

Investigation of the Synthesis of a Novel Glycidyl Ether-amine Epoxy Tanning Agents and their Tanning Performance

by

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Abstract

Isophorone diamine (IPDA) and epichlorohydrin (ECH) were used to fabricate the epoxy tanning agents, and polyalcohol compounds (glycerol, polyethylene glycol, ethylene glycol) were employed to introduce the ether bonds into the epoxy tanning agents to improve their compatibility with water. The prepared epoxy tanning agents were named IGE, IPE and IEE for the introduction of glycerol, polyethylene glycol and ethylene glycol, respectively. FT-IR and ¹H NMR analysis indicated that epoxy groups, ether bonds and hexatomic rings were successfully introduced into IGE, IPE and IEE. The tanning performances of the epoxy tanning agents were further evaluated in water, ethanol-50 (50% of ethanol in water) and ethanol-95 (95% of ethanol in water) medium, which suggested that ethanol-50 was the most favorable one for the epoxy tanning agents. The IGE tanned leather exhibited the highest shrinkage temperature of 83°C in ethanol-50 due to its low viscosity, high epoxy value and wide molecular dispersion. Morphology observation indicated that the IGE tanned leather exhibited better dispersion of fiber network than that of IPE and IEE tanned leathers. These results illustrated that IGE was an appropriate tanning agent in water-ethanol medium, which could be considered as a candidate for the organic tanning agents.

Introduction

Tanning is the critical process in leather manufacture as it converts a raw hide or skin into leather. In the tanning process, tanning agent can combine with the -COOH, -NH₂, and -OH groups of collagen to establish a crosslink among collagen fibers, resulting in the enhancement of leather hydrothermal stability.¹ Up to now, chrome tanning agent is still the most widely used one as it can endow the resultant leather with excellent features.^{2,3}

However, a vast amount of Cr(III) contained wastewater and solid waste will be generated during the process, creating a roadblock for the sustainable development of leather manufacturing.^{4,5} Besides, the possibility that Cr(VI) exists in leather products, wastewater and tannery solid wastes presents a potential risk to the human body and environment.⁶⁻⁸ Thus, it is the chrome-related issues that stimulate researchers to develop chrome-free tanning agent to ensure the sustainability of the leather industry.

To date, organic tanning agents with favorable tanning effect are an important alternative for the chrome tanning agent, in which aldehyde tanning agent is widely used.^{1,9} However, the leather tanned with aldehyde tanning agents can release formaldehyde during both manufacture and commercial application processes, which may lead to the potential hazards to human health.^{10,11} Thus, to avoid the drawback of aldehyde tanning agents, more substitutions are considered for the organic tanning process. Epoxide is a promising alternative organic tanning agent that can be used for leather tanning due to the prospect of high cross-reactivity with collagen. On the other hand, epoxide tanning agent can eliminate the disadvantages of aldehyde agent because it is aldehyde free. Recent studies reported that epoxide performs significant crosslink effect among collagen fibers.¹²⁻¹⁸ However, the shrinkage temperature, appearance, physical and chemical performances of epoxide tanned leather cannot compare with that of chrome tanned leather.^{1,19} Therefore, it remains a challenge to synthesize a novel epoxide with special molecular structure and excellent tanning performance.

In our previous work, a novel epoxide tanning agent (IEGA) with aliphatic ring was prepared, and the shrinkage temperature (Ts) of IEGA tanned sheep leather could be enhanced significantly. However, the promising tanning effect of the IEGA could only be obtained in ethanol-95 medium due to its poor water solubility, which would limit its practical application even

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though it was considered as one of the cleaner tanning processes in ethanol medium.²⁰ As is well known, ether bonds contained in a polymer can result in soft segments and a certain compatibility with water,²¹ thus it is supposed that the introduction of ether bonds into the molecular structure of an epoxide will also improve its water-compatibility and reduce its viscosity, leading to a significant performance enhancement of epoxide in tanning process.

In this work, three kinds of ether bonds contained in epoxide tanning agents (IGE, IPE and IEE) were prepared using isophorone diamine (IPDA), epichlorohydrin (ECH) and polyalcohol compounds (glycerol, polyethylene glycol and ethylene glycol were employed, and corresponding epoxides were named as IGE, IPE and IEE, respectively) as starting materials. The structural features of prepared epoxide tanning agents were characterized using FT-IR, ¹H NMR and GPC (gel permeation chromatography) analysis, and their tanning performances in the different tanning medium (water, water-ethanol) were further investigated.

Experimental

Materials

Isophorone diamine (IPDA) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., China. Glycerol (GLY), polyethylene glycol (PEG, 400 g/mol), ethylene glycol (EG), epichlorohydrin (ECH), sodium hydroxide and Boron (tri) fluoride etherate (BFE) were supplied by Sinopharm Chemical Reagent Co. Ltd., China. Monopotassium phosphate and acetic acid were supplied by Beijing Chemical Works, China. All chemicals employed in the present work were analytical grade.

Synthesis of Epoxide Tanning Agents

The synthetic process was carried out in a 500 mL three-necked flask equipped with stirrer, reflux condenser and temperature-controlled water bath. In optimal conditions, IPDA (1 mol) was added into the three-necked flask under stirring, and then ECH (4 mol) was slowly dropwise added into the flask. After reaction at 35°C for 2 h, the mixture was heated to 60°C and then continuously reacted for 4 h, and the intermediate was obtained. Afterward, the polyalcohol compound (GLY, PEG or EG, respectively) was reacted with intermediate catalyzed by BFE at 60°C for 4 h for the introduction of ether bonds, followed by continuous reaction with ECH at 60°C for another 4 h. The resultant solution was then cooled down to 35°C, and 40 wt% sodium hydroxide solution was employed to conduct the ring closing reaction (1.5 h). Finally, the resultant solution was neutralized by using both monopotassium phosphate and acetic acid. After neutralization, the organic phase was separated. Vacuum rotary evaporation at 45 °C was employed to remove the unreacted ECH in the organic phase, and epoxide tanning agents

were finally obtained, which were named IGE, IPE and IEE. The detailed information for the synthesis of the epoxide tanning agents are presented in Table I and reaction illustration of the IGE and IEGA (previous work) are shown in Figure 1.

Characterization of Epoxide Tanning Agents

Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR spectra of epoxy tanning agents were obtained in a Bruker Tensor 27, using a Bruker/Pike MIRacle ATR Accessory (A529-P, Bruker, Germany). All the samples were scanned in the range from 600 to 4000 cm⁻¹ using 64 scans with a resolution of 1 cm⁻¹. The obtained spectra were further processed by using OPUS software.

Molecular Weight Determination

The weight-average molecular weight (M_w), number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the prepared epoxy tanning agents were determined by GPC (HLC-8320, Japan Tosoh Corporation) equipped with a refractive index detector (RID). The tanning agent was dissolved in THF to prepare a test sample with a concentration of 0.5 mg/mL. Before the measurement, the test samples were filtered with 0.22 μm filters. The styragel columns of HR3, HR4 and HR5 were employed. The columns and detector were thermostated at 35°C, and the samples were analyzed at a flow rate of 1.0 mL/min in the tetrahydrofuran moving phase. Polystyrene was used as standard calibration for chromatography.

¹H NMR Analysis

¹H NMR spectra were recorded by the superconducting pulse Fourier transform nuclear magnetic resonance spectrometer (600MHz, AV II type, Bruker, Switzerland). The chemical shifts relative to that of deuterated chloroform (d=7.26) were recorded.

Determination of Viscosity

The viscosity of the prepared epoxy tanning agents was determined by rotary viscometer (DV-T2, Shanghai Nirun intelligent technology Co. Ltd., China) at 25°C.

Table I
The optimal processes for the synthesis of epoxide tanning agents.

Samples	IPDA (mol)	ECH (mol)	GLY (mol)	PEG (mol)	EG (mol)	BFE (mmol)	NaOH (mol)
IGE	1	14	3	0	0	7.8	14
IPE	1	11	0	3	0	6.0	11
IEE	1	11	0	0	3	6.0	11

Tanning Trials

The performances of the prepared tanning agents were determined by using limed sheep skin, which was split and cut along the back bone into matched pieces (20 cm × 20 cm) for tanning trials. The dosage of subsequent chemicals was calculated based on the weight of limed skin. The tanning process was performed according to the process described in Table II. After deliming and bating, pH value of the bated sheep skin was adjusted, and then the bated skin was tanned with IGE, IPE and IEE in water, ethanol-50, ethanol-95, respectively.

Furthermore, the tanning conditions of epoxy tanning agent IGE in various water-ethanol media were investigated in detail. The bated sheep skin was tanned in water and water-ethanol media (water, ethanol-50 and ethanol-95) with a certain dosage (2%, 4%, 6%, 8%, 10%, 12% and 14%, respectively) of tanning agent. The pre-penetration process was conducted at 30°C with a certain pH (pre-penetration pH: 5, 6, 7 and 8, respectively). After running for a certain time (pre-penetration time: 1, 2, 3 and 4 h, respectively), the fixation pH was raised by adding sodium bicarbonate (pH: 6, 7, 8, 9, 10, respectively) with the fixation temperature of 35°C, 45°C and 50°C, respectively. After continuously running 2, 4, 6, 8, 10, 12, 14 and 16 h, respectively,

the tanned leather was washed for 10 min in water. The pickled sheep skin tanned by 8% chrome tanning agent according to the conventional chrome tanning process was used as a control. The leather obtained was piled for 24 h, and then it was fatliquored in standard manner.

Evaluation of Tanning Performance

Shrinkage Temperature

The shrinkage temperature of tanned sheep leather was measured using digital leather shrinkage temperature tester (MSW-YD4, Shaanxi University of Science and Technology, China). The heating rate was maintained at 2°C/min constantly.²²

Absorption Rate of Tanning Agent

The initial weight of epoxy tanning agent (m_1) was recorded and the tanning apparatus remained airtight during the tanning of sheep skin. After tanning, the weight of waste liquid was recorded (m_2) and then the weighted waste liquid was used to test the residual content of epoxy tanning agent (x). The absorption rate of epoxy tanning agent (A) was calculated according to the following equation:

$$A = \frac{m_1 - m_2 \times x}{m_1} \times 100\% \quad (1)$$

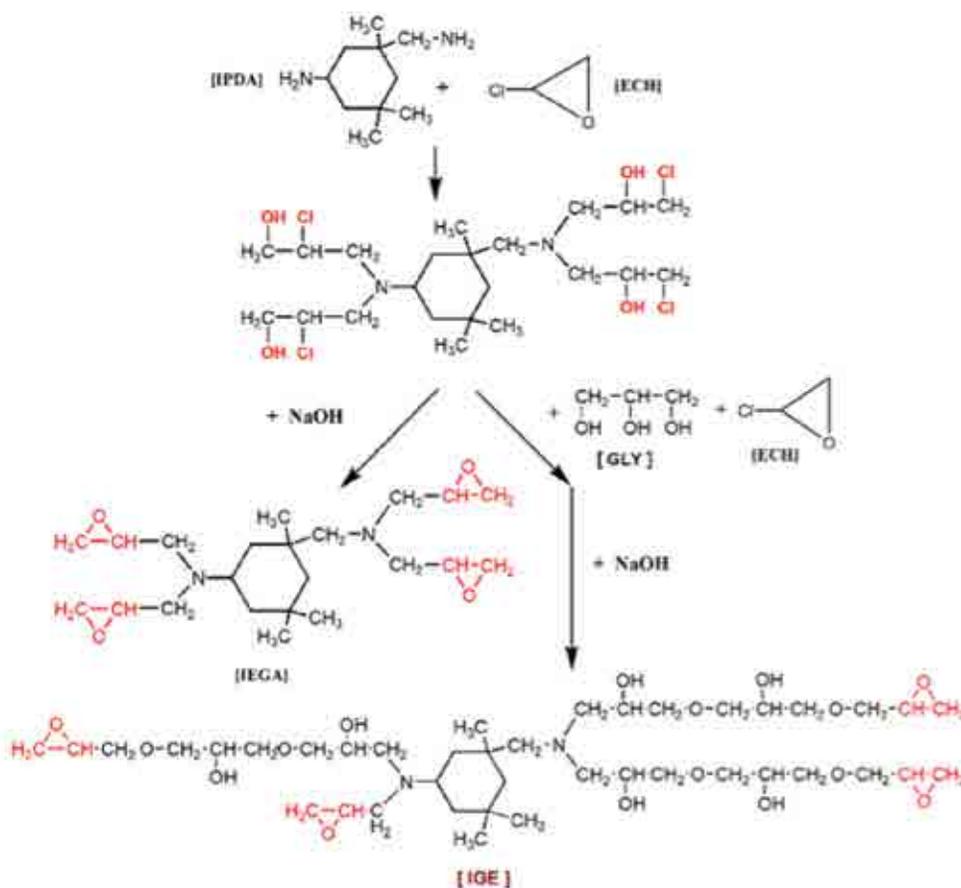


Figure 1. The reaction illustration of IGE and IEGA.

Physical Properties

All tanned sheep leathers were fatliquored according to conventional process. Then, the fatliquored leathers were dried and softened to obtain crust leathers. The crust leather samples were conditioned at 20°C with a relative humidity of 65% for 48 h according to the official sampling method,²³ and tensile strength, tear strength and elongation at break were measured.²⁴ The hand feeling of these crust leathers were evaluated by professional skilled tanners.

Scanning Electron Microscope (SEM) Observation

The dried crust leathers were cut into 2 mm × 5 mm pieces. Then, the cross section of leather sample was coated with gold in vacuum. The SEM observation was carried out by using a scanning electron microscope (JSM-7500F, JEOL Ltd.) with a magnification of 500 times, acceleration voltage of 15 kV and resolution ratio of 1.0 nm.

Results and Discussion

Chemical Structure Analysis

The chemical structure analysis of the prepared epoxy tanning agents was conducted by FT-IR and ¹H NMR. The FT-IR spectra of IPDA, IGE, IPE and IEE are presented in Figure 2. It can be found that the absorption peaks (Figure 2b, 2c and 2d) at 842 cm⁻¹, 916 cm⁻¹ and 1261 cm⁻¹ are attributed to skeleton vibrations of epoxy rings, which evidenced the existence of epoxy group in the samples.²⁵⁻²⁷ The peaks at 1155 cm⁻¹ are attributed to the stretching vibration of C-O-C, which confirmed the presence of ether bonds. The presence of these peaks reveals the successfully introduction of epoxy groups and ether bonds in the prepared epoxides. In Figure 2a, the double peaks at 3364 cm⁻¹ and 3283 cm⁻¹ correspond to the stretching vibration of -NH₂ and the peak at 1597 cm⁻¹ is attributed to the bending vibration of N-H of IPDA,²⁸⁻²⁹ while the absence of these peaks in the spectra of IGE, IPE and IEE (Figure 2b, 2c and 2d) suggested that the amine group had been involved in the reaction. The absorption peak at 1414 cm⁻¹ is assigned to C-N structure, and the peak at 1069 cm⁻¹ is attributed to the carbon skeletal vibration of hexatomic ring. The peaks at 2949 cm⁻¹, 2869 cm⁻¹ and 1455 cm⁻¹ are assigned to the dissymmetry, symmetry stretching and bending vibration band of -CH₂- group.

Table II
Deliming, bating and tanning process of as prepared epoxy tanning agents.

Process	Chemicals	Dosage (%)	Temp. (°C)	Time (h)	pH	Remarks
Deliming	Water	100	35	60		
	Deliming agent	1.0			8.0-8.5	Drain
Washing	Water	200	35	10×2		Drain
Bating	Water	100			8.0-8.5	
	Trypsin compound	0.5	40	60		
	Degreasing agent	2	40	30	8.0	Drain
Washing	Water	200	25	10×3		Drain
Tanning	Medium*	100			6.0	
	IGE, IPE or IEE	10	30	2		
Basification	NaHCO ₃				8.0	
			45	10		
Washing	Water	200	25	10		Drain

*Water and water-ethanol medium of ethanol-50 and ethanol-95.

Figure 3 shows the ^1H NMR spectra of IPDA, IGE, IPE and IEE, respectively. The peaks at 1.19 and 1.21 ppm of Figure 3a are attributed to the H of amine group (9H and 10H). By contrast, these peaks disappear in the corresponding locations in the spectra of IGE, IPE and IEE, indicating the introduction of additional chemical groups in these samples at the position of $-\text{NH}_2$ group. The signals at ~ 2.65 and ~ 3.05 ppm correspond to the 10H of epoxide rings, suggesting that the epoxide group was introduced.³⁰⁻³¹ Furthermore, the signals of $-\text{CH}_2-\text{O}-$ (~ 3.54 ppm) and $-\text{CH}-\text{O}-$ (~ 3.71 ppm) are observed in the spectra of IGE, IPE and IEE. ^1H NMR and FT-IR results indicated that epoxy groups, ether bonds and hexatomic ring were imported into the prepared epoxides, and the possible chemical structures of IGE, IPE and IEE are shown in Figure 4.

Molecular Weight and Viscosity of as Prepared Epoxides

Table III shows the weight average molecular weight (M_w), number average molecular weight (M_n), polydispersity index (M_w/M_n) and viscosity of IGE, IPE and IEE. The M_w of IGE is 813 g/mol, while the M_w of IPE is 921 g/mol. However, the polydispersity of IGE was larger as compared with IPE and IEE, demonstrating that IGE had a wider molecular weight distribution and higher polydispersity index.³² Therefore, IGE might be able to enter different hierarchical structures of collagen fibers and perform crosslinking reactions with collagen matrix during the tanning process.³³ In addition, the viscosity of IGE is 224 mPa·s, much lower than that of IPE and IEE, indicating a potential better penetration in tanning process.

Evaluation of the Tanning Performance of Prepared Epoxides

Shrinkage temperature (Ts) of leather is one of the most critical indexes for measuring tanning ability. This was used in the present work to investigate the tanning performance of prepared epoxides.⁸ The Ts of leather tanned by IGE, IPE and IEE in different tanning media is summarized in Figure 5. As shown in Figure 5a, it can be found that IPE tanned leather exhibited the highest Ts in pure water, while IGE tanned leather showed the best tanning effect in ethanol-50 tanning medium, which corresponds with their uptake rate, as shown in Figure 5b. It might be because IPE had higher ether bond proportion compared with IGE and IEE, resulting in a higher water-solubility in pure water. On the other hand, the epoxy value of IGE (Figure 5c) is higher than that of IPE and IEE, resulting in a better tanning effect in ethanol-50 tanning medium. In addition, the molecular size of IGE is smaller than that of IPE and IEE, which is favorable for penetration in leather. These facts suggested that the epoxide with higher epoxy value and smaller molecular size could result in good tanning effects.

Optimization of IGE Tanning Conditions

According to the above results, IGE exhibited better tanning performance than that of IPE and IEE in ethanol-50 tanning

medium. Thus, the detail tanning performances of IGE were further investigated. The effect of IGE dosage on Ts of sheep leather was investigated, as shown in Figure 6a. In general, the Ts increased a lot by adding more tanning agent in all kinds of tanning medium. As compared with ethanol-95, ethanol-50 could be recognized as a promising tanning medium candidate for IGE, which is safer due to the relatively lower ethanol content. This fact confirmed that the introduction of ether bonds can increase the compatibility of the prepared epoxides with water. Furthermore, the Ts of tanned leather was raised to 83.8°C as the dosage increased to 10% when tanning process was conducted in ethanol-50. As compared with tanning in water, the Ts of leather obtained in ethanol-50 was higher than 80°C when the IGE dosage was 8%. After 8%, the Ts of tanned leather raised slightly with the increase of the dosage, especially when the dosage reached 10%, which suggested that 10% is a promising dosage for IGE.

pH is one of the most critical parameters for tanning process, which was investigated in the present study. As shown in Figure 6b, it can be observed that the leather tanned in ethanol-50 medium exhibited almost the same Ts with the leather tanned in ethanol-95, which was much higher than that of in pure water at the same fixation pH of 8.0~9.0, suggesting that IGE could be used in ethanol-50 tanning medium to achieve excellent tanning performance. It was believed that the epoxy groups of epoxide tanning agents more easily react with the free amino groups of collagen fiber at alkali conditions.³⁴⁻³⁵ However, further increasing pH may destroy collagen fiber, thus, the optimal fixation pH value in the present study should be in the range of 8.0~9.0.

Furthermore, the influence of pre-penetration pH and time on the tanning effect of IGE in ethanol-50 was also investigated (Figure 6c,

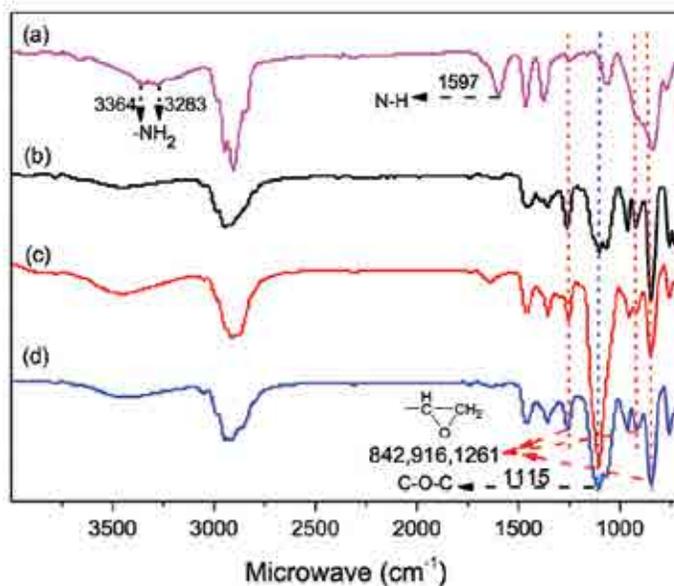
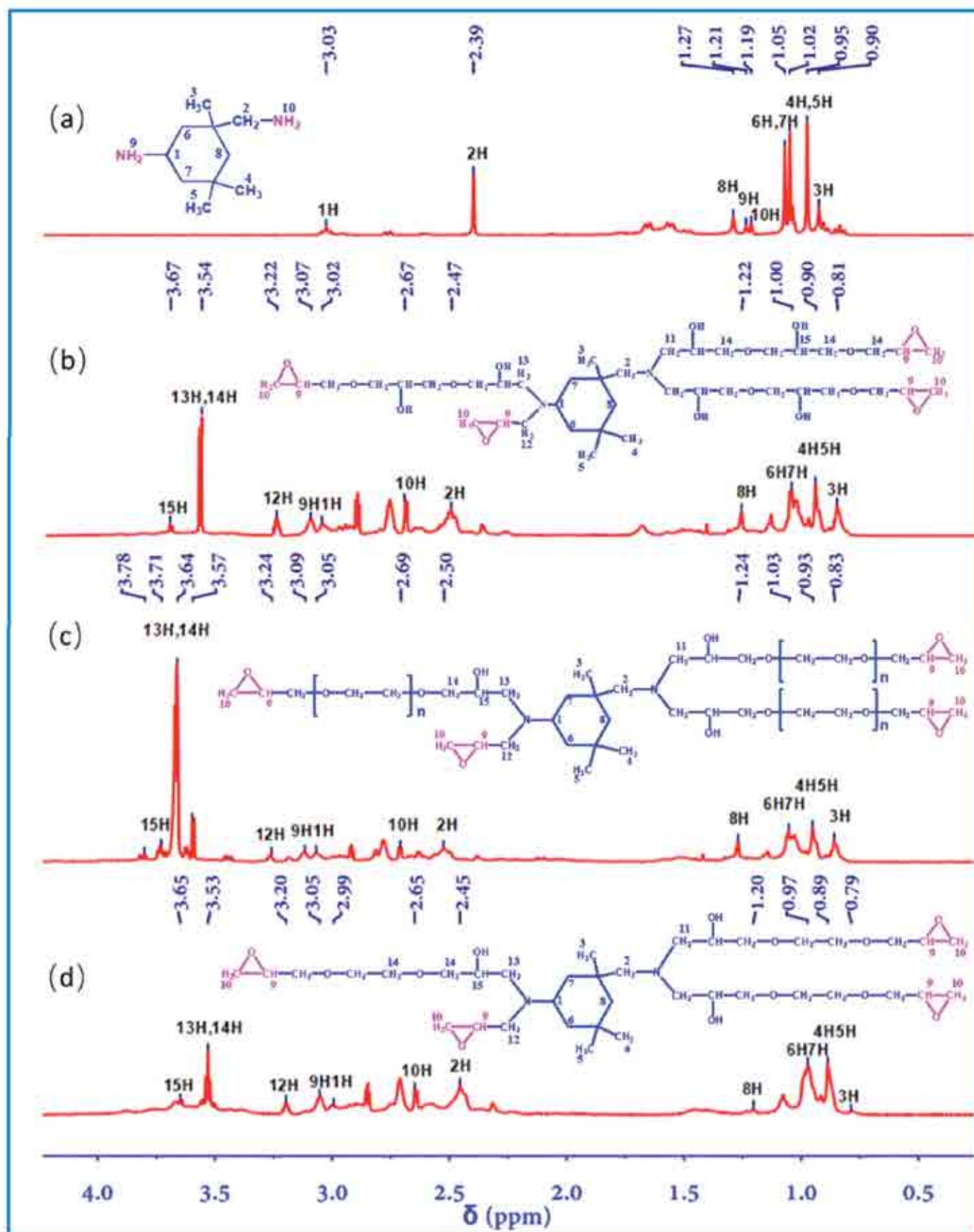


Figure 2. FT-IR Spectra of (a)-IPDA, (b)-IGE, (c)-IPE and (d)-IEE.

Figure 3. ^1H NMR spectra of (a)-IPDA, (b)-IGE, (c)-IPE and (d)-IEE.

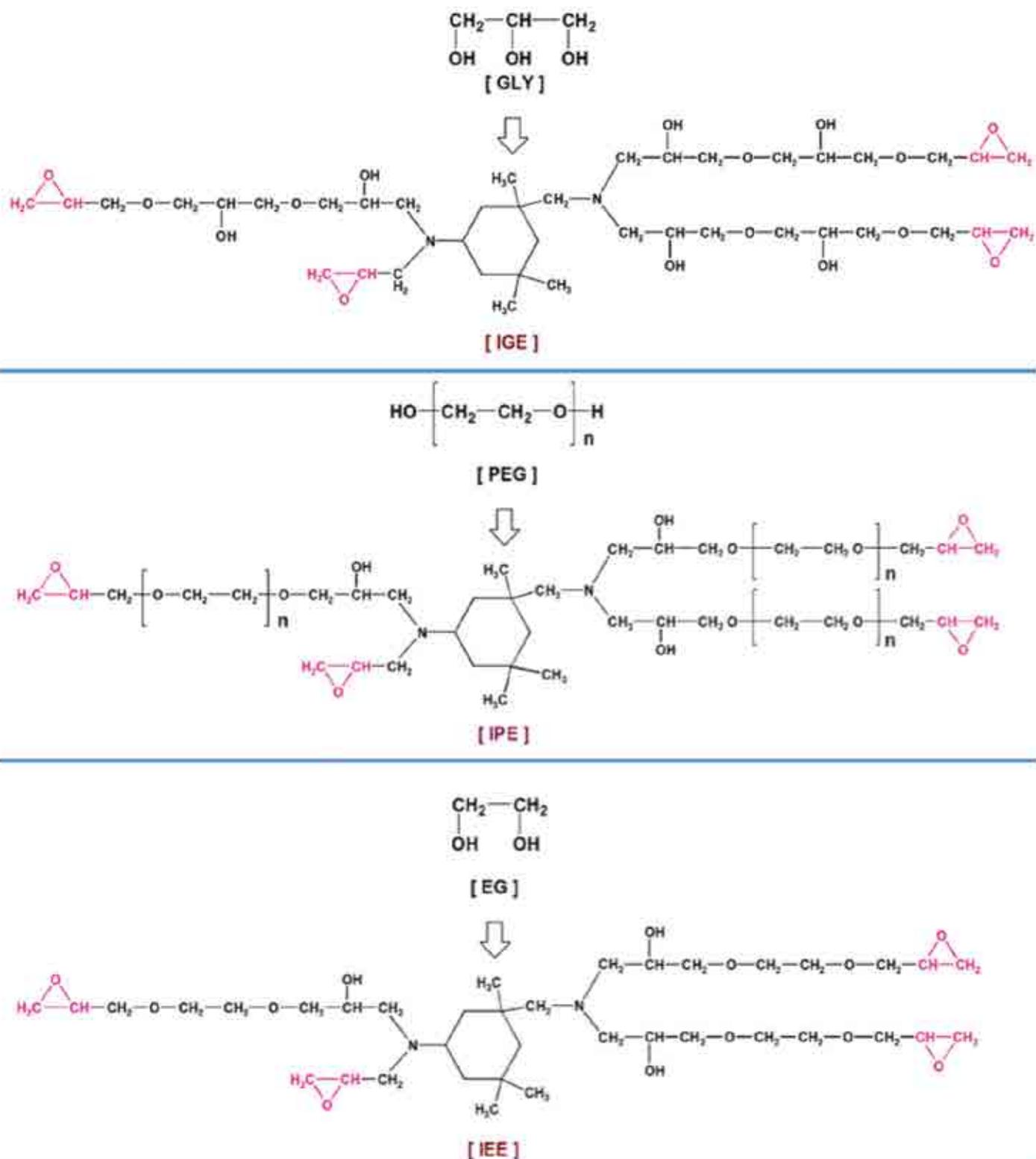


Figure 4. Possible chemical structures of IGE, IPE and IEE

6d). The results suggested that pre-penetration pH had significant impact on the Ts of the tanned leather. In particular, the epoxy groups and amino groups would react with each other quickly on the surface of skin/hide when the pre-penetration pH value was higher than 7.0, and thus will prevent the further penetration of IGE. On the other hand, the hydrolysis of epoxy group would take place when the pre-penetration pH value was lower than 6.0, which resulted in the decline of the epoxy value, leading to the decrease of Ts of IGE tanned leather. Therefore, controlling the pre-penetration pH in a range 6.0 to 7.0 was desirable for the IGE tanning process. The impact of the pre-penetration time on tanning performance was also evaluated, which is shown in Figure 6d. The result suggested that pre-penetration time significantly impacts the tanning effect, and Ts was raised with prolonging of the pre-penetration time to 2 h. Additional increasing in pre-penetration time would not improve the Ts, indicating that the pre-penetration time could be set at 2 h to 3 h. Therefore, it could be concluded that the pre-penetration pH and time are of essential importance for the epoxide tanning process.

The effect of fixation time and fixation temperature were also investigated in ethanol-50 to evaluated the tanning performance of IGE. As illustrated in Figure 6e, fixation time and fixation temperature obviously affected the Ts of IGE tanned leather, in which the Ts of the leather raised with the elevation of the fixation temperature and fixation time. The Ts of the leather was only 76°C when it was tanned at 35°C for 16 h, while it increased to about 84°C if the fixation temperature raised to 50°C, due to the poor reactivity of epoxide groups and amino groups at low temperature. However, further increasing fixation temperature would decrease the tanning performance, due to the high risk of leather damage or area yield reduction if the tanning process was conducted in a fixation temperature higher than 50°C. As compared with the epoxide tanning agent synthesized in our previous work,²⁰ IGE with ether bonds significantly promoted its water compatibility, which remarkably reduced the ethanol demand, making the tanning process safer.

Table III
The molecular weight and viscosity
of IGE, IPE and IEE.

Epoxy tanning agent	M_w	M_n	M_w/M_n	Viscosity/ (mPa·s)
IGE	813	398	2.04	224
IPE	921	463	1.99	435
IEE	827	422	1.96	460

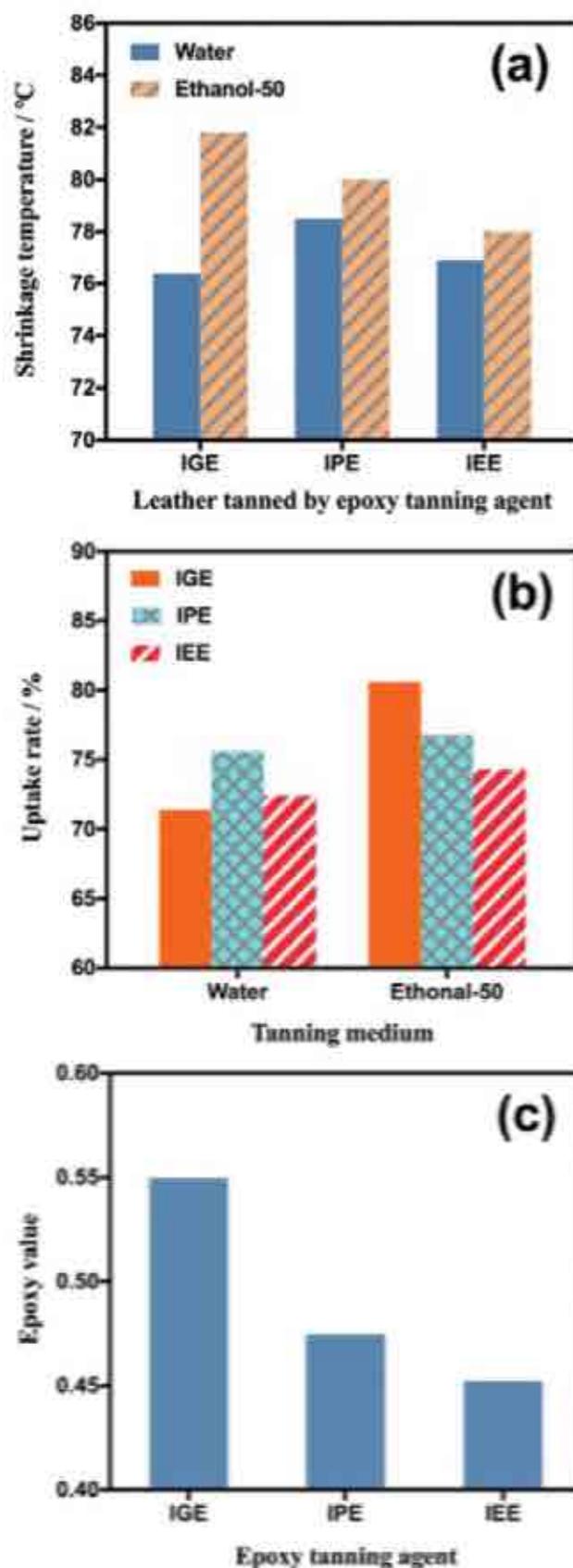


Figure 5. Tanning performance of prepared epoxides: (a)-Ts of leather tanned in different media; (b)-uptake rate of IGE, IPE and IEE; (c)- epoxy value of IGE, IPE and IEE.

Morphological Observation of Tanned Leather

Morphology of the tanned leather is an important factor for the evaluation of tanning effects, which provide an intuitive vision of the tanned leather. Figure 7 shows the morphological observation of the cross section of the bated skin, the leather tanned by epoxides in ethanol-50 and the leather tanned by chrome tanning agent. It was found that the fiber network dispersion of epoxides tanned leather was better than that of the bated skin (Figure 7a). The chrome tanned leather (Figure 7e) showed the best network dispersion among the tanned leathers, and IGE performed with comparable effect compared to that of chrome. The SEM image of the IGE tanned leather (Figure 7b) showed a high fiber network dispersion, and exhibited similar tanning effect compared to chrome tanned leather. Among the epoxy tanning agents tanned leathers, IGE tanned leather (Figure 7b) showed higher fiber network dispersion as compared with IPE and IEE tanned leathers (Figure 7c, 7d), which suggested that IGE exhibited a better tanning effect than IPE and IEE at the same tanning condition. Furthermore, the morphologies of the cross section of the leathers tanned by IGE

in water and water-ethanol medium were also illustrated in Figure 8. Higher dispersion of fiber network could be obtained as the ethanol content increased in the tanning medium, which achieved a satisfactory tanning performance if the ethanol content was 50%. After that, further increase in ethanol content would not significantly promote the tanning effect, and there was no remarkable network dispersion improvement observed in Figure 8c (leather tanned by IGE in ethanol-95), indicating that the introduction of ether segments into the tanning agent outstandingly reduced the ethanol demand as compared with the IGE tanning agent prepared in our previous work,²⁰ which is beneficial for the tanning process. Such a result was in accordance with the T_s change of IGE tanned leathers in different water-ethanol media (Figure 5a). It can be well explained using the theory of tanning chemistry that good cross-linking effects will be beneficial to higher opening-up and degree of fixation for collagen fibers.³⁶⁻³⁷ Thus, IGE exhibited more satisfactory tanning properties compared with IPE and IEE, and was a competitive tanning agent candidate in water-ethanol tanning medium.

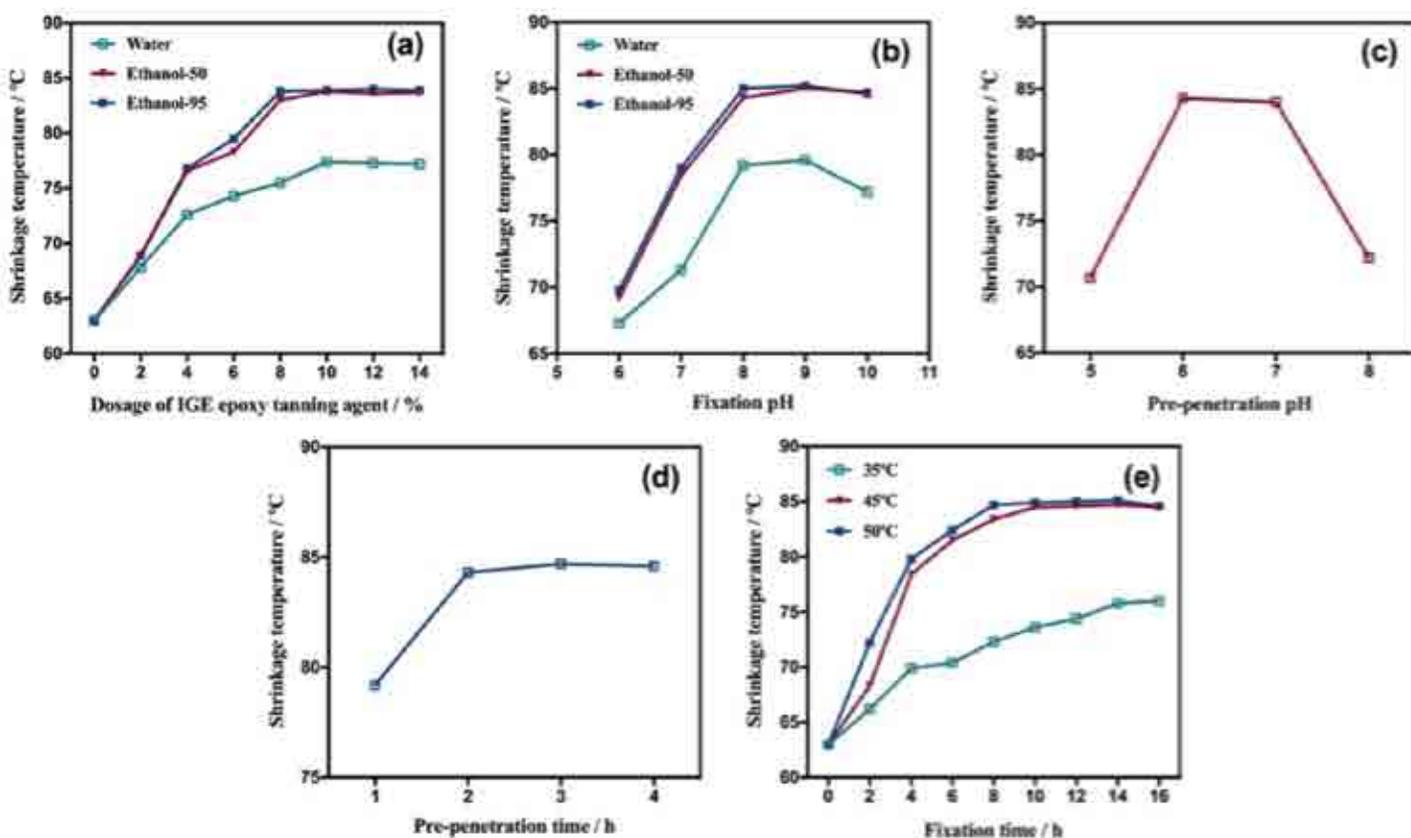


Figure 6. Effect of IGE tanning conditions on shrinkage temperature of sheep leather in ethanol-50: (a) pre-penetration pH was 6.0, pre-penetration time was 2 h, fixation pH was 8.0, fixation time was 10 h, and fixation temperature was 45 °C; (b) dosage of IGE was 10%, pre-penetration pH was 6.0, pre-penetration time was 2 h, fixation time was 10 h, and fixation temperature was 45 °C; (c) dosage of IGE was 10%, fixation pH was 8.0, fixation time was 10 h, and fixation temperature was 45 °C; (d) dosage of IGE was 10%, fixation pH was 8.0, fixation time was 10 h, and fixation temperature was 45 °C; (e) dosage of IGE was 10%, pre-penetration pH was 6.0, pre-penetration time was 2 h, fixation pH was 8.0.

Physical Properties

The physical properties of fatliquored leather are shown in Table IV. The result suggested that the IGE tanned leathers in water-ethanol medium (TM-II) generally exhibited a higher mechanical strength (tensile and tear strength) and a better hand feeling than the IGE tanned leathers in water medium. Among these, IGE tanned leather performed the most favorably for mechanical strength with tensile and tear strength of 16.62 and 65.46 N/m² in water (TM-I) respectively, and 20.77 and 73.28 N/m² in ethanol (TM-II) respectively. The mechanical performance of the IGE tanned leather was not only better than that of other epoxy agent tanned leather, but also better than that of traditional chrome

tanned leather. This might be due to the covalent crosslinking among IGE and collagen fibers and the rigid hexatomic-ring structures in IGE, which has been explained in our previous work.²⁰ Accordingly, it can be inferred that the epoxide with higher epoxy value and rigid hexatomic-ring structure could provide higher strength for-tanned leather. Additionally, the hand feeling of IGE tanned leather is almost same as the chrome tanned leather. As compared with the epoxide tanning agent in our previous work, IGE with ether bonds exhibited much better water solubility and lower viscosity, and therefore its outstanding tanning performance can be expected.-

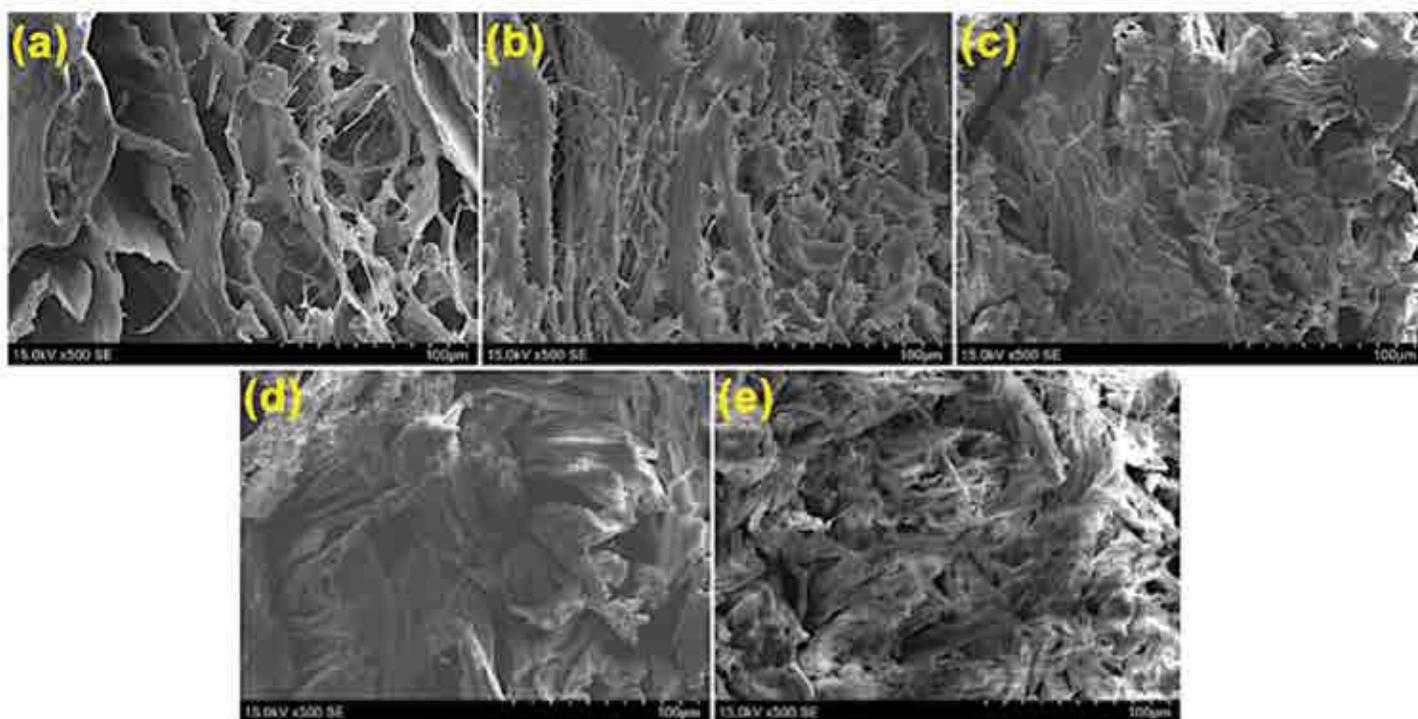


Figure 7. SEM images of bated skin and leathers tanned by prepared epoxides and chrome tanning agent: (a)-bated skin; (b)-leather tanned by IGE in ethanol-50; (c)-leather tanned by IPE in ethanol-50; (d)-leather tanned by IEE in ethanol-50; (e)-leather tanned by chrome tanning agent.

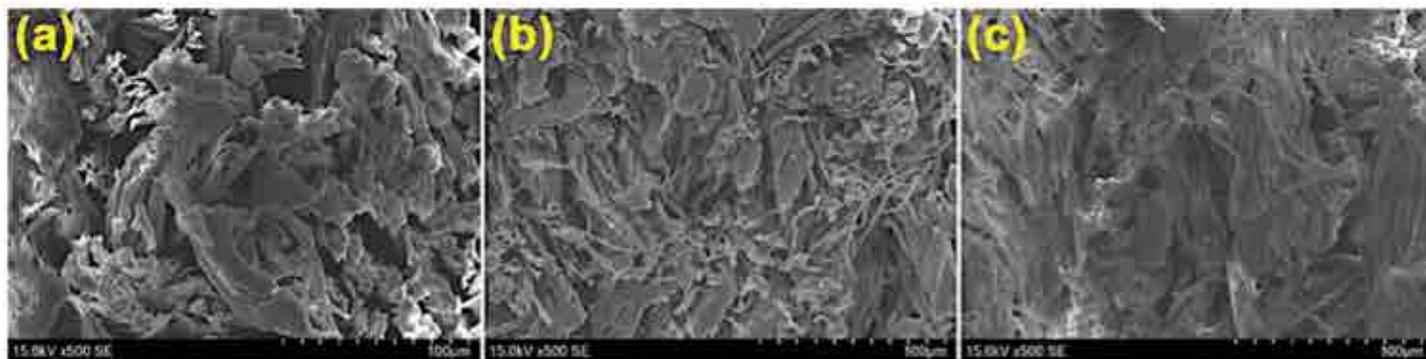


Figure 8. SEM images of leathers tanned by IGE in different water-ethanol media: (a)-leather tanned by IGE in water; (b)-leather tanned by IGE in ethanol-50; (c)-leather tanned by IGE in ethanol-95.

Table IV
Physical properties of leather tanned by as prepared epoxides.

	IGE		IPE		IEE		Chrome
	TM-I ^a	TM-II ^b	TM-I	TM-II	TM-I	TM-II	TM-I
Bath liquid	TM-I ^a	TM-II ^b	TM-I	TM-II	TM-I	TM-II	TM-I
Tensile strength/(N/m ²)	16.62	20.77	13.52	16.73	12.95	14.65	14.47
Tear strength/(N/mm)	65.46	73.28	66.78	68.09	60.04	63.87	42.2
Elongation at break/%	73.71	54.63	70.45	53.21	69.33	65.42	82.23
Hand feeling ^c	8	10	7	6	4	5	10

^a TM-I: tanning in water medium.

^b TM-II: tanning in ethanol-50 medium.

^c The 0-10 point is used to judge the hand feeling of leather, 10 points is the best one.

Conclusion

Three epoxy tanning agents with multi-epoxy groups, ether bonds and hexatomic rings were synthesized. The water solubility of prepared epoxy tanning agents was greatly improved due to the introduction of ether bonds. These epoxides exhibited good tanning effect in water-ethanol medium, suggesting a safer tanning process. Compared with IPE and IEE, IGE showed more favorable tanning performance in terms of the Ts and fiber network dispersion of the tanned leather due to its high epoxy value and low molecular weight. Besides, the leather tanned by IGE showed competitive physical properties compared to conventional chrome tanned leather on account of its rigid hexatomic-ring structures and good crosslinking effect for collagen fiber in water-ethanol medium. As a result, IGE can be recognized as an effective tanning agent candidate in the leather manufacturing.

Acknowledgement

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