

# Insight into Understanding Incorporation of Glycidoxypropyltrimethoxysilane for Improving Hydrothermal Stability and Porous Structure of Silicic Acid Tanned Leather

by

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## Abstract

Tanning with silicic acid, a kind of silicon-containing materials, is considered as a more environmentally benign process; however, the obtained leather would become stiff and brittle during storage in spite of possessing acceptable shrinkage temperature (Ts). Herein, we incorporated organosilicon material attaching silicon atoms with T linkage structure (e.g. glycidoxypropyltrimethoxysilane, GPTMS) in the leather-making process to investigate hydrothermal stability and porous structure, in particular their variation along with different storage time, through Ts determination, DSC analysis, SEM observation and SEM-EDS test. The results confirmed that the introduction of GPTMS stabilized properties of the resultant leather during accelerated ageing process, which may be ascribed to that GPTMS could prevent silicon hydroxyl groups existing in collagen fiber matrix from further condensation. Besides, the tanning mechanism of chrome-free tanning agent based on silicon materials such as silicic acid and GPTMS was investigated preliminarily by means of FT-IR and XPS analysis, indicating hydrogen bonds between silicon hydroxyl groups and amino groups in collagen molecules, and the covalent bonding formed by epoxy group of GPTMS and carboxyl groups of collagen fibers are beneficial to improvement of the properties of silicon-based materials tanned leather. These findings provide an effective and promising strategy to control condensation of silicon hydroxyl groups, and are of great significance to the development of a chrome-free tanning technology based on silicon materials.

## Introduction

Basic chromium (III) sulfate is the most significant and widely-used tanning agent in leather-making industry, due to chrome-tanned leather with superior comprehensive properties such as high hydrothermal stability, excellent mechanical strength, pleasing sensory performance, and versatile applicability. However, chrome tanning method suffers from shortcomings including lack of chromium mineral resource, huge amounts of chrome-containing leather wastes generated, and potential toxicity concerns relating to chromium (VI), resulting in investigation of more environment-friendly tanning agents.<sup>1-3</sup> Although large numbers of tanning agents, e.g. other metal salts, vegetable tannins, aldehyde derivatives and syntans, have been explored,<sup>4-7</sup> the corresponding leather suffers from lower shrinkage temperature (Ts), poorer mechanical property, or inferior storage stability and so on. Therefore, exploration of environment benign chrome-free tanning technology for manufacturing leather with properties matching with chrome-tanned leather is still a great challenge.

The element silicon presents in abundance as a variety of silicate in the earth's crust. Scientists have long known that silicic acid derived from acidification of silicate can precipitate gelatin solution, implying its potential tanning effect. Subsequently, it was discovered that leather tanned with silicic acid alone possessed acceptable shrinkage temperature in spite of being inferior to that of chrome-tanned leather, while it would become stiff and brittle after storage for a period of time,<sup>8</sup> which should be addressed. The interpretation of this phenomenon was supposed that the gel generated from silicic acid deposited between collagen fibers in leather matrix would be further subjected to dehydration and condensation, and then formed a rigid silica network. However, the real reason why this issue

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proceeds should be definitely revealed and how to control it should be investigated intensively. They are highly indispensable to achieve successfully a chrome-free tanning technology based on silicon chemistry.

With development of organosilicon chemistry and progress of organic-inorganic hybrid technology, study on silicon-based tanning technology has drawn more increasing attention in recent years. For example, nano-silica derived from tetraethyl orthosilicate improved physical-mechanical properties and shrinkage temperature of the obtained leather, which was close to chrome tanning leather.<sup>9</sup> Zhang et al. researched the effect of sodium silicate on collagen fiber structure, and found that sodium silicate formed aggregates of silica particles and coated on the surface of collagen fibrils by the electrostatic interactions, however the treated leather showed almost no improved stabilization.<sup>1</sup> In addition, the variation of porous structure and shrinkage temperature of leather treated with glycidoxypropyltrimethoxysilane (GPTMS) and tetraethoxysilane was explored previously in our group, and we discovered the fact that incorporation of GPTMS under alkaline condition effectively enhanced the porosity and hydrothermal stability of collagen matrix.<sup>10</sup> Nevertheless, there is no report on an effective strategy to prevent leather from becoming brittle during storage, and the tanning mechanism is not entirely clear. They are the major hindrance to progress of chrome-free tanning technology based mainly on silicic acid chemistry.

Taking into consideration the fact that silicon-containing materials exhibit properties similar to either inorganic or organic materials depending on their different linkage structure of silicon atoms, such as Q, T and D species. Herein, Q ( $\text{SiO}_2$ ) represents four-functional silicon-oxygen linkage, T ( $\text{RSiO}_{1.5}$ ) stands for tri-functional silicon-oxygen linkage, and D ( $\text{R}_2\text{SiO}$ ) is double-functional silicon-oxygen linkage. Thus, it is expected that the condensation degree of silicon hydroxyl groups in silicic acid molecules and the corresponding properties can be controlled and regulated by incorporation of organosilicon attaching T or even D linkage structure silicon atoms. The aim of this present study was to explore a method of controlling condensation of silicon hydroxyl groups and the tanning mechanism of silicic acid, which is great significance for the development of tanning technology based on silicon chemistry. Firstly, shrinkage temperature ( $T_s$ ) was used to identify better conditions of silicic acid tanning process. Then the influence of different dosage of glycidoxypropyltrimethoxysilane (GPTMS) on properties such as hydrothermal stability and porous structure of obtained leather were investigated by  $T_s$  determination, differential scanning calorimeter (DSC) and scanning electron microscopy and couple energy dispersive X-ray spectroscopy detector (SEM-EDS). In particular, variation of stability and porous structure of leather along with different storage time was investigated. Furthermore, the tanning

mechanism of silicic acid was explored by Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS) and so on. The findings of this work would be greatly beneficial to develop an improved and practical chrome-free tanning technology based on silicon chemistry.

## Experimental

### Materials

Pickled goat skin prepared by conventional process was chosen for leather tanning, of which thickness is  $\sim 1.3\text{mm}$ , area is at about  $\sim 0.54\text{m}^2$ , wet weight of a piece of skin is  $\sim 1.65\text{kg}$ , and the pH is  $\sim 2.2$ . Sodium silicate nonahydrate ( $\text{Na}_2\text{O}:\text{SiO}_2=1.03\pm 0.03$ ), sulphuric acid, sodium chloride and sodium hydrogen carbonate were purchased from Kelong Reagent Co. Ltd (Chengdu, China). All of the reagents mentioned above are analytical-reagent grade. The GPTMS was provided by Jingzhou Jiangnan Fine Chemical Company (Jingzhou, China).

### Preparation of the Silicic Acid Solution

The silicic acid solution was prepared from sulfuric acid and sodium silicate solution. Briefly, a definite amount of concentrated sulfuric acid was first diluted with water by the weight ratio of 1:1. Then the sodium silicate was dissolved into the water to constitute a solution of 10% concentration. After that, the sodium silicate solution was slowly added into diluted sulfuric acid solution according to stoichiometric ratio of 1: 1.1 under stirring condition. Finally, the mixed solution was placed carefully, and the temperature dropped to room temperature. The silicic acid solution (3% w/v, pH 2.0-2.5), of which the average particle size was  $366.19\pm 17.08\text{nm}$  determined by using a Nano-ZS90 nanoparticle size and zeta potential measurement instrument (Malvern, UK), thus obtained would be employed in tanning experiments.

### Tanning Process and Accelerated Ageing Test of Leather Samples Selection of Tanning Conditions

The tanning experiments were carried out utilizing pickled goat skins (S). At first, the suitable dosage of silicic acid was confirmed at the final tanning pH value 4 and tanning time 5 h. Secondly, the tanning procedure was conducted at the suitable dosage of silicic acid selected above and tanning time 5 h, while the final tanning pH was adjusted to 4 and 5, respectively to optimize pH value. Finally, the tanning time was adjusted to 1, 3, 5, 7, 9 h, respectively at the dosage of silicic acid and the pH value selected above. The better condition for silicic acid tanning process was thus achieved based on  $T_s$  of the obtained leather.

### Addition of GPTMS and Accelerated Aging Test

Considering the fact that the difference in different regions of a goat skin may influence negatively the measurement results, the sampling method for trial was selected according to Figure 1.<sup>10</sup> In

this article each part labeled number 1 is corresponding to leather tanned by silicic acid alone (SA), and number 2, 3 and 4 is that sample tanned by combination of silicic acid and GPTMS, i.e. molar ratio of silicic acid to GPTMS is 15:1 (SAG-1), 10:1 (SAG-2) and 5:1 (SAG-3), respectively. The chemicals used in the experiment were based on the weight of pickled skin. The tanning process of this article is shown in Table I.

To explore the variation of stability and porous structure of the obtained leather samples under storage process, an accelerated ageing test was performed. Briefly, representative samples SA and SAG-2 were put in a bake oven at 40°C and the change of pore structure and thermal stability of the samples were measured after 0, 1, 3, 5d, respectively.

#### Test of the Shrinkage Temperature

Shrinkage temperature of the sample was tested on a MSW-YD4 apparatus (China) under the bath of water according to ASTM method D 6076-97. Each sample was cut into rectangular (10 mm×60 mm) by the model. Then the specimen was heated in water at a rate of 2°C/min. Every sample was repeated at least five times.<sup>11</sup>

#### Test of the Denaturation Temperature

Denaturation temperature of the representative dried samples was characterized by DSC-200PC (Netzsch, Germany) under nitrogen protection, as a sign of thermal stability of the tanned leather. Briefly, the samples were cut into appropriate piece and scanned from 20°C to 140°C at the rate of 5°C/min.<sup>12</sup>

#### Measurement of the Total Porosity

Porosity of the sample was measured by the liquid displacement method.<sup>13</sup> In brief, the pre-weighted sample ( $W_s$ ) was immersed in a graduated bottle filled with anhydrous ethanol at 25°C, and the whole weight was recorded as  $W_1$ . After 24 h, the liquid above the maximum degree scale was imbibed, and the weight of the remains was recorded as  $W_2$ . Then the total bottle was weighted as

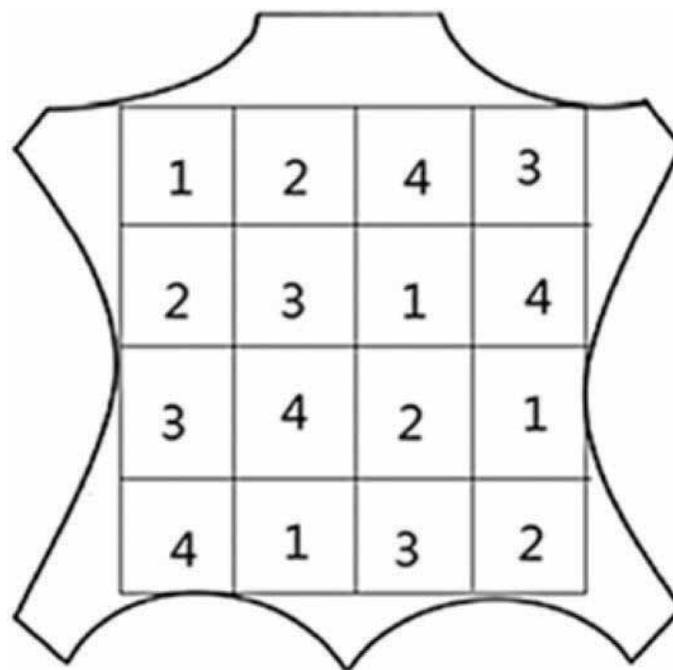


Figure 1. Sampling method <sup>10</sup>

**Table I**  
Tanning process of pickled goat skins.

Process	Material	Dosage (%)	T (°C)	Time (h)	pH	Remark
Tanning	Pickled skin	100	25			
	Water	100				
	NaCl	8		0.5		
	GPTMS	x		1		
	Silicic acid	10 (15, 20)		1 (3, 5, 7, 9)	2.0-2.5	
Adjust pH	NaHCO <sub>3</sub>	x		2	4 (5)	
Overnight						
	Water	100	45	1.5		Increase the liquid ratio and heating-up
Drying						Waiting detection

$W_3$  after the sample was separated from the bottle. The porosity was calculated according to formula (1). Five measurements were conducted and the average data were calculated.

$$\text{porosity (\%)} = \frac{W_2 - W_3 - W_s}{W_1 - W_3} \times 100 \quad (1)$$

#### SEM Observation and SEM-EDS Analysis

Leather samples were freeze-dried at  $-60^\circ\text{C}$  for 24 h in the freeze dryer (SCIENTZ-10N, China), and cut into slices with uniform thickness. Then the grain surface and fracture section of these specimens were observed by operating JSM-5900 scanning electron microscopy (SEM) (JEOL, Japan) at an accelerating voltage of 15 KV with different magnification level. After that, average pore size and its distribution of the leather were calculated with the help of Nano-measure software.<sup>11, 14</sup> In addition, the distribution of silicon element in leather was recorded by coupling energy dispersive X-ray spectroscopy detector (EDS).

#### FT-IR Measurement

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet is10 spectrometer (Thermo Fisher Scientific, USA). In brief, the leather sample was ground into powder, and mixed evenly with potassium iodide powder to be pressed into a cake-like structure in the mold. Finally, the sample was scanned in the range of  $500\text{--}4000\text{ cm}^{-1}$  with a resolution of  $4\text{ cm}^{-1}$ .<sup>15</sup>

#### XPS Measurement

X-ray photoelectron spectroscopy (XPS) measurement was performed on an Escalab 220i-XL (Kratos, Japan) spectrometer using a monochromated Al  $K\alpha$  ( $h\nu = 1100\text{ eV}$ ) X-ray source of 250W at 15 kV. The C, O, N and Si atoms semi-quantitative elemental percentages were obtained by calculating the relative XPS peaks.<sup>16-17</sup>

## Results and Discussion

#### Optimization of Parameters in Silicic Acid Tanning Process

It is known fact that, tanning conditions such as dosage of tanning agent, pH value, and tanning time are of great significant parameters for determining properties of leather. Although the tanning effect can be usually characterized by three main aspects including shrinkage temperature ( $T_s$ ), porous structure parameters, and enzymatic resistance of leather,  $T_s$  was utilized herein as one primary indicator to optimize the tanning conditions in silicic acid tanning process, which is the foundation for further studying enhanced silicon tanning technology.

Firstly, with respect to the different dosage of tanning agent, it can be seen from Table II that  $T_s$  value of the tanned leather increased greatly from that of the pickled skin. When the dosage

**Table II**  
 **$T_s$  of silicic acid tanned leather obtained from different condition.**

	Dosage (%)	pH value	Time (h)	$T_s$ ( $^\circ\text{C}$ )
S				$43.18 \pm 0.78$
I	10	4	5	$74.13 \pm 0.52$
	15	4	5	$83.69 \pm 0.70$
	20	4	5	$85.00 \pm 0.33$
II	15	4	5	$83.85 \pm 0.25$
	15	5	5	$78.83 \pm 1.21$
III	15	4	1	$76.70 \pm 0.36$
	15	4	3	$79.20 \pm 0.25$
	15	4	5	$84.05 \pm 0.40$
	15	4	7	$84.25 \pm 0.28$
	15	4	9	$84.95 \pm 0.35$

of silicic acid increased from 10% to 15% w/w, the  $T_s$  increased about 10°C; while the dosage increased further from 15% to 20% w/w,  $T_s$  value of leather increased slightly, and there is no significant difference in grain fineness and handle. This may be due to the fact that collagen fibers have reached a maximum binding level to silicic acid. Therefore, 15% w/w silicic acid was chosen in the subsequent tanning tests.

Secondly, pH value is another important parameter in the tanning process. In fact, it is one of the decisive factors influencing gelation of silicate. Si-OH groups of silicic acid molecule derived from silicate will make into polycondensation in the presence of mineral acid or base. Under basic condition, fewer, larger, and denser particles would be achieved as a result of easier condensation and aggregation, leading to smaller specific surface areas and larger pores, which are unfavorable to the condensation of clusters with each other. On the other hand, when the condensation reaction of Si-OH groups was catalyzed in acidic condition (pH<5), a chain-like network could be obtained, that retained more active silicon hydroxyl groups, which was considered to be beneficial to tanning action.<sup>18-20</sup> Thus, pH value 4 and 5 was selected in tanning process, respectively, and make a comparison. From Table II, we can conclude that hydrothermal stability of the leather tanned at pH 4 is greater than at pH 5. This result is likely to be ascribed to the rate of diffusion or condensation of silicic acid in relation to the kinetics of aggregation. At higher pH value, the rate of diffusion decreased, while the rate of condensation increased.<sup>21-22</sup> The shrinkage temperature of leather was therefore lower at pH 5 than that of at pH 4. This may be the reason that condensation of more silicic acid molecules at pH 5 occurred on the surface of leather matrix, leading to a nonuniform distribution of the silicon atom in the cross section of leather.

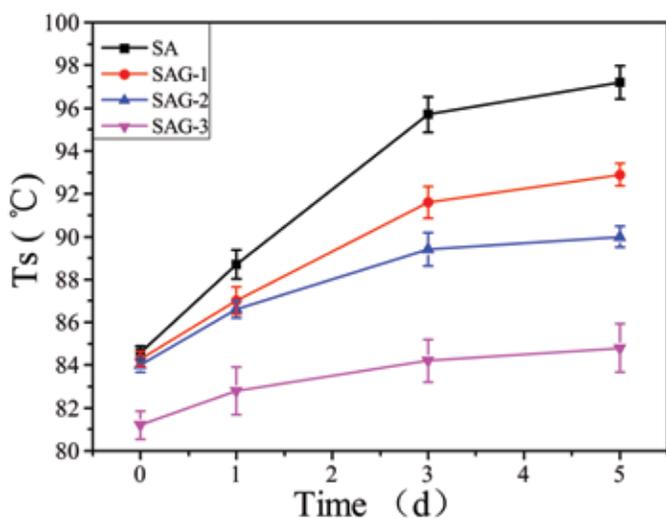


Figure 2. Shrinkage temperature of SA, SAG-1, SAG-2 and SAG-3 as a function of accelerated ageing time.

Finally, the  $T_s$  values as a function of tanning time (Table II) demonstrated that the hydrothermal stability of leather improved obviously with the prolongation of tanning time from 1 to 5 hours; while the  $T_s$  increased slightly when the tanning time was further extended, from 5 to 7 and 9 hours. This is likely to be the active groups of collagen fiber matrix reacted completely for five hours after start of the tanning process. As a consequence, the optimized parameters in tanning process using silicic acid alone are 15% dosage of silicic acid, pH value 4, and tanning time 5 h, which was employed as basic conditions to further investigate variation of stability and porous structure of leather manufactured by a chrome-free tanning technology based on silicon chemistry.

#### Effect of GPTMS on Stability and Porous Structure of Leather

To address the issue that silicic acid tanned leather become rigid and brittle under storage, GPTMS was introduced and expected

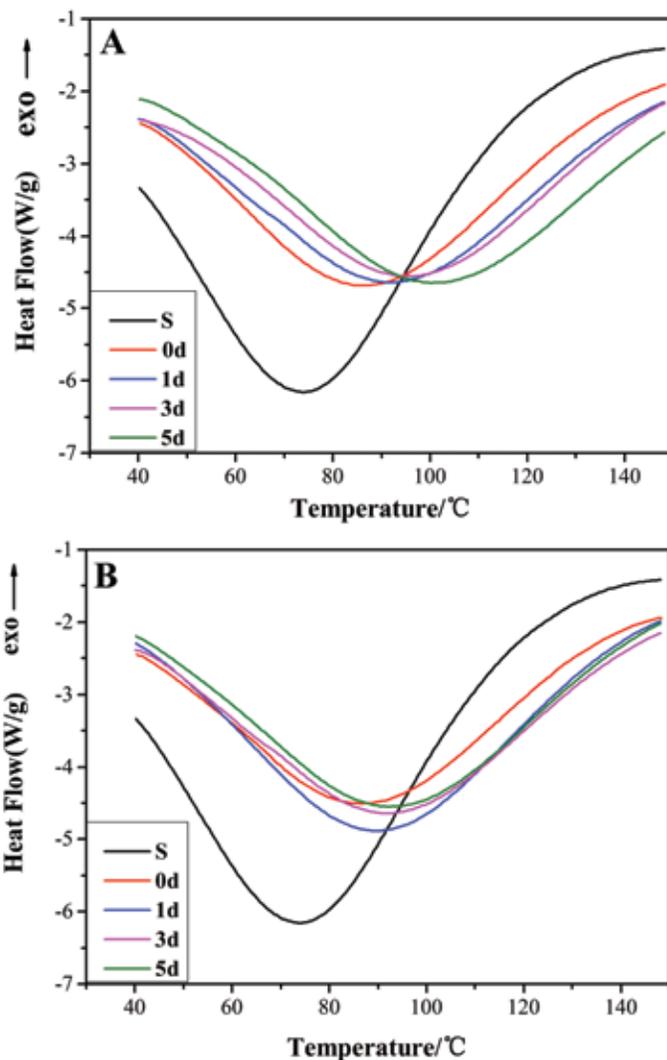


Figure 3. DSC curves of SA (A) and SAG-2 (B) during accelerated ageing process.

to make co-condensation with silicic acid via Tri-type Si-OH groups derived from hydrolysis of its three Si-OR groups, and to impede the possible tendency of lasting condensation of Q-type Si-OH groups from silicic acid molecules. To insight into understanding the reason, different amount of GPTMS was employed in combination with silicic acid in tanning process, and the obtained leather was characterized by Ts measurement, DSC analysis, SEM observation and SEM-EDS analysis.

#### Effect of GPTMS and Accelerated Ageing on Stability of Leather

Shrinkage temperature (Ts) of silicic acid tanned leather (SA) and silicic acid-GPTMS combination tanned leather (SAG-1, SAG-2 and SAG-3), as well as the corresponding change trend with accelerated ageing time was recorded at Figure 2. Ts value of leather decreased to different degrees when a conjunction of GPTMS with silicic acid in the tanning process. It can be seen that Ts of SAG-1 and SAG-2 decreased slightly, respectively, while that of SAG-3 decreased

evidently. On the other hand, all Ts of samples increased with the prolongation of accelerated ageing time, but there were some different degrees of them. Clearly, the Ts of SA increased significantly, while the Ts of SAG-1, SAG-2 and SAG-3 increased to a lesser extent. The results suggested that the introduction of GPTMS can reduce the Ts change tendency of leather, and the more GPTMS was added, the smaller the Ts change degree of leather was. This may be related to the co-condensation reaction of silicon hydroxyl groups of silicic acid and GPTMS molecules. At first, methoxyl groups in GPTMS were hydrolyzed to form silicon hydroxyl groups. Then Si-OH groups of GPTMS took dehydration and co-condensation reaction with Si-OH groups in silicic acid molecule. Meanwhile, the epoxy group in GPTMS molecule reacted with carboxyl groups in collagen molecules under acidic condition. Therefore, continued condensation of intramolecular Si-OH groups of silicic acid molecules was partly suppressed, thus leading to a slight variation of hydrothermal stability of leather.<sup>23-26</sup>

**Table III**  
Average pore diameter and total porosity of leather

Samples	S	SA	SAG-1	SAG-2	SAG-3
Average pore diameter ( $\mu\text{m}$ )	65.72 $\pm$ 1.02	13.45 $\pm$ 2.09	18.46 $\pm$ 1.29	31.44 $\pm$ 2.03	54.72 $\pm$ 1.58
Total porosity (%)	40.56 $\pm$ 1.4	52.69 $\pm$ 1.95	51.31 $\pm$ 1.84	51.40 $\pm$ 1.48	44.59 $\pm$ 1.37

**Table IV**  
Relative content of elements in leather (%).

Element types		O	C	N	Si
Surface	S	50.64 $\pm$ 0.21	29.67 $\pm$ 0.17	19.68 $\pm$ 0.13	0
	SA	52.46 $\pm$ 0.29	21.80 $\pm$ 0.33	17.16 $\pm$ 0.46	8.57 $\pm$ 0.22
	SAG-1	51.94 $\pm$ 0.18	22.71 $\pm$ 0.25	17.35 $\pm$ 0.11	7.99 $\pm$ 0.56
	SAG-2	51.40 $\pm$ 0.35	23.46 $\pm$ 0.32	17.54 $\pm$ 0.35	7.59 $\pm$ 0.17
	SAG-3	50.92 $\pm$ 0.28	24.47 $\pm$ 0.14	17.70 $\pm$ 0.21	6.90 $\pm$ 0.35
Cross section	S	42.14 $\pm$ 0.32	30.40 $\pm$ 0.22	27.45 $\pm$ 0.15	0
	SA	43.16 $\pm$ 0.19	29.12 $\pm$ 0.30	22.30 $\pm$ 0.22	5.41 $\pm$ 0.30
	SAG-1	41.97 $\pm$ 0.25	30.00 $\pm$ 0.45	23.00 $\pm$ 0.13	5.02 $\pm$ 0.21
	SAG-2	40.82 $\pm$ 0.11	30.65 $\pm$ 0.23	23.60 $\pm$ 0.23	4.92 $\pm$ 0.56
	SAG-3	39.45 $\pm$ 0.27	30.76 $\pm$ 0.19	25.84 $\pm$ 0.54	3.94 $\pm$ 0.27

To further study the effect of addition of GPTMS on thermal stability of leather, and its change with accelerated ageing time, samples SA and SAG-2 selected as representatives were measured by DSC (Figure 3). Thermal denaturation temperature of SA increased

13.9°C, while the thermal denaturation temperature of the SAG-2 just increased 4.5°C. The results further verified combination of GPTMS and silicic acid in tanning process stabilized appropriately properties of leather during the aging process.

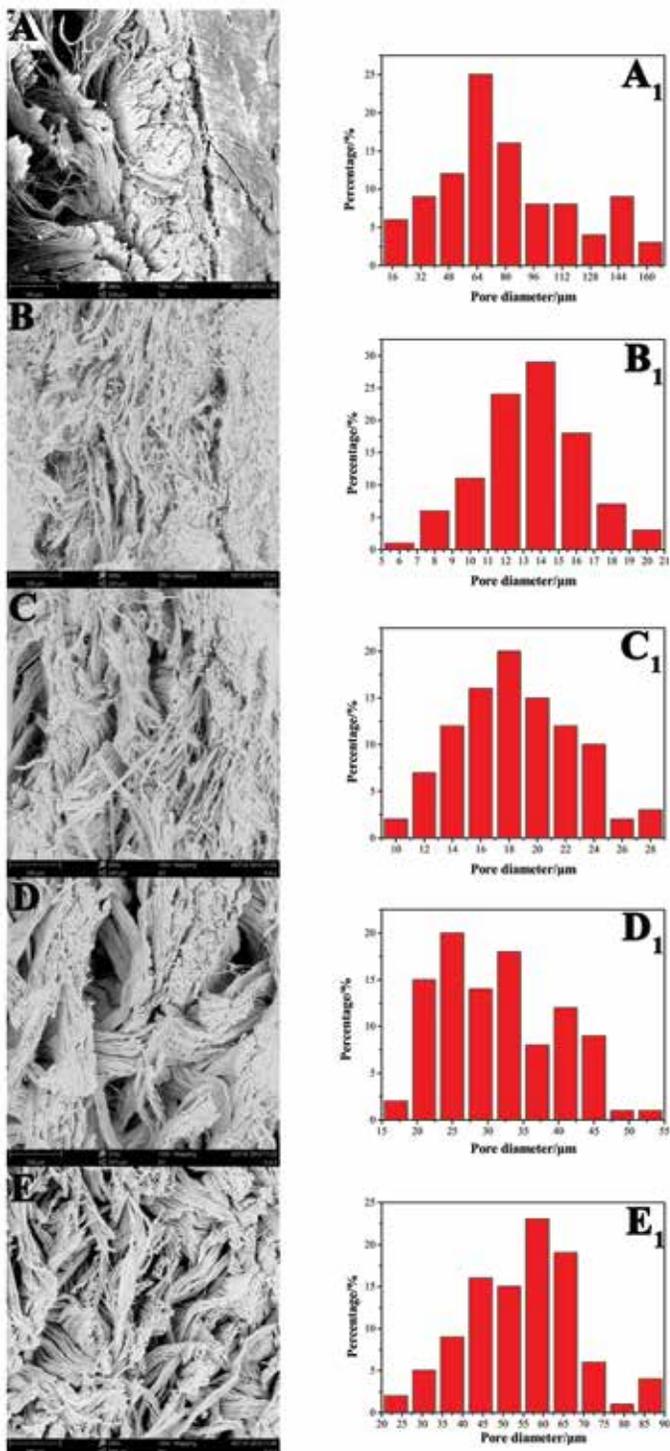


Figure 4. Cross section morphology and pore diameter distribution of S, SA, SAG-1, SAG-2 and SAG-3.

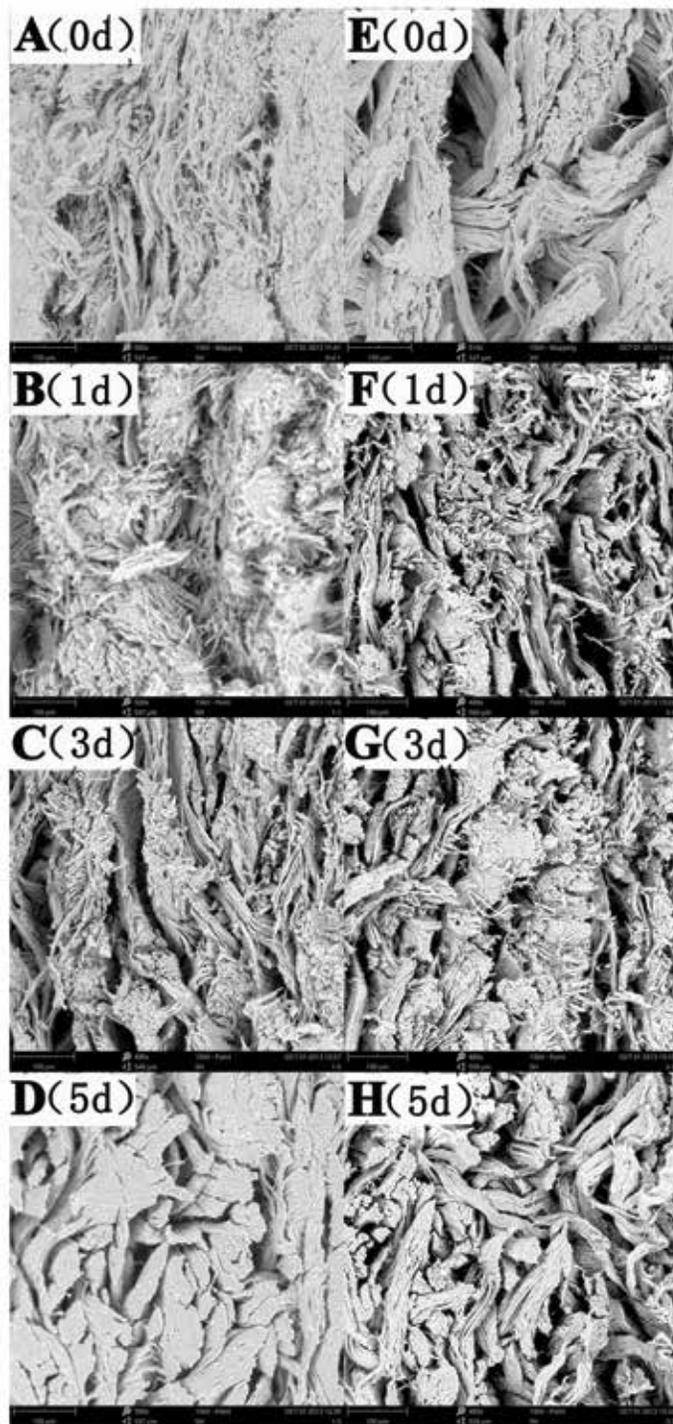


Figure 5. Morphology change of cross section of SA (A-D) and SAG-2 (E-H) at different time.

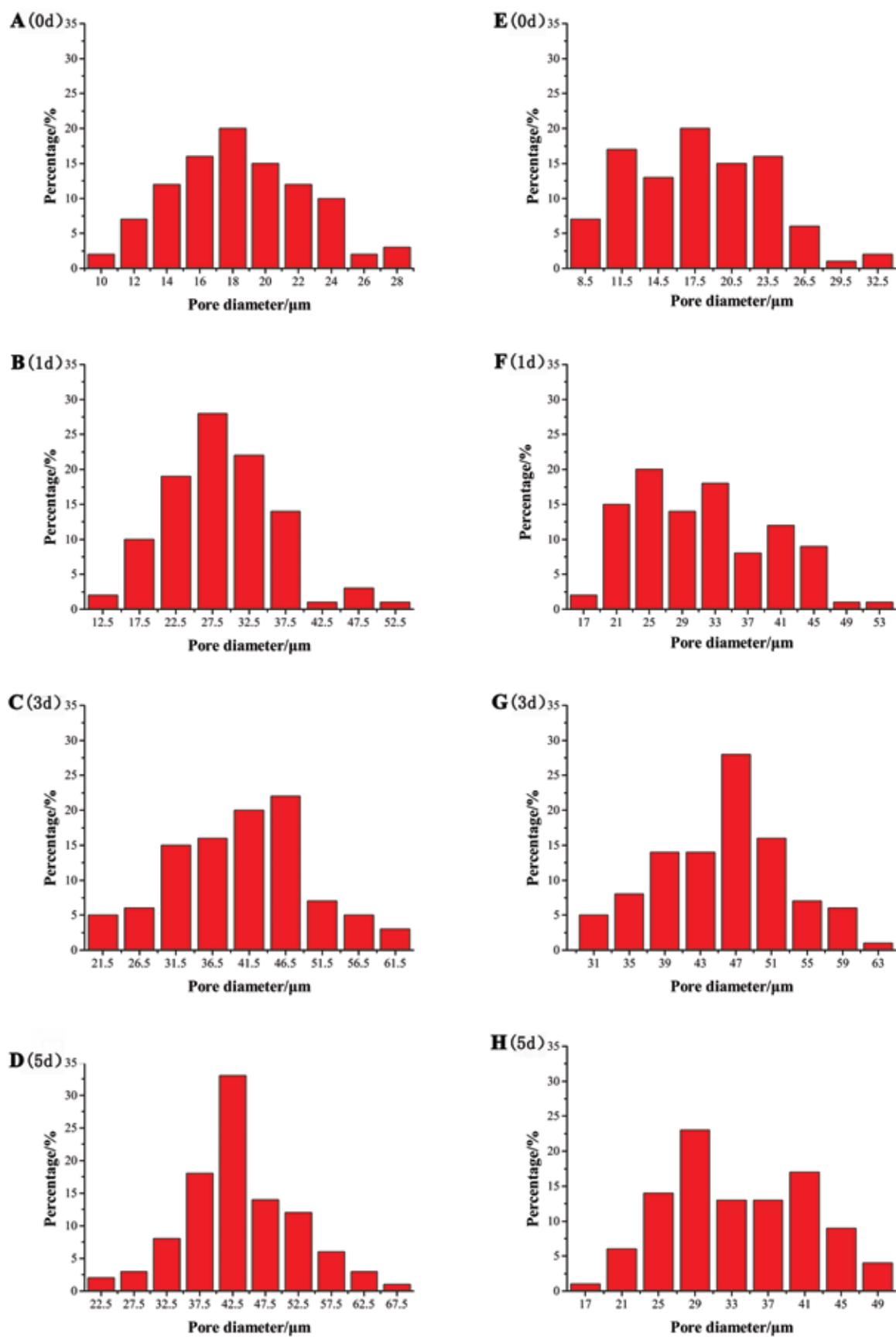


Figure 6. Distribution of pore diameter of SA (A-D) and SAG-2 (E-H) at different time.

**Effect of GPTMS and Accelerated Ageing on Porous Structure of Leather**

To gain a better understanding of the effect of GPTMS addition on the porous structure of leather, cross section morphology of samples S, SA, SAG-1, SAG-2, and SAG-3 was observed by SEM respectively (Figure 4). Pickled skin (Figure 4A) showed a compacted and uneven structure of collagen fiber bundles, whereas separate and unique collagenous fibers were observed after tanning (Figure 4B-4E). With respect to SA (Figure 4B), denser but separated evenly collagen fibers were observed. However, SAG-1, SAG-2, and SAG-3 (Figure 4C-E) showed that addition of GPTMS brought about the formation of well-dispersed collagen fiber bundle-like structure. Furthermore, with the increasing dosage of GPTMS, the separated degree of fiber bundles decreased, while the average pore size between fiber bundles increased. This is consistent with the total porosity of collagen fibers observed from liquid displacement method (Table III), which may be due to the incorporated GPTMS controlled the condensation of silicic acid.

The distribution of pore diameter in pickled skin was in a wider range from 15-170 μm (Figure 4A<sub>1</sub>), while that of tanned leather concentrated between 10-90 μm (Figure 4B<sub>1</sub>-E<sub>1</sub>). This phenomenon suggested that inorganic silicon materials (e.g. silicic acid) dispersed

collagen bundles more obviously, while organosilicon materials (e.g. GPTMS) improved clearly the pore size between collagen fibers. This result is in agreement with our previous study on the modification of skin collagen matrix by organosilicon.<sup>10</sup>

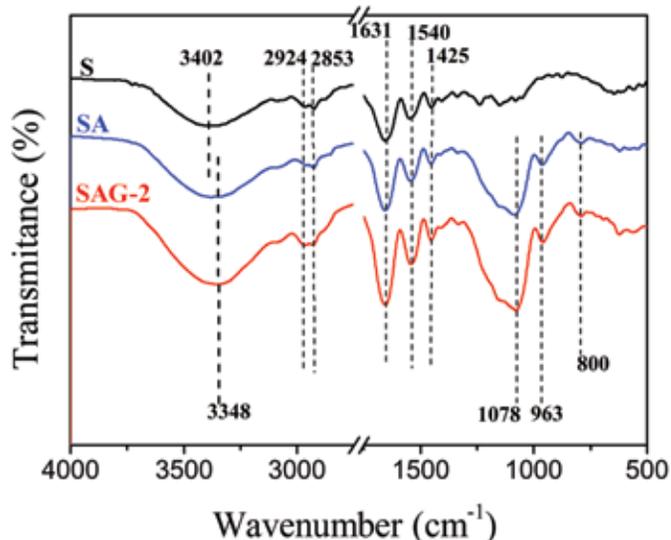
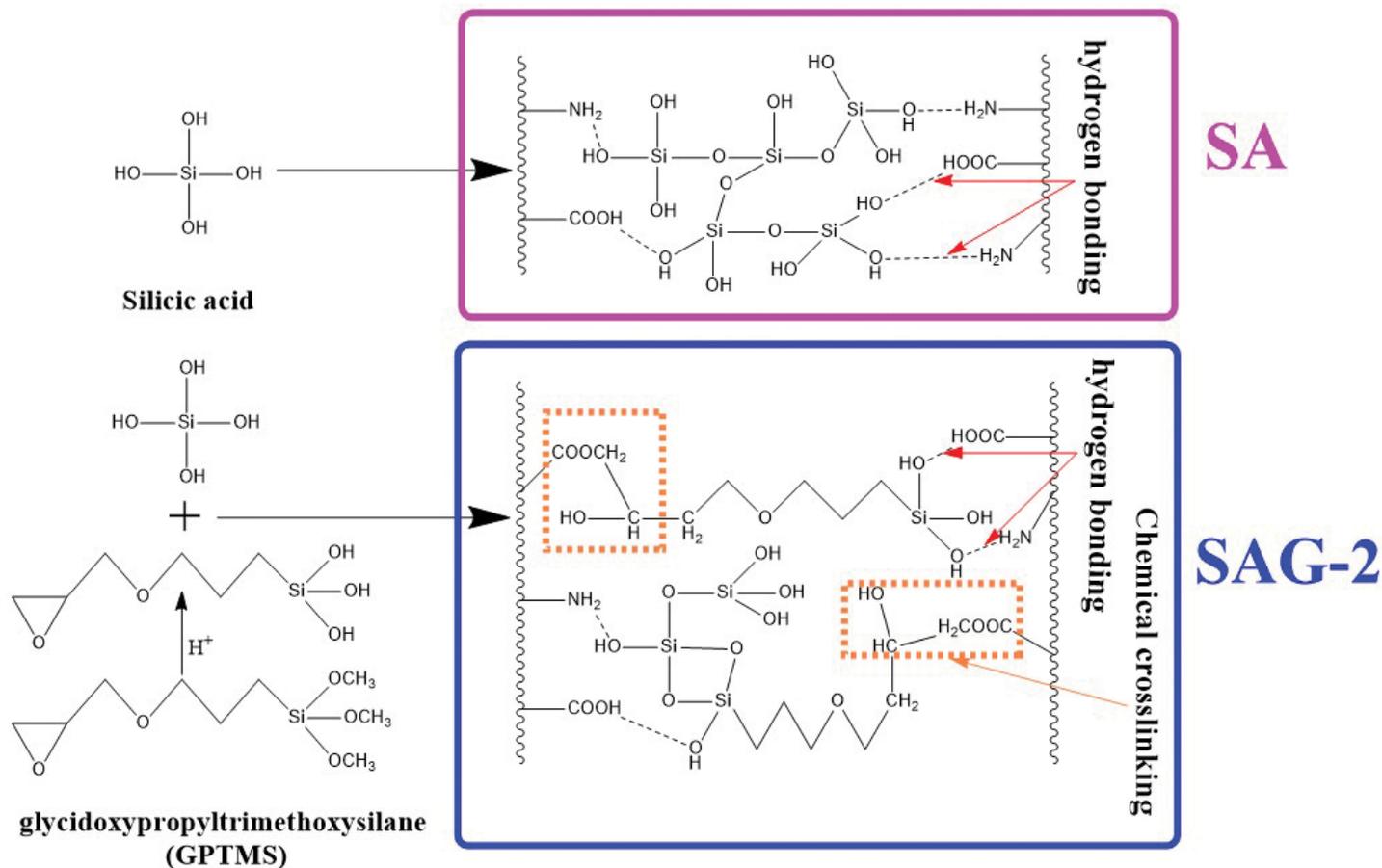


Figure 7. FT-IR spectra of S, SA and SAG-2.



Scheme 1. Preliminary tanning mechanism of silicon-based materials.

In addition, distribution of elements in the leather surface and cross section was then studied by EDS analysis, respectively (Table IV). With respect to leather surface, compared with the pickled skin, increase of Si and O element content in tanned leather may be attributed to incorporation of silicon materials including silicic acid and GPTMS to collagen fiber matrix as a result of deposition via hydrogen bonds and covalent bonding behavior. Content of C element increased with increasing proportion of GPTMS, owing to the organic carbon chain attached to GPTMS molecule. It is worthy to note that the

relevant content of N element in pickled skin and tanned leather has no noticeable change, which indicated that the silicon materials were conjugated with collagen fibers rather than covered on the surface of leather. Most interestingly, the change trend of element contents in leather cross section is similar to that of grain (Table IV). However, the content of Si element in the leather cross section was lower than that of the grain surface. Furthermore, the content of Si element is almost the same in the cross section of SA, SAG-1 and SAG-2, which is consistent with their Ts, being no significant difference, measured at 0 d

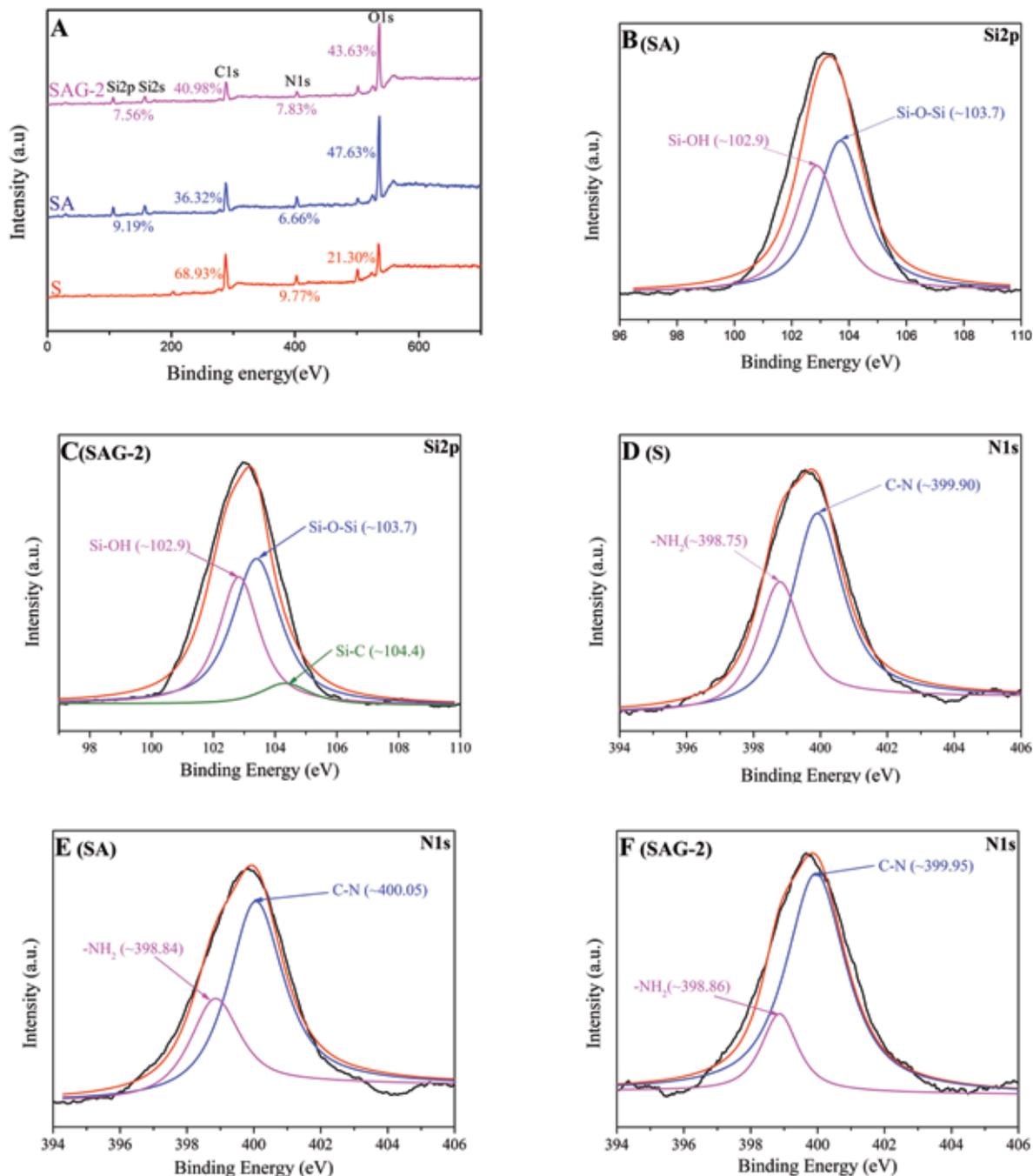


Figure 8. XPS spectra of S, SA and SAG-2.

(Figure 2). Subsequently, SA and SAG-2 were also selected for further studying influence of GPTMS on morphology and porous structure of leather during the accelerated ageing process.

The morphology of cross sections of SA and SAG-2 samples at different period of time were recorded by SEM observation (Figure 5). It can be observed that the collagen fibers combined with each other to form bundles of collagen fibers with a relatively regular structure during accelerated ageing process. Formation of ordered collagenous fibers is also one of the important signs of tanning reaction.<sup>14, 27-28</sup> Moreover, porous structure of SAG-2 changed more slightly than that of SA. In addition, incorporation of GPTMS resulted in the pore size distribution of leather more uniform (Figure 6).

The findings about changes of properties of SA and SAG-2 such as  $T_s$ , thermal denaturation temperature, morphology and distribution of pore diameter showed a good consistency, and demonstrated that addition of GPTMS could inhibit change of collagen fibers during accelerated ageing process, suggesting that the addition of GPTMS can stabilize properties of leather during storage. However, the tanning mechanism of silicic acid, in particular, combination of GPTMS and silicic acid, still needs to be further explored.

#### Preliminary Research of Tanning Mechanism

The probable mechanism of tanning with silicic acid alone, and silicic acid-GPTMS combination was speculated and shown in Scheme 1. For silicic acid tanned leather (SA), firstly silicic acid molecule penetrated into the pickled skin collagen fiber matrix at pH 2-3, and then its silicon hydroxyl groups took dehydration and condensation to form Si-O-Si bonds when the pH value increased to 4. On the other hand, silicon hydroxyl groups also reacted with active groups (e.g.  $-\text{NH}_2$ ,  $-\text{COOH}$ ) of collagen fibers by hydrogen bonds. Thus, a rigid and stable three-dimensional silica network was obtained, which could improve hydrothermal stability and some other performances of leather. In the case of silicic acid-GPTMS combination tanned leather (SAG-2), there was Si-O-Si bonds generated from intermolecular co-condensation of Si-OH groups of silicic acid and GPTMS, besides that formed by intramolecular condensation of silicic acid molecules. Additionally, ester bonds were easily formed between epoxides of GPTMS and carboxyl groups of collagen molecules in an acidic aqueous medium.<sup>29-30</sup>

To verify tanning mechanism of silicon-based materials, FT-IR analysis was carried out (Figure 7). For the pickled skin sample (S), the peaks at  $3402\text{ cm}^{-1}$ ,  $1540\text{ cm}^{-1}$  and  $1425\text{ cm}^{-1}$  can be assigned to the N-H stretching (amide A), N-H bending vibrations (amide II) and C-N stretching vibrations, respectively.<sup>31</sup> And for the silicic acid tanned leather (SA), there are some new peaks at  $1078\text{ cm}^{-1}$  (Si-O-Si, stretching vibrations),  $963\text{ cm}^{-1}$  (Si-OH, stretching) and  $800\text{ cm}^{-1}$  (Si-O-Si, bending vibrations), indicating the successful of

tanning reaction.<sup>15, 32-33</sup> Furthermore, the red-shifted band of N-H stretching ( $3402\text{ cm}^{-1}$ ) and increased intensity of peak at  $1631\text{ cm}^{-1}$  (C=O, stretching vibrations) demonstrated the reaction of silicic acid with amino groups on collagen molecules, thus exposing more carboxyl groups.<sup>34</sup> In addition, intensity of the peaks at  $2924\text{ cm}^{-1}$  ( $-\text{CH}_2-$ , asymmetric vibrations) and  $2853\text{ cm}^{-1}$  ( $-\text{CH}_2-$ , symmetric vibrations) of silicic acid-GPTMS combination tanned leather (SAG-2) was stronger than that of SA, respectively, which can be attributed to the hydrocarbon segments of GPTMS attached onto the collagen fibers surface.<sup>35</sup>

In addition, the XPS analysis was conducted to further investigate tanning mechanism through revealing difference of chemical components of S, SA and SAG-2. In full XPS spectra (Figure 8 A), there are three main peaks located at 284.6, 532.7 and 400.0 eV, which assigned to C1s, O1s and N1s, respectively. It must be mentioned that two new peaks appeared coming from Si2p and Si2s in SA and SAG-2, owing to the tanning result of silicon-based materials. Moreover, there is a remarkable difference in the peak intensities of the samples. The O1s peak intensity increased from 20.80% (S) to 47.63% (SA) and 43.63% (SAG-2), respectively, indicating oxygen-containing functional groups (especially hydroxyl groups) were successfully introduced into the leather; while the C1s peak intensity of SAG-2 (40.98%) was different slightly from that of SA (36.52%), maybe attributed to the incorporation of organic hydrocarbon segment of GPTMS.<sup>36</sup>

The shift of peaks in SA and SAG-2 when compared with S sample provides evidence of interactions between the silicon materials and collagen fibers (Figure 8 B-F). In the Si2p spectrum of SA (Figure 8B) and SAG-2 (Figure 8C), the peaks at 102.9 eV and 103.7 eV can be assigned to the Si-OH and Si-O-Si, respectively.<sup>37-39</sup> The decrease in the relative ratio of Si-OH to Si-O-Si maybe the reason that the co-condensation of silicon hydroxyl groups of GPTMS after hydrolysis with that of silicic acid promoted the degree of condensation of Si-OH groups as a result of incorporation of GPTMS. While the additional peak at 104.4 eV (Figure 8C) is characteristic of Si-C group, clearly ascribed to the addition of GPTMS. Figure 8 (D-F) exhibits the peaks of nitrogen. The increase of  $-\text{NH}_2$  binding energy can be attributed to the formation of hydrogen bonds between silicon hydroxyl groups and primary amino groups of collagen fibers. Decrease of the intensity area of C-N of SAG-2, accompanied by increase of binding energy of C-N, which maybe owing to some epoxy groups in GPTMS reacted with amino groups,<sup>40</sup> despite the dominant reaction of the epoxy groups in GPTMS with the  $-\text{COOH}$  groups in collagen fibers at acidic condition.

## Conclusions

In this work, it was found firstly that leather possessed appropriate shrinkage temperature, which obtained when

employing silicic acid alone in tanning process under the parameters such as 15% w/w dosage of silicic acid (3% w/v), pH value 4, and tanning time 5 h. Subsequently, investigation of effect of different amount of GPTMS on variation of properties of leather including shrinkage temperature, thermal denaturation temperature, micromorphology and distribution of porous diameter confirmed incorporation of GPTMS could prevent properties of leather from alteration during accelerated ageing process, implying that addition of GPTMS could control further condensation of silicon hydroxyl groups existing in collagen fiber matrix, and then stabilize properties of leather during storage. In addition, the preliminary tanning mechanism of chrome-free tanning agent based on silicic acid and GPTMS was revealed by Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS) analysis. These findings of this work therefore provide an effective and promising strategy to explore enhanced and practical chrome-free tanning technology based on silicon materials, which are ongoing in our research group.

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