained by IEGA tanned is higher than that of GTE. In addition, as shown in Figure 5c, the T_s of leather was enhanced with the increase of dosage, but it did not increase when the dosage higher than 10%, which is thought to be associated with the increasing of single-point combination between the epoxy group and collagen fiber in the excess amount of tanning agent.¹¹

As shown in Figure 5b, it can be observed that tanning temperature is one of the most important factors for the tanning effect of IEGA. It was found that the T_s was increased with the increasing of tanning temperature. The T_s was only 79.9°C tanned at 35°C for 12 h, while it was increased to 85°C tanned at 45°C. In addition, tanning rate was also significantly affected by tanning temperature. At temperature of 50°C, only 10h was needed to complete the tanning process, while it was greatly

prolonged to more than 20 h when the temperature was 35°C. In optimal manner, the tanning temperature of IEGA was controlled to 40°C for 12 h. It has been reported that the reaction of $-\text{NH}_2$ and epoxy group can take place even at room temperature, but it must be taken more than 7 days to complete this reaction with an un-catalyzed system.^{9,30} Therefore, the as prepared IEGA exhibited great potential in the practical application.

The bath pH value also has great impact on the tanning effect, as shown in Figure 5d. The highest T_s was obtained when the pH value was around 7.0~8.0 and T_s began to decrease when pH value was higher than 8.0. As reported in literatures, the reason is that epoxy group has a fast reaction rate with amine group and lower hydrolysis rate at alkali condition.^{8,9} Whereas the reaction between epoxy group and carboxy group at acidic conditions is emphasized the substantial hydrolysis for epoxide.^{30,31} Moreover, there is a potential damage for collagen fiber when the pH value is higher than 8.0. Hence, the optimal pH value in the tanning process of IEGA appears at 8.0, and the experimental results indicated that IEGA can be directly used to carry out tanning process after bating without pickling.

Investigation for Tanning Mechanism of IEGA

Hide powder is commonly used as the model substrate to study the tanning mechanism of tanning agent.³²⁻³³ Theoretically, epoxy group of IEGA was first reacted with primary amine and

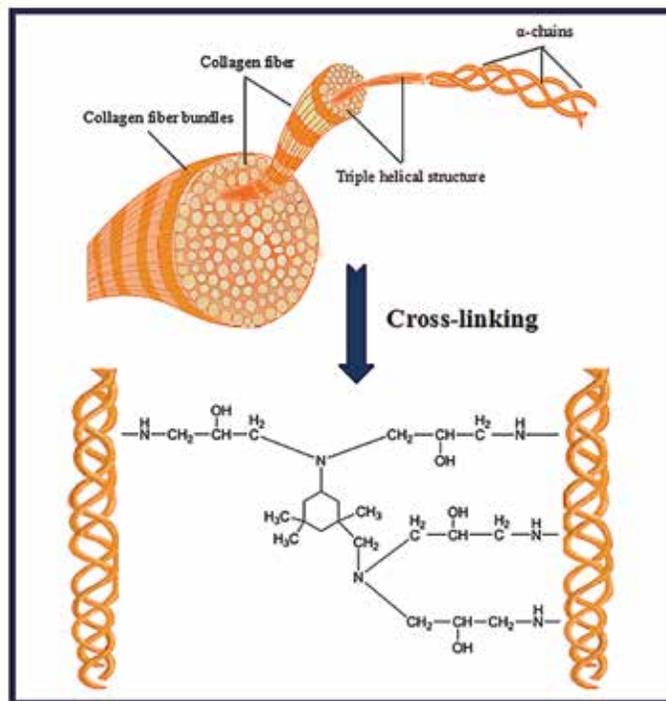


Figure 6. The schematic illustration of cross-linking of IEGA among primary amino groups of collagen fibers.

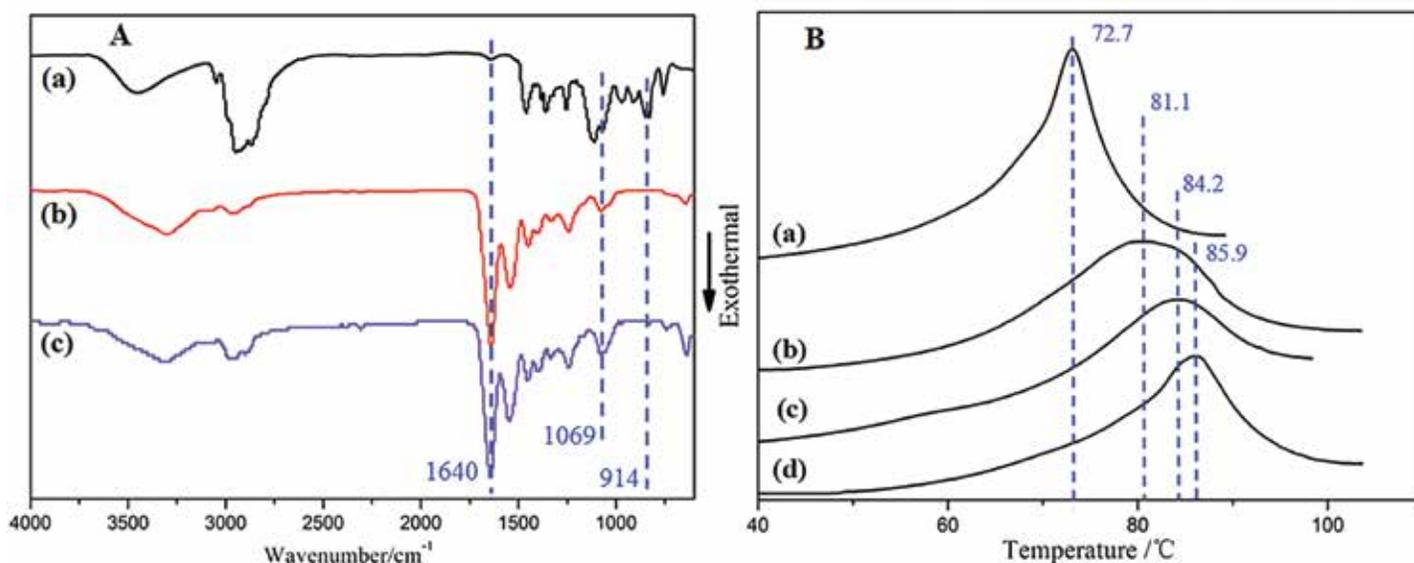


Figure 7. A: FTIR images of (a) IEGA, (b) hide powder, (c) hide powder tanned by IEGA; B: DSC of hide powder (a), cross-linking hide powder by IEGA with the dosage of 6% (b), 8% (c) and 10% (d).

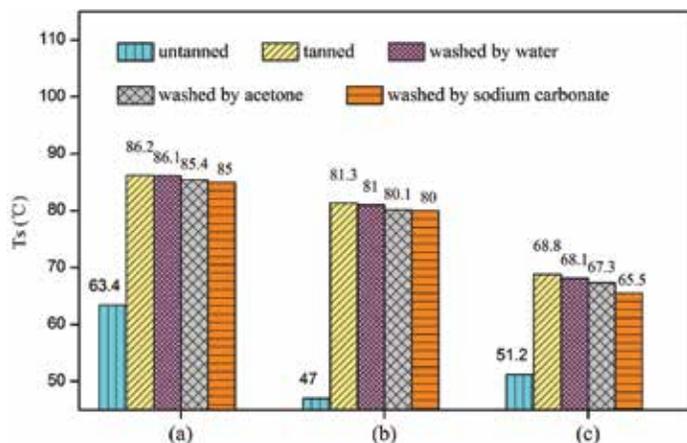


Figure 8. T_s of sheep skin and its tanned leather with different washing solvents. (a) bated skin and its tanned leather, (b) esterified skin and its tanned leather, and (c) deaminized skin and its tanned leather.

then reacted with secondary amine of collagen molecules. However, the time factor for reaction with the second amino group is most likely a matter of reaching an alignment where an epoxy group is in close enough proximity to a primary amine for the cross-linking to form. It was found that reaction of the primary amine with epoxy group is much faster than that of secondary amine.^{34,35} Therefore, the cross-linking of IEGA should be predominately taking place among the primary amino groups of collagen molecules, as shown in Figure 6.

Figure 7 shows the FT-IR of hide powder before and after IEGA tanning. In Figure 7A (a), the FT-IR spectrum mainly shows the absorption peaks of the epoxy group of IEGA at 914 cm^{-1} . By contrast, as shown in Figure 7A(c), this peak of 914 cm^{-1} is disappeared for hider powder tanned with IEGA, and the peak at 1069 cm^{-1} attributed to the carbon skeletal vibration of

isophenone diamine hexadecyclic ring has appeared, indicating the epoxy groups of IEGA have reacted with collagen. In Figure 7A(b), the peak at 1640 cm^{-1} should be the stretching vibration of N-H group of collagen, which is overlapped with the stretching vibration of N-H possibly resulted from the cross-linking reaction of -NH_2 of collagen fibers by the epoxy groups of IEGA, as shown in Figure 7(c).

Figure 7B shows that the T_s for raw hide powder is 72.8°C , which is close to literature data ($T_s=72.6^\circ\text{C}$).⁶ The thermal stability of hide powder was enhanced after cross-linking with IEGA. With increasing the dosage of IEGA from 6% to 10%, the T_s of hide powder was increased from 81.1°C to 85.9°C , which is likely to relate with the increasing of epoxy groups.

In order to further understand the tanning mechanism of IEGA, the chemical modified sheep skins were used in this investigation. Furthermore, the interaction stability between IEGA and the functional groups of collagen fiber was studied using the washing test. The chemical modification for sheep skin includes two methods. One is the esterification reaction in order to block the -COOH groups of collagen, and the other is the deamination reaction that -NH_2 groups in collagen were changed to -OH groups at the conditions of sodium nitrite and glacial acetic acid.³⁶

Figure 8 is the T_s of bated sheep skin, chemical modification sheep skin, and their corresponding tanned leather. Meanwhile, the T_s of tanned leathers washed using different solvents were also presented. In case of bated sheep skin without chemical modification, its T_s was increased to 86.2°C after tanned with IEGA. For esterified sheep skin, its T_s after tanned with IEGA was increased to 81.3°C . Meanwhile, it was slightly increased to

68.8°C for that of deaminated sheep skin. These facts suggested that the cross-linking reaction should be mainly taking place among the $-NH_2$ groups of collagen fibers by the epoxy groups of IEGA.³⁷

The Ts of tanned leather washed with different solvents was also summarized in Figure 8 to further verify the cross-linking mechanism of collagen and IEGA. In general, just physical adsorbed tanning agent should be taken away when the tanned leather washed by water. If the tanning agent is hydrogen bonded or electrovalent bonded with collagen fiber, it will be broken down when washed by acetone or sodium carbonate, leading to the significantly reducing of Ts. In Figure 8, it can be observed that the Ts of leather obtained from bated skin, esterified skin and deaminated skin is slightly decreased after washed with different solvents. Therefore, IEGA should be covalently bonded with $-NH_2$ groups of collagen fibers, resulting much higher stability.

Conclusions

A novel tanning agent (IEGA) with multi-epoxy groups has been successfully synthesized using IPDA and ECH as starting materials. Experimental results indicated that IEGA exhibited strong tanning effect for sheep skin in the ethanol bath. Due to the hexatomic ring structure contained, the Ts of tanned leather with IEGA is higher than that of epoxide with only aliphatic chain. Furthermore, appropriate increase of the IEGA dosage, tanning pH and tanning temperature would increase the Ts of leather. The covalently cross-linking among $-NH_2$ groups of collagen fibers by the epoxy groups of IEGA should be the main tanning mechanism of IEGA.

Acknowledgement

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