# STUDY ON THE APPLICATION OF A NEW MULTI-EPOXY REINFORCEMENT AGENT FOR SHEEP LEATHER

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**Abstract.** Leather is a kind of natural biomass composite material using animal skin as raw material. Its main structure is collagen fibre with three-dimensional network structure. Sheep leather is one of the important leathers except cattle and pig leather. However, it always exhibits weak mechanical strengths. Through the past decades, many methods have been tried to improve the strength of sheep leather, but the strength enhancement of sheep leather is extremely limited, although the fullness and softness may be improved. In this work, a new type of multi-epoxy reinforcement agent (IGE) and polyamine synergistic IGE (IGE-PA) were used to enhance the strength of sheep leather in tanning and fatliquoring process. Compared with chrome tanned leather, the tearing strength of tanned leather increased 56.8% when IGE was used as a reinforcement agent in tanning process. In addition, the tearing strength was significantly increased 97.9% when IGE-PA2000 was used. Furthermore, when IGE and IGE-PA were used in fatliquoring process, it has significant reinforcement effect for tetrakis hydroxymethyl phosphonium (THPS) salt tanned leather. Under the optimized conditions with IGE in fatliquoring process, the tear strength increased 50.2%, while when the IGE-PA400 was used, the tear strength increased 64.3% compared with blank experiment. In addition, the optimized conditions of IGE-PA2000 used in tanning process was obtained by orthogonal experiment: the dosage of PA-2000 and IGE were 0.5% and 10%, respectively, pH was 8, temperature was 35°C for penetration and 45°C for fixation, and tanning time was 10 h. The optimized conditions of IGE-PA400 in fatliquoring process was also obtained by orthogonal experiment: the dosage of IGE and PA-400 were 3% and 1%, respectively, meanwhile the treated temperature was 55°C, pH was 7.5 and time was 2h. Furthermore, TG and DTG results showed that the decomposition temperatures of IGE-PA enhanced leather were all higher than IGE. In addition, SEM results showed that IGE and IGE-PA enhanced leather obtained better opened-up fibre structure.

## 1 Introduction

Sheep leather has the properties of soft, large extension, smooth hand feeling, clear and beautiful leather grain. However, it has low strength owing to not only the large number of hair bunches, fat glands, sweat glands and erector hairs but also the finer collagen fibre bundle of reticular layer, loose braid, and parallel weave horn. Until now, the strength problem of sheep skin has not been effectively solved.[1]

The characterization methods for leather strength mainly include tensile strength and tear strength. Tensile strength refers to the number of loads per unit cross-sectional area when the leather is stretched and broken, represented by $N/mm^2$. Tear strength refers to the number of loads per unit thickness of the leather crack when the leather is stretched, expressed as N/mm. The strength of the leather is closely related to the direction of the fibre bundle. The more parallel fibre bundle, the greater the strength will be. And when the bent fibre bundle has greater bending degree, it has bigger total stress and is easier to be destroyed, and then it has lower strength.

To date, weakening the mechanical force in processing has been proved to be an effective approach to reinforce the network structure of sheep leather, such as choosing sharp cutting equipment to reduce the damage of mechanical force on collagen fibre network, large liquid ratio and run combined stop processing mode, etc. On the other hand, the application of retanning or fatliquoring agent was common method to improve the strength for sheep leather, such as using sulfated cattle shoe oil, acrylic polymer retanning agent or alkyl sulfonyl chloride. However, due to the failure of effective cross-linking with the leather collagen or the limitation of application conditions, the improvement for strength of sheep leather is limited. [2-8] In fact, in-stiu polymerization of acrylate monomers and PVA has been reported to reinforce the strength of split leather, [9,10] but due to the complex process, it is difficult to get industrialized application. In this work, the reinforcement effect of a new type of epoxide on sheep leather was investigated. At the same time, the investigation on the synergistic reinforcement effect of polyamine (PA) and IGE was conducted, and the reinforcement effect of IGE-PA were characterized using tensile strength, tear strength, TG and SEM.

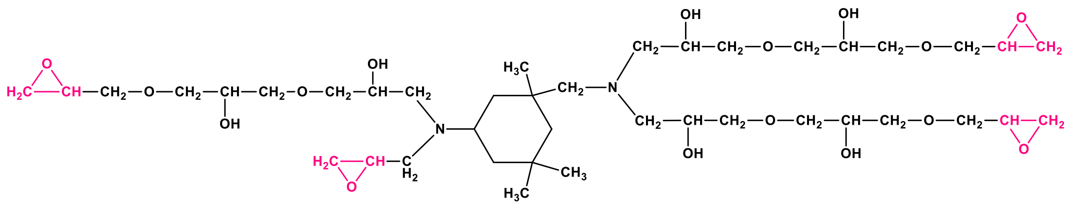
## 2 Experiment

### 2.1 Main materials

Melamine (MEL), ethanol, formic acid, sulfuric acid, sodium bicarbonate and sodium acetate were purchased from Sinopharm Chemical Reagent Co., Ltd. Polyether amine 400 (PA-400) and polyether amine 2000 (PA-2000) were purchased from Aladdin (Shanghai) Reagent Co. Ltd. Ctalix U Paste (U). Tetrahydroxymethyl quaternary phosphine salt (THPS), Granofin F90 (F90) were provided by Zhongpi Tianyuan Co. Ltd. Liming sheep skin was provided by Hebei Dongming Group Company.

### 2.2 Synthesis of epoxide reinforcement agents

The synthetic process was carried out in a 1000 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 4 mol of ECH was slowly dropwise added into the flask. After reaction at 35 ºC for 2 h, the mixture was heated to 60 ºC and then continuously reacted for 4 h to obtain the intermediate. Afterward, the polyalcohol compound GLY was reacted with intermediate catalysed by BFE at 60 ºC for 4 h to introduce ether bonds, following with the continuously reaction with ECH at 60 ºC for another 4 h. The resultant was then cooled down to 35 ºC, and 40 wt. % sodium hydroxide solution was employed to conduct the ring closing reaction (1.5 h). Finally, the resultant was neutralized by using both monopotassium phosphate and the acetic acid. After neutralization, the organic phase was separated and washed three times by distilled water to remove the sodium chloride and catalyst. Vacuum rotary evaporation at 45 ºC was conducted to remove the unreacted ECH in the organic phase, and the epoxide tanning agents were finally obtained, which was named as IGE.[11] The main proposed chemical structure of IGE was shown in Fig. 1.



[ IGE ]

**Fig. 1.** The proposed chemical structure of IGE.

### 2.3 Reinforcement experiments for IGE

Leather was treated with IGE and IGE-PA in the tanning process and fatting process respectively, and the physical strength were tested. Meanwhile, the strength was compared with F90, THPS and chrome tanned leather when IGE was used in tanning process, while it was contrasted with commercial product of reinforcement agent U in the fatting process. The reinforcement process using IGE in tanning and fatliquoring process are shown in Tab. 1 and Tab. 2.

**Table 1.** IGE reinforcement in tanning process.

| | Chemicals | Dosage (%) | Time (min) | Tem. (°C) | pH |
|---|---|---|---|---|---|
| Tanning process | The bated skin as the raw materials | | | | |
| | Ethanol-50* | 80 | 20 | 35 | 6.0～6.5 |
| | Polyamine** | 0～1.5 | 60 | 35 | |
| | IGE | 10% | 120 | 30 | |
| | $NaHCO_3$ | | 30 | 30 | 8.0 |
| | | | 600 | 45 | |
| washing | water | 200% | 10 ×2 | 25 | |

* Ethanol-50 represents 50 wt. % of ethanol in water; **polyamine refers to MEL, PA-400 and PA-2000.

**Table 2.** IGE reinforcement in fatliquoring process.

| | Chemicals | Dosage (%) | Tem. (°C) | Time（min） | pH |
|---|---|---|---|---|---|
| fatliquoring | the THPS tanned leather as the raw materials | | | | |
| | water | 150 | | | |
| | Mixture Fatliquoring agent | 14 | 55 | | |
| | IGE or U | x | | 60 | |
| | Formic acid | 1 | | 20×2 | 3.6 |
| washing | Water | 300 | 25 | 10×2 | |

**Table 3.** Orthogonal experiment for IGE reinforcement in tanning process.

| No. | A | B | C | D |
|---|---|---|---|---|
| | Dosage of PA-2000 (%) | Dosage of IGE (%) | Penetrating time (h) | Tanning time (h) |
| 1 | 0.5 | 6 | 0.5 | 10 |
| 2 | 0.5 | 8 | 1 | 12 |
| 3 | 0.5 | 10 | 2 | 14 |
| 4 | 1.0 | 6 | 1 | 14 |
| 5 | 1.0 | 8 | 2 | 10 |
| 6 | 1.0 | 10 | 0.5 | 12 |
| 7 | 1.5 | 6 | 2 | 12 |
| 8 | 1.5 | 8 | 0.5 | 14 |
| 9 | 1.5 | 10 | 1 | 10 |

Orthogonal tests of three levels and four factors were designed respectively, choosing the strength of leather as the evaluation index, the reinforcement effect of IGE at different conditions in tanning and fatting processes were determined. The orthogonal experiments are shown in Tab. 3 and Tab. 4. At the same time, the effect of IGE dosage on sheep skin was investigated by single factor experiment.

**Table 4.** Orthogonal experiment for IGE reinforcement in fatliquoring process.

| No. | A | B | C | D |
|---|---|---|---|---|
| | Dosage of PA-400 (%) | Tem. (℃) | pH | Time (h) |
| 1 | 0.5 | 50 | 5.5 | 1 |
| 2 | 0.5 | 55 | 6.5 | 2 |
| 3 | 0.5 | 60 | 7.5 | 3 |
| 4 | 1 | 50 | 6.5 | 3 |
| 5 | 1 | 55 | 7.5 | 1 |
| 6 | 1 | 60 | 5.5 | 2 |
| 7 | 1.5 | 50 | 7.5 | 2 |
| 8 | 1.5 | 55 | 5.5 | 3 |
| 9 | 1.5 | 60 | 6.5 | 1 |

## 2.4 Evaluation of reinforcement performances

### *2.4.1 Physical properties*

All the sheep leathers samples were fatliquored according to the conventional process. Then, the fatiliquored 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 demand,[12] and tensile strength and tear strength were measured.[13]

### *2.4.2 TGA determination*

The sample of 6～8 mg was put into a standard pan and the thermal decomposition behaviour of sample was measured using TGA (Netzsch 209 F1， Germany) in dynamic mode from 30 °C to 500 °C at a heating rate of 10 °C/min under $N_2$ atmosphere.

### *2.4.3 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.

# 3 Results and discussions

## 3.1 Evaluation of the reinforcement performance

### *3.1.1 Orthogonal experiment results for IGE reinforcement in tanning process*

Tab. 5 and Tab.6 are the orthogonal experiment results for IGE reinforcement and range analysis for IGE reinforcement in tanning process. As shown in Tab. 5 and Tab. 6, the optimum process combination is A1B2C3D2 when the tensile strength was performance indicator, while the optimum process combination is A1B2C3D1 when the tear strength was performance indicator. From the range analysis, it can be concluded that the influence order of various factors on tensile strength was PA-2000 dosage, tanning time, osmotic time, IGE dosage in sequence and the influence order of various factors on tearing strength was penetrating time, IGE dosage, PA-2000 dosage, tanning time in turn.

**Table 5.** Orthogonal experiment results for IGE reinforcement in tanning process.

| No. | Dosage of PA-2000（%） | Dosage of IGE（%） | Penetrating time（h） | Tanning time（h） | Tensile strength ($N/mm^2$) | Tear strength (N/mm) |
|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 11.95 | 79.36 |
| 2 | 1 | 2 | 2 | 2 | 13.21 | 74.76 |
| 3 | 1 | 3 | 3 | 3 | 11.71 | 76.47 |
| 4 | 2 | 1 | 2 | 3 | 10.75 | 65.06 |
| 5 | 2 | 2 | 3 | 1 | 13.44 | 84.92 |
| 6 | 2 | 3 | 1 | 2 | 11.95 | 56.81 |
| 7 | 3 | 1 | 3 | 2 | 11.9 | 80.82 |
| 8 | 3 | 2 | 1 | 3 | 8.62 | 73.52 |
| 9 | 3 | 3 | 2 | 1 | 9.01 | 53.9 |

**Table 6.** Range analysis for IGE reinforcement in tanning process.

| | Tensile strength | | | | Tear strength | | | |
|---|---|---|---|---|---|---|---|---|
| Mean value 1 | 12.297 | 11.533 | 10.840 | 11.467 | 76.863 | 75.080 | 69.897 | 72.727 |
| Mean value 2 | 12.047 | 11.757 | 10.990 | 12.353 | 68.930 | 77.733 | 64.573 | 70.797 |
| Mean value 3 | 9.843 | 10.897 | 12.457 | 10.367 | 63.413 | 62.393 | 80.737 | 71.683 |
| Range | 2.454 | 0.860 | 1.517 | 1.986 | 7.933 | 15.340 | 16.164 | 1.930 |

**Table 7.** Results of optimum conditions.

| No. | Dosage of PA-2000（%） | Dosage of IGE（%） | Penetrating time（h） | Tanning time（h） | Tensile strength ($N/mm^2$) | Tear strength (N/mm) |
|---|---|---|---|---|---|---|
| 10 | 1 | 2 | 3 | 2 | 13.95 | 84.36 |
| 11 | 1 | 2 | 3 | 1 | 13.21 | 89.76 |

Tab. 7 is the results of optimum conditions for the orthogonal experiments. As shown in Tab. 7, in the optimal conditions, the better tensile strength and tear strength were obtained. Therefore, for the optimum condition on tensile strength for reinforcement in tanning process, the dosage of PA-2000 and IGE was 0.5% and 10%, respectively, the penetrating time was 2h, tanning time was 10h. In case of the optimum condition on tear strength, the process combination was same except that the tanning time was 8h.

***3.1.2 Orthogonal experiment results for IGE reinforcement in fatliquoring process***

Tab. 8 is the orthogonal experiment results and Tab. 9 is the range analysis for IGE reinforcement in tanning process. It can be found that the optimum process combination is A2B2C3D2 when the tensile strength was set as indicator, while the optimum process combination is A2B3C2D1 when the tear strength was performance indicator. From the range analysis, it can be concluded that the influence order of various factors on tensile strength is the dosage of PA-400, dosage of IGE, penetrating time, tanning time in sequence and the influence order of various factors on tearing strength is the tanning time, penetrating time, dosage of IGE and dosage of PA-400 in turn.

Tab. 10 is the results of optimum conditions for the orthogonal experiments. In the optimal conditions, better tensile strength and tear strength were obtained. Therefore, for the optimum condition on tensile strength for reinforcement in tanning process, the dosage of PA-400 was 1.0%, temperature was 55℃, pH was 7.5 and time was 2h. In case of the optimum condition on tear strength, the dosage of PA-400 was 1.0%, temperature was 60℃, pH was 6.5 and time was 1h.

**Table 8.** Orthogonal experiment results for IGE reinforcement in fatliquoring process.

| NO. | Dosage of PA-400 (%) | Tem.(°C) | pH | Time (h) | Tensile strength (N/mm²) | Tear strength (N/mm) |
|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 11.4 | 65.32 |
| 2 | 1 | 2 | 2 | 2 | 15.39 | 56.29 |
| 3 | 1 | 3 | 3 | 3 | 15.28 | 59.78 |
| 4 | 2 | 1 | 2 | 3 | 13.02 | 68.92 |
| 5 | 2 | 2 | 3 | 1 | 16.43 | 60.78 |
| 6 | 2 | 3 | 1 | 2 | 13.77 | 62.32 |
| 7 | 3 | 1 | 3 | 2 | 10.49 | 46.89 |
| 8 | 3 | 2 | 1 | 3 | 11.51 | 64.83 |
| 9 | 3 | 3 | 2 | 1 | 9.69 | 71.65 |

**Table 9.** Range analysis for IGE reinforcement in fatliquoring process.

| | Tensile strength | | | | Tear strength | | | |
|---|---|---|---|---|---|---|---|---|
| Mean value 1 | 14.023 | 11.637 | 12.227 | 12.507 | 60.463 | 60.377 | 64.157 | 65.917 |
| Mean value 2 | 14.407 | 14.443 | 12.700 | 13.217 | 64.007 | 60.633 | 66.620 | 56.168 |
| Mean value 3 | 10.563 | 12.913 | 14.067 | 13.270 | 61.123 | 64.583 | 55.817 | 64.510 |
| Range | 3.844 | 2.806 | 1.840 | 0.763 | 3.544 | 4.206 | 9.803 | 10.750 |

**Table 10.** Experimental results of optimal combination in fatliquoring process.

| No. | Dosage of PA-400（%） | Dosage of IGE（%） | Penetrating time（h） | Tanning time（h） | Tensile strength (N/mm²) | Tear strength (N/mm) |
|---|---|---|---|---|---|---|
| 10 | 2 | 2 | 3 | 2 | 17.57 | 69.66 |
| 11 | 2 | 3 | 2 | 1 | 16.31 | 71.76 |

#### *3.1.3 Effect of Dosage of IGE on physical property in fatliquoring process*

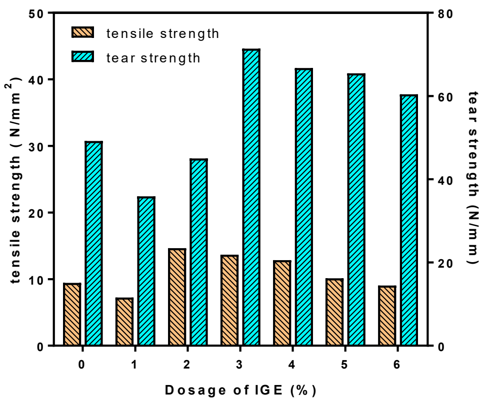



**Fig. 2.** Effect of IGE dosage on physical property in fatliquoring process.

As shown in Fig. 2, IGE exhibited obvious reinforcement effect on sheep skin in the fatliquoring process. The tensile strength and tear strength were enhanced with the increase of dosage of IGE, but they did not further increase when the dosage of IGE exceeded 2%, which may be attributed to the increasing of single-point combination between the epoxy group and collagen fibre when excess amount of IGE was used. [14]

### *3.1.4 Physical properties of different chemicals in tanning and fatliquoring process*

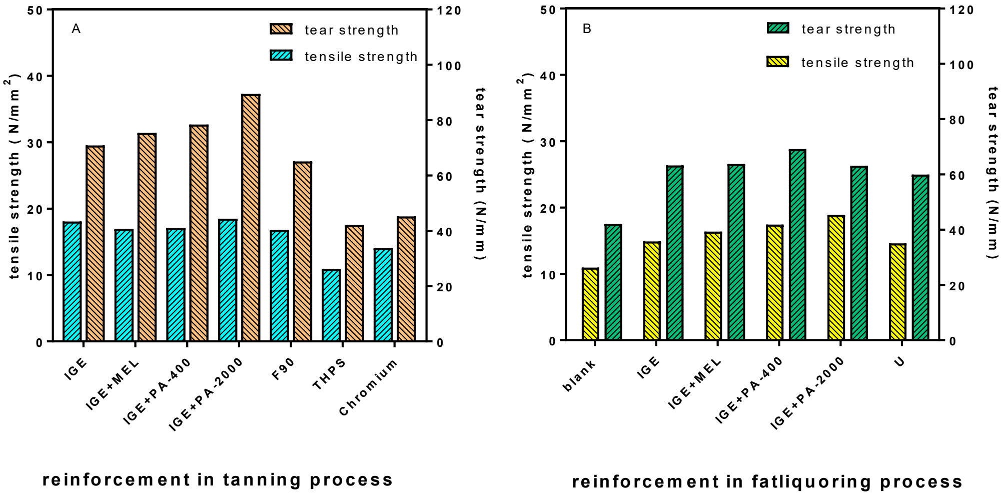



**Fig. 3.** Physical properties of sheep leather treated by different chemicals in tanning and fatliquoring process.

Fig. 3-A and Fig. 3-B illustrate the physical properties of sheep leather treated by different chemicals in tanning process and fatting process. Fig. 3-A shows that IGE and PA-2000 had the most obvious improvement on the tensile strength and tearing strength of sheep leather. Compared with chrome tanned leather, the tearing strength of tanned leather increased 56.8% when IGE was used as a reinforcement agent in tanning process. In addition, the tearing strength was significantly increased 97.9% when IGE-PA2000 was used. It can be seen from Fig. 3-B that the enhancement effect of IGE was similar to that of controlled chemical U, but the tensile strength and tearing strength of IGE treated sheep leather were significantly improved when polyamine was applicated. When IGE and IGE-PA were used in fatliquoring process, it was found that the tear strength of leather increased 50.2%, while when the IGE-PA400 was used, the tear strength increased 64.3% compared with blank experiment. It could be suggested that PA-2000 or PA-400 first penetrated into the collagen fibre, and then the cross-linking should be mainly conducted among the epoxy groups of IGE, and amino groups of collagens and PA-2000 or PA-400, resulting the formation of interpenetrating network structure "rigid module" inside the collagen fibres (see Fig. 4).[15,16] However, as compared with reinforcement in fatliquoring process, the improvement was higher for IGE-PA in tanning process, due to more amine group of collagen fibre exposed for IGE. But the interpenetrating network structure was difficult to form in fatliquoring process owing to more tanning and retanning agent have combined with the amine group of collagen fibre. Thus, IGE-PA exhibited more satisfactory reinforcement properties and was a competitive reinforcement candidate for sheep leather. It could be concluded the "rigid module" can increase the rigidity of the collagen fibres and improve the physical and mechanical strength of the leather.

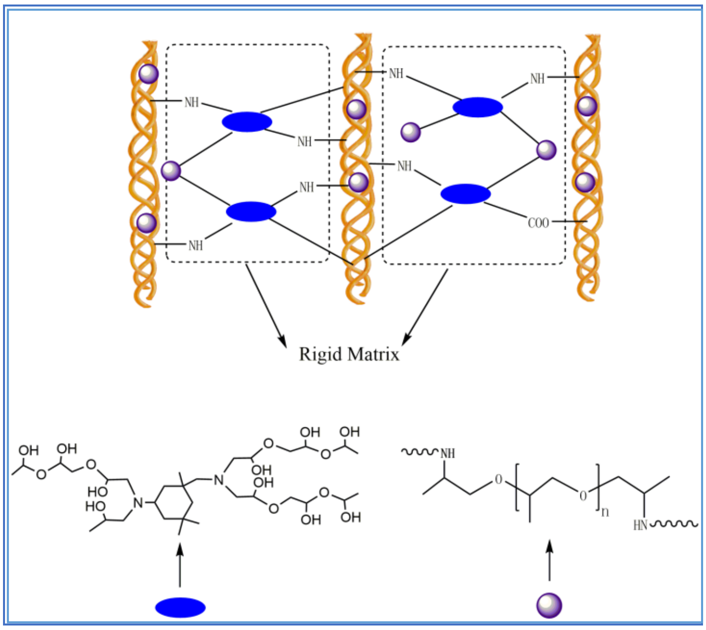



**Fig. 4.** Diagram of "rigid matrix" between IGE, PA and collagen fibre.

### 3.2 TGA analysis

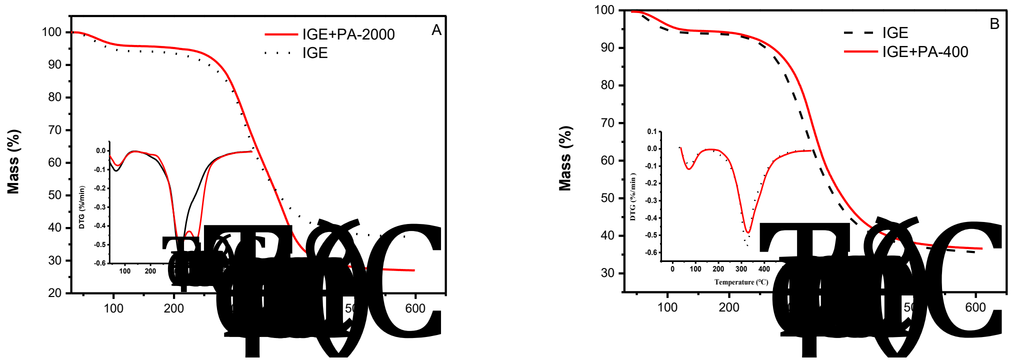



**Fig. 5.** TG and DTG thermograms of leather reinforced in tanning process (A) and fatliquoring process (B).

Fig. 5 is TG and DTG diagrams of leather reinforced in tanning and fatliquoring process. The decomposition temperature of samples was the second weightless peak of DTG. As shown in Fig. 5A, the decomposition temperature IGE treated leather was 315.2°C, while PA-2000+IGE treated leather appeared two decomposition peak temperature, the highest was 377.1°C. In combination with Fig. 3-A, the strength of IGE+ PA-2000 strengthened leather was the highest, indicating that IGE and polyether amine 2000 formed cross-linking among the collagen fibres and increased the decomposition temperature of the leather. It can be seen from Fig. 5B that the addition of PA-400 in the fatliquoring process can increase the thermal decomposition temperature of leather to a certain extent, but it was not as higher as that in the tanning process. It can be inferred that the covalent crosslinks between IGE, PA2000 and collagen fibres had formed to improve the thermal stability for sheep leather.

### 3.3 SEM analysis

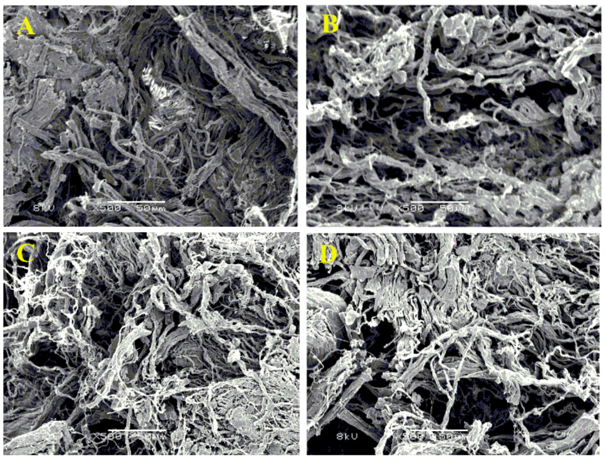



**Fig. 6** SEM of leather (A: reinforced by IGE in tanning process, B: reinforced by IGE+PA-2000 in tanning process, C: reinforced by IGE in fatliqouring process, D: reinforced by IGE+PA-400 in fatliqouring process)

It can be seen from Fig. 6 that the dispersion of leather fibres with polyether amine participating in synergistic tanning and fatliquoring is significantly better than that of leather reinforced by IGE tanning alone. Generally, better fibre dispersion is in favour of the penetration of chemical materials into the collagen fibre network and react with the active groups on the collagen fibre, thus leading to increasing the mechanical strength of leather. As a result, IGE-PA exhibited more satisfactory fibre dispersion and therefore its outstanding reinforcement performance can be expected.

## 4 Conclusions

A new type of multi-epoxy tanning agent (IGE) was prepared and it proved that IGE had reinforcement effect on the strengths of sheep leather especially on tear strength. IGE and polyether amine can be used in tanning process with ethanol medium, and IGE-PA could show synergistic effect, resulting in a significant enhancement for sheep leather. IGE and IGE-PA can be also used in fatliquoring process to enhance the strength of sheep leather in water medium owing to the emulsification effect of fatliquoring agent. As a result, IGE-PA could be recognized as an effective reinforcement agent candidate for sheep leather.

## Acknowledgement

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