

## SYNTHESIS AND APPLICATION OF DENDRITIC-LINEAR POLYMER PAMAM-Si FOR LEATHER FATLIQUORING PROCESS

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**Abstract.** Environmental pollution caused by leather making is the primary concern in the development of leather industry. The use of safe, effective and multi-functional green chemical products has the advantages of reducing leather operations, increasing chemicals utilization, decreasing the environmental burden, improving leather quality. In this study, dendritic-linear polymers of PAMAM-Si 1G and PAMAM-Si 2G were applied to fatliquoring process, which were prepared by branching polysiloxane on the dendritic polyamide-amine (PAMAM). Then the emulsion properties, fatliquoring properties and fatliquoring mechanism were studied by EDS, SEM, XRD, TG and washing experiments. The conclusion was drawn that PAMAM-Si are weak alkali products with high emulsion stability. The particle size of PAMAM-Si 1G was 35.8 nm, and that of PAMAM-Si 2G was 26.7 nm. They can improve the softness, shrinkage temperature and physical and mechanical properties of leather. The softness of leather with PAMAM-Si 1G and PAMAM-Si 2G increased by 115.6% and 104.7% respectively. The shrinkage temperature of leather with PAMAM-Si 2G increased by 2.9 °C. The Breaking elongation of leather with PAMAM-Si 1G and PAMAM-Si 2G increased by 38.6% and 32.4% respectively. At the same time, PAMAM-Si not only increased the distance and disorder of fiber but combined with collagen fiber through hydrogen bond, electrovalent bond and a certain amount of physical adsorption and covalent bond.

### 1 Introduction

Environmental pollution caused by leather making is the primary concern in the development of leather industry <sup>[1]</sup>. Currently, the methods adopted to improve it are strengthening terminal treatment <sup>[2]</sup>, promoting clean production technology <sup>[3]</sup> and developing new eco-friendly material <sup>[4-5]</sup>. The use of safe, effective and multi-functional green chemical products has the advantages of reducing leather operations, increasing chemicals utilization, lowering the cost of consumption, decreasing the environmental burden, improving leather quality and so on <sup>[6-7]</sup>. Therefore, it is considered the necessary product in reducing leather pollution.

Fatliquor agent is among the most important leather chemicals to decide the leather handle and applicability <sup>[8]</sup>. The earliest method is to put animal and plant oil in leather by soaking and painting. The oil is only effective on the surface but cannot penetrate into the leather sample, so the improvement on leather softness is not obvious. Later, a method of adding additional emulsifier was developed. But apart from the disadvantage of too many processes, the emulsion performance proved to be unstable, and the property of fatliquored leather was not uniform <sup>[9]</sup>. Therefore, some researchers developed a partial modifying method in which sulfate, sulfite oxidation, sulfonation and phosphorylation were employed to partly modify animal and plant oil for forming a self-emulsification system <sup>[10]</sup>. However, a large amount of abandoned fat and salt solutions will be produced in the modification process, thus, polluting the environment. In recent years, with the development of the petroleum products, synthetic oils based on petroleum products as fatliquoring agent gradually shows its unique performance, whose varieties and dosage are increasing <sup>[11]</sup>. The characteristic of this kind of product is the structure in accordance with the requirements of people, integrating various functions <sup>[12]</sup>. Bao et al. <sup>[13]</sup> synthesized polyurethane microemulsions (MC-PURs) by maleic anhydride modified castor oil (MCO),

PEG1000 (polyethylene glycol) and IPDI (isophorone diisocyanate) for leather to improve its softness. Nashy et al. [14] studied two different nano-emulsions based on methyl methacrylate/butyl acrylate copolymers as retanning and lubricating agents for chrome-tanned leather. But its linear molecular structure affects modification, resulting in poor leather quality, and failing to meet the various needs of fatliquoring.

Dendritic molecular, however, has three-dimensional molecular structure, making certain filling possible [15-16]. Moreover, its multiterminal reactive group can produce a large number of active site reaction to introduce functional groups and combine leather fiber closely. Qiang et al. [17] prepared a series of hyperbranched linear surfactants (HLS) by using oleic acid to modify the first generation hydroxyl-terminated hyperbranched polymer (HBP-1), which was obtained through a step synthesis method using trimethylolpropane and N,N-dihydroxyethyl dodecylamine-3-amine-methyl propionate (AB(2)-type monomer). Ibrahim et al [18] studied polyamidoamine hyperbranched polymer (HPAM), which significantly improves the shrinkage temperature, and the texture and softness of the leather. Li et al. [19] synthesized a novel leather chemical product from pentaerythritol, phosphorus oxychloride, melamine and tetrakis-hydroxymethyl phosphonium chloride (THPC) by three steps, which effectively inhibits leather burning and improve leather properties like fullness, softness, grain tightness.

In this study, dendritic-linear polymers of PAMAM-Si 1G and PAMAM-Si 2G were prepared respectively by branching polydimethylsiloxane which has excellent softness on the dendritic polyamide-amine (PAMAM). Then the emulsion properties of PAMAM-Si were studied. Finally, PAMAM-Si were applied to fatliquoring process. The properties of fatliquored leather were examined, and the interaction mechanism of PAMAM-Si and leather were discussed.

## 2 Experimental section

### 2.1 Materials

Hydrogen-terminated polydimethylsiloxane (H%=0.5, commercial product), allyl glycidyl ether and chloroplatinic acid (analytically pure) were obtained from Nanjing Chengong Silicon Co., Ltd., Jiangsu, China. Dendritic polyamide-amine (commercial product), which were purified by n-butyl alcohol, was purchased from Weihai Chenyuan Molecular New Materials Co., Ltd., Shandong, China. Synthetic fatliquor (DESOPON LQ-5, commercial product) was purchased from Decision Chemical Industrial Co. Ltd.

### 2.2 Synthesis

#### 2.2.1 Synthesis of SEPDMS

First, HTPDMS (11.70 g, 27.68 mmol), AGE (3.00 g, 26.27 mmol) and toluene (20 g) were firstly charged into a 250 ml four-necked flask along with a low stream of nitrogen. When the temperature was heated to 75 °C, 0.15 wt% of Pt-catalyst was added to the flask. Then the mixture was heated to 90 °C and stirred for 6 h. The trace of platinum was removed by stirring with activated charcoal. The toluene of solvent was removed by rotary evaporator, and unreacted HPDMS was separated from the raw products in methanol. The prepared SEPDMS was colorless transparent oily liquid.<sup>[20]</sup> IR (KBr,  $\text{cm}^{-1}$ ): 2963, 2873 (aliphatic C-H stretching), 2129 (Si-H stretching), 1260 (Si-C-H bending), 1130~1000 (Si-O-Si stretching), 911 (Si-H bending), 798 (Si-C-H stretching); <sup>1</sup>H-NMR (300MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  4.72(s, 1H, -Si-H), 3.75 (d, 2H, -O-CH<sub>2</sub>-CH-), 3.46 (t, 2H, -CH<sub>2</sub>-O-), 3.18 (m, 1H, -CH-CH<sub>2</sub>-), 2.61, 2.82 (d, 2H, -CH-CH<sub>2</sub>-), 1.64 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 0.6 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-), 0.20 (s, -Si-CH<sub>3</sub>).

#### 2.2.2 Synthesis of PAMAM-Si 1G

PAMAM 1G (8.33 g, 16.11 mmol) and isopropanol were mixed with constant stirring in a 250 ml four-necked flask. Then SEPDMS (10.00 g, 15.30 mmol) was dropwise added into the mixture for

30min. And the reaction of epoxy group and amino group was taken at a certain temperature and time. Then the product was redissolved in dichloromethane, and then precipitated and centrifugally separated several times to remove the excess PAMAM. The pale yellow viscous PAMAM-Si 1G was obtained by removing the solvent with rotary evaporator.<sup>[16]</sup> IR (KBr,  $\text{cm}^{-1}$ ): 3478, 3300 (primary amino N-H stretching), 2943, 2860 (aliphatic C-H stretching), 1648, 1550 (-NH-CO-), 2129 (Si-H stretching), 1260 (Si-C-H bending), 1130~1000 (Si-O-Si stretching), 911 (Si-H bending), 798 (Si-C-H stretching); <sup>1</sup>H-NMR (300MHz, D<sub>2</sub>O, ppm): PAMAM 1G:  $\delta$  3.07 (m, 8H, -CO-NH-CH<sub>2</sub>-), 2.61 (m, 8H, -CH<sub>2</sub>-NH<sub>2</sub>), 2.55 (m, 8H, -N-CH<sub>2</sub>-), 2.44 (m, 4H, -CH<sub>2</sub>-N-), 2.27 (m, 2H, -CH<sub>2</sub>-CO-); PAMAM-Si 1G:  $\delta$  3.87 (d, 2H, -O-CH<sub>2</sub>-CH-), 1.55 (m, 8H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 0.52 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-), 0.08 (s, -Si-CH<sub>3</sub>).

### 2.2.3 Synthesis of PAMAM-Si 2G

PAMAM 2G (11.91 g, 8.05 mmol) and isopropanol were mixed with constant stirring in a 250 ml four-necked flask. Then SEPDMMS (5.00 g, 7.65 mmol) was dropwise added into the mixture for 30 min. And the reaction of epoxy group and amino group was taken at a certain temperature and time. Then the product was redissolved in dichloromethane, and then precipitated and centrifugally separated several times to remove the excess PAMAM. The pale yellow viscous PAMAM-Si 2G was obtained by removing the solvent with rotary evaporator.<sup>[16]</sup> IR (KBr,  $\text{cm}^{-1}$ ): 3500~3300 (primary amino N-H stretching), 2958, 2860 (aliphatic C-H stretching), 1648, 1550 (-NH-CO-), 2129 (Si-H stretching), 1260 (Si-C-H bending), 1130~1000 (Si-O-Si stretching), 911 (Si-H bending), 798 (Si-C-H stretching); <sup>1</sup>H-NMR (300MHz, D<sub>2</sub>O, ppm): PAMAM 2G:  $\delta$  3.29~3.20 (m, 24H, -CO-NH-CH<sub>2</sub>-), 2.78 (m, 16H, -CH<sub>2</sub>-NH<sub>2</sub>), 2.75 (m, 24H, -N-CH<sub>2</sub>-), 2.69 (m, 8H, -CH<sub>2</sub>-N-), 2.55 (m, 4H, centre -CH<sub>2</sub>-CH<sub>2</sub>-), 2.38 (m, 24H, -CH<sub>2</sub>-CO-); PAMAM-Si 2G:  $\delta$  3.87 (d, 2H, -O-CH<sub>2</sub>-CH-), 1.56 (m, 8H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 0.52 (m, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-), 0.08 (s, -Si-CH<sub>3</sub>).

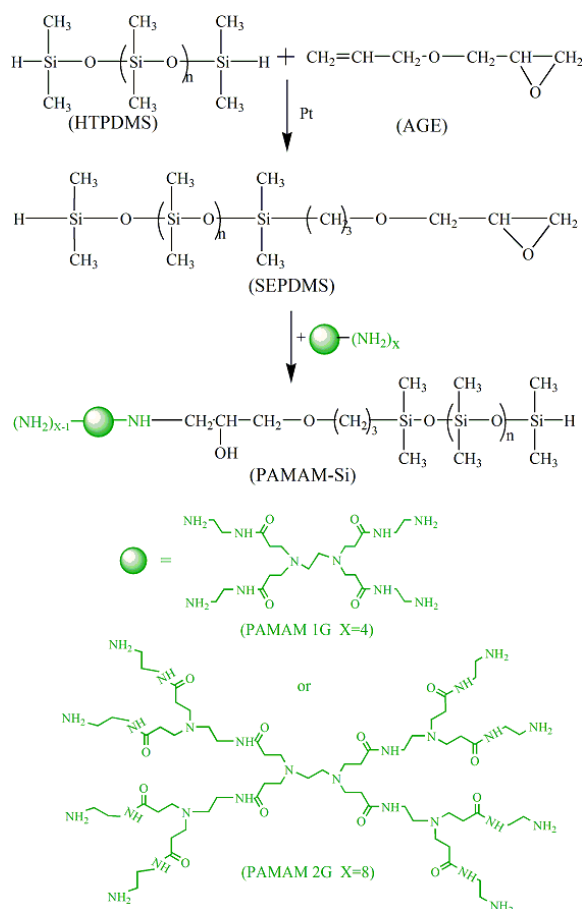


Fig. 1. Synthesis route of PAMAM-Si 1G and PAMAM-Si 2G.

### 2.3 Application in leather fatliquoring

For the fatliquoring research there were used sheepskin chrome tanned (wet-blue). The leather thickness was 0.8~1.1 mm. The leather was cut into 25 cm x 25 cm size samples. The shaved weight of the leather samples was recorded. Fatliquoring process with PAMAM-Si 1G, with PAMAM-Si 2G, with the commercial product (DESOPON LQ-5) and without any fatliquor was respectively carried out according to detailed methodology (Table 1) <sup>[21]</sup>.

**Table 1.** The fatliquoring technology.

Process	Materials	Dosage ( $\omega$ )/%	Temperature/ $^{\circ}$ C	Time/min	PH	Remarks
Washing	water	300	30	10		
	water	100	30			
Neutralization	NaHCO <sub>3</sub> (1:10)	1.5		120	5.5	
	fatliquor	10	55	60		
Fatliquoring	formic acid (1:10)	1.5		10+10+30	4.0	
Washing	water	200	30	10		Setting out

### 2.4 Analytical Methods

#### 2.4.1 FT-IR and <sup>1</sup>H-NMR

The structure of PAMAM-Si obtained under optimal conditions was characterized using fourier infrared spectrometer (Vector-22, Bruker Daltronics Co., Ltd.), and proton nuclear magnetic resonance spectra (Avance-400MHz, Bruker Daltronics Co., Ltd.) <sup>[22]</sup>.

#### 2.4.2 Emulsion property

The stability of emulsion was measured by the particle size (Zetasizer NANO-ZS90, Malvern Instruments Co. Ltd.) and the property of that in acid, alkali or salt base fluid was conducted according to the reference <sup>[23]</sup>.

#### 2.4.3 Fatliquored leather property

Energy dispersive spectrometer (Octane Prime, EDAX Co. Ltd.) was used to observe the distribution of silicon in leather. The loose degree of collagen fiber was observed by scanning electron microscope (SEM Q45, FEI Company.). The distance of collagen fiber was obtained by X-ray diffraction instrument (D/Max2200PC, Rigaku Co. Ltd.), equipped with Cu-Ka radiation source to identify the d-spacing of MMT. The X-ray generator operated at 40 kV, 40 mV, with a scanning speed of 2 $^{\circ}$ /min and  $\theta=5^{\circ} \sim 60^{\circ}$ . Thermogravimetry was used to determine the thermostability of leather, in which the heating rate was 10  $^{\circ}$ C/min and the range of temperature was from 25  $^{\circ}$ C to 600  $^{\circ}$ C.

#### 2.4.4 Binding form

The combination rate of PAMAM-Si refers to the ratio of the changed weight of sample before and after processing and the combined PAMAM-Si total weight with sample. Samples without any fatliquor, with PAMAM-Si 1G, and PAMAM-Si 2G were washed by water, acetone solution ( $m_{\text{acetone}}:m_{\text{water}}=1:1$ ) and dilute alkali solution ( $\omega_{\text{Na}_2\text{CO}_3}=0.5\%$ ) in turn. Every treatment was repeated many

times until a constant weight (difference between parallel measurements < 1%) was obtained. It was kept washing until a constant weight (1% difference between parallel measurements)

### 3 Results and discussion

#### 3.1 Emulsion property

**Table 2.** Emulsion properties of PAMAM-Si.

Parameters	PAMAM-Si 1G	PAMAM-Si 2G
Appearance	Pale yellow transparent oily dope	Pale yellow transparent oily dope
pH	8.5~9.0	8.5~9.0
Particle size ( $\omega=10\%$ )	35.8 nm	26.7nm
1:9 dilution emulsion (48 h)	uniformity	uniformity
Potassium chromium sulfate solution (1 mol/L)	uniformity	uniformity
Hydrochloric acid solution (1 mol/L)	uniformity	uniformity
Ammonia solution(1 mol/L)	uniformity	uniformity

Table 2 shows that PAMAM-Si 1G and PAMAM-Si 2G were weak alkali products with high stability against acids, alkalies and chromium salts. There was not a sedimentation in the PAMAM-Si dilution ( $\omega=10\%$ ) for 48 h at 25 °C. It is worth noting that the particle size of PAMAM-Si 1G was 35.8 nm, and PAMAM-Si 2G was 26.7, far less than the collagen fiber distance of 50~300nm<sup>[24]</sup>, which was better to permeate into leather and distribute uniformly for PAMAM-Si.

#### 3.2 Leather property

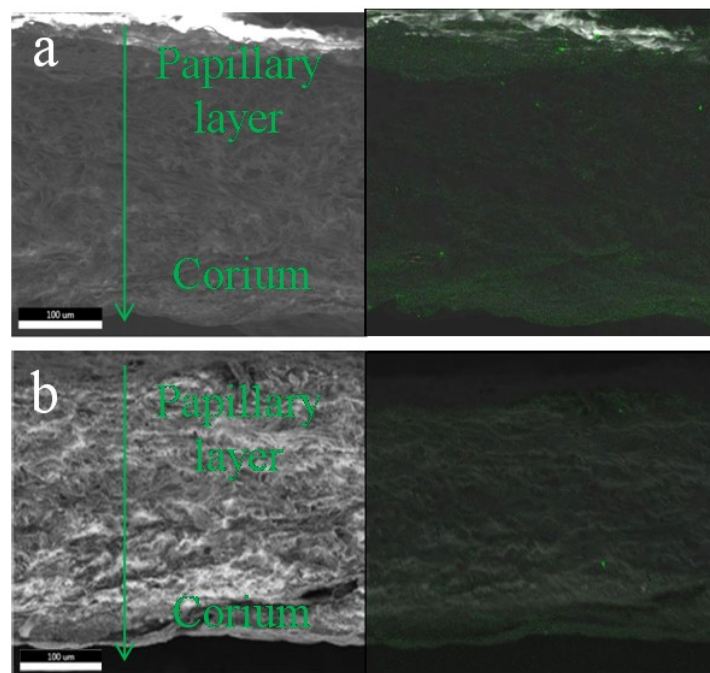
**Table 3.** Properties of the leather by Fatliquor.

Parameters of leather	Experiments			
	I Without	II Commercial	III PAMAM-Si 1G	IV PAMAM-Si 2G
Softness/mm	1.92	4.54	4.14	3.93
Thickness/%	-3.33	5.88	12.35	5.49
Shrinkage temperature /°C	99.40	98.10	100.50	102.30
Tensile strength/MPa	27.61	27.14	29.84	35.91
Breaking elongation/%	77.69	114.04	107.71	102.84
Tear strength/(N/mm)	67.73	68.56	68.72	73.03
Permeability of water /{mg/(10cm <sup>2</sup> ·24h)}	0.50	0.52	0.54	0.54

Wet-blue leather was fatliquored using PAMAM-Si 1G and PAMAM-Si 2G, as well as commercial product (LQ-5) and anything with comparable aim. The properties of leather fatliquored were presented in Table 3. Compared with blank, the properties of leather fatliquored by PAMAM-Si

were improved in softness, thickness, shrinkage temperature, mechanical properties and permeability of water. To softness, leather fatliquored by PAMAM-Si 1G and PAMAM-Si 2G were similar with leather fatliquored by commercial product. The softness of leather with PAMAM-Si 1G and PAMAM-Si 2G increased by 115.6% and 104.7% respectively. The thickness of sample with PAMAM-Si 1G was the highest among these samples, which was due to that the spheric structure of PAMAM-Si has better filling effect than the line structure of commercial product. And it is important to note that the thickness changed rarely, because the more active groups (e.g. amine group) PAMAM-Si 2G contains, the stronger it's interconnection with leather. The results of shrinkage temperature and mechanical properties were as what described above. Especially, the shrinkage temperature of leather with PAMAM-Si 2G increased by 2.9°C. The Breaking elongation of leather with PAMAM-Si 1G and PAMAM-Si 2G increased by 38.6% and 32.4% respectively. That is to say, PAMAM-Si serves as a bridge between fiber-to-fiber, in which the active groups offer interconnecting site with fiber, and the spheric structure fills interfiber. In addition, the improvement of water permeability of leather fatliquored by PAMAM-Si indicated that hygienic property improved.

### 3.3 Distribution of PAMAM-Si in leather

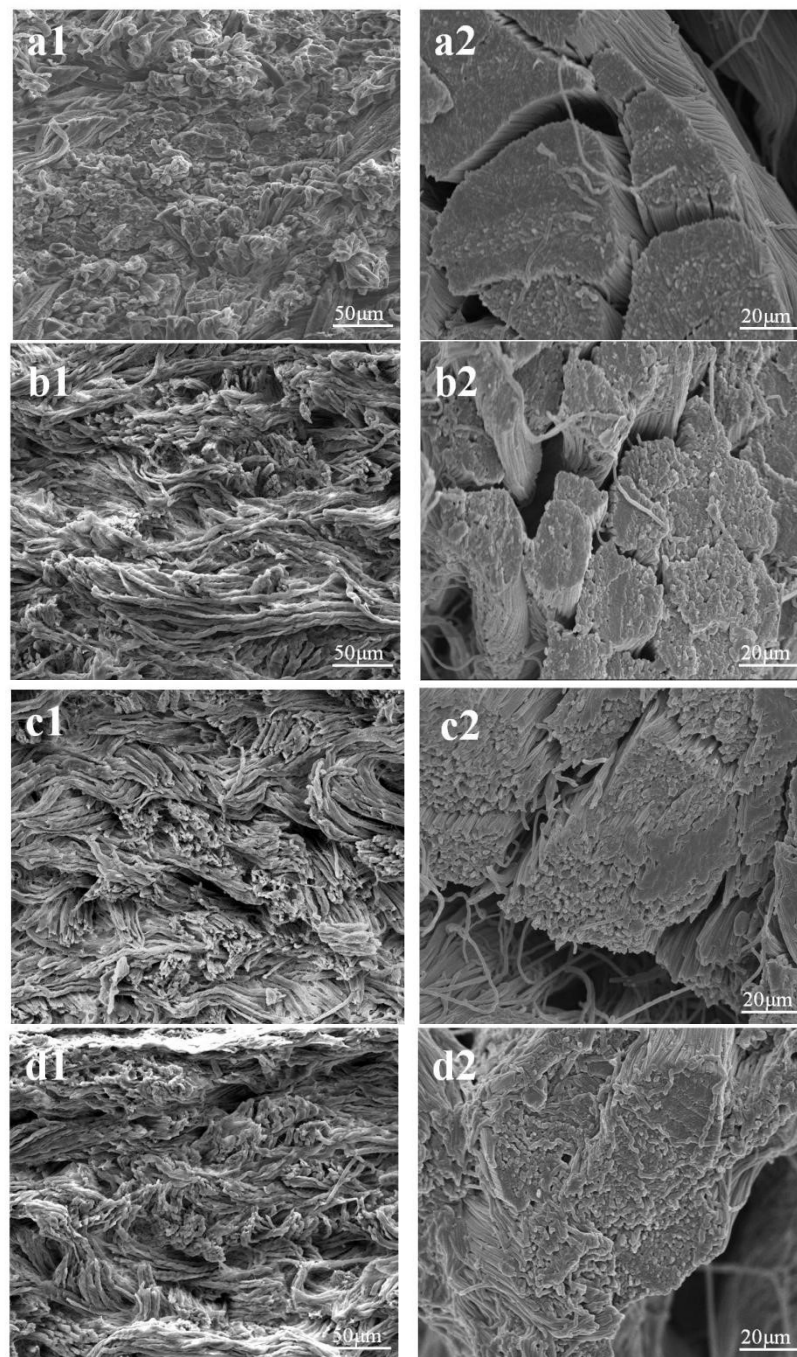


**Fig. 2.** EDS results of silicon by scanning of longitudinal section with PAMAM-Si 1G (a) and PAMAM-Si 2G (b).

Figure 2 shows the EDS results of silicon by scanning of longitudinal section of crust leather with PAMAM-Si. The green point stands for the silicon, which shows the distribution of PAMAM-Si in leather. Fatliquoring process is the balance between permeating and combining, rather than physical filling for fatliqur in leather. Since leather has papillary layer and corium, different fiber waving structures which leads to different degree of interaction between fatliqur and leather, the distribution of fatliqur in longitudinal section is not uniform. From the samples with PAMAM-Si 1G (Fig. 2a) and PAMAM-Si 2G (Fig. 2b), it can be noted that silicon was distributed in the whole section, but it can be also noted that the content of silicon decreased first, then increased, along with papillary layer to corium, revealing that the content is higher in papillary layer than that in corium, and lowest in the centre of the whole section. It also indicated that PAMAM-Si was distributed into

the whole leather, and enriched on both sides, which was attributed to the fact that the excess combined PAMAM-Si with leather took effect on further permeation. Moreover, the content of silicon in sample containing PAMAM-Si 1G was higher than that in sample containing PAMAM-Si 2G, consistent with that in molecule.

### 3.4 Loose degree of collagen fiber



**Fig. 3.** SEM of leather fatliquored without anything (a), with commercial product (b), with PAMAM-Si 1G (c) and with PAMAM-Si 2G (d); 1:x1 k, 2:x10 k.

Fatliquoring agent is mainly used to reduce friction and increase space between fibers, so as to achieve soft leather. Therefore the fiber loose degree of fatliquored leather proves the soft performance. Fiber arrangement of longitudinal section under low multiple can be observed from Fig. 3(1). The sample without any fatliquror was arranged closely, and that with commercial product, PAMAM-Si 1G and PAMAM-Si 2G distributed loosely and random, indicating that the spheric structure of PAMAM-Si has filling effect on increasing interfiber space, meanwhile there was more flexible long chain in commercial fatliquror and PAMAM-Si 1G attached fiber surface to decrease resistance force for fibers movement than that in PAMAM-Si 2G. Under high multiple, the above phenomenon was more noticeable (Fig. 3(2)). Fibril packing without any fatliquror arranged neatly and closely, dividing clearly, but that with commercial product distributed to small clusters and increased the gap. It is worth noting that the disorder of arrangement and mutual crosslinking degree increased and some small random fibers appeared among fibril packing with PAMAM-Si 1G and PAMAM-Si 2G, on account of the increased combination of multi terminal active groups and fibers.

### 3.5 Fiber distance

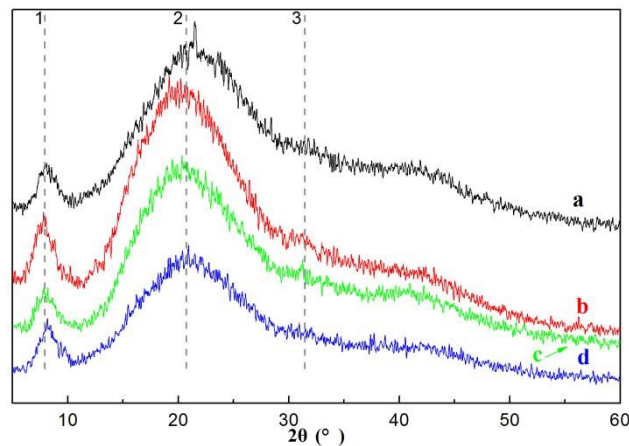


Fig. 4. XRD curves of leather samples without any fatliquror (a), with commercial product (b), with PAMAM-Si 1G (c) and with PAMAM-Si 2G (d).

Table 4. XRD results of leather samples without any fatliquror (a), with commercial product (b), PAMAM-Si 1G (c) and PAMAM-Si 2G (d).

Sample	2θ <sub>1</sub>	2θ <sub>2</sub>	2θ <sub>3</sub>	d <sub>1a</sub>	d <sub>2a</sub>	d <sub>3a</sub>
Without	7.967	21.522	31.425	1.108	0.412	0.284
Commercial	7.715	20.044	31.133	1.144	0.442	0.287
1GPAMAM-Si	7.847	19.501	31.080	1.125	0.455	0.287
2GPAMAM-Si	8.168	20.409	31.242	1.081	0.435	0.286

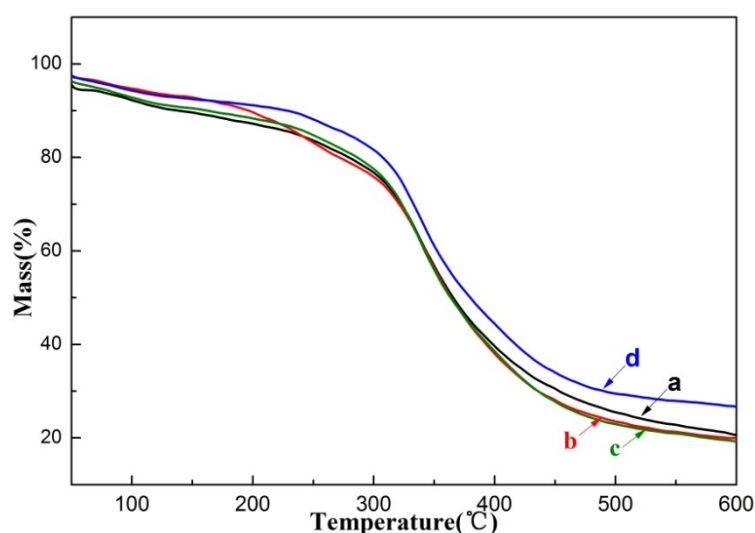
<sup>a</sup> Bragg equation:  $2d\sin\theta=\lambda$ ,  $\lambda=0.154$ ,  $d=\lambda/2\sin\theta=0.077/\sin(\theta/2)$ .

The loose degree of fatliquored leather fiber increased and the order degree of fatliquored collagen fibril packing with PAMAM-Si decreased significantly against the blank sample, (Fig. 3). The progress of fatliquror could not only change the external form of the leather fibril packing, to a certain extent, but change its internal structure as well. XRD curves of leather samples without any fatliquror (a) and with PAMAM-Si (b) are shown in Fig.4. Three main diffraction peaks appeared in the XRD curves of leather fiber: the first sharp peak at 7°~8° indicates the distance between the molecular chains,



the broad peak at  $20^\circ$  is due to diffuse scattering and the third peak at  $30^\circ$  corresponding to the unit height, typical of the triple helical structure [25-26]. According to Bragg equation to calculate the spacing of area corresponding to  $2\theta$ , the results were summarized in Table 4.  $2\theta_1$  of leather fatliquored by PAMAM-Si 2G was in comparison with blank, but that by commercial product and PAMAM-Si 1G significantly reduced, indicating that the distance between the collagen fiber molecular chains increased.  $2\theta_2$  of leather fatliquored is smaller than that of leather without any fatliquor, revealing that the disorder of arrangement increased. Meanwhile  $2\theta_3$  of various samples were very close, in accordance with a single residue triplex pitch. Combined with the size of PAMAM-Si 1G and PAMAM-Si 2G emulsion, PAMAM-Si can permeate into fiber, increase fiber distance, combine with fiber active groups and enhance fiber arrangement disorder. In addition, PAMMA-Si 2G has larger molecule structure and more amino groups, which formed stronger bonds with fibers, resulting in that fiber distance changed insignificantly. Notably, the progress of various fatliquors did not destroy the molecular structure of collagen.

### 3.6 Leather thermal property



**Fig. 5.** TG curves of leather samples without any fatliquor (a), with commercial product (b), with PAMAM-Si 1G (c) and with PAMAM-Si 2G (d).

The thermal degradation curve of leather samples after fatliquoring was divided into two stage (Fig.5): When the temperature remained from  $25^\circ\text{C}$  to  $230^\circ\text{C}$ , the loss weight was mainly evaporable moisture and small molecules; At the second stage, the temperature was ranged from  $230^\circ\text{C}$  to  $600^\circ\text{C}$ , during which under the action of heat, the collagen intermolecular hydrogen bond, Vander Waals force and coordination bond ruptured, collagen structure destroyed and molecular chain distorted, then collagen was degraded to peptide and amino acid, finally amino acid residues were destroyed, deaminated and dehydrated [27-28].

At the first stage, the sample with commercial fatliquor thermal weight loss was the highest. Commercial fatliquor contained small molecules volatile oil, which led to the increase of degradation rate and decrease of the weight.

The order of sample thermal degradation rate at the second stage is described as follows: with PAMAM-Si 2G < with PAMAM-Si 1G < without any fatliquor << with commercial Fatliquor. It was attributed to the fact that a large number of active groups of PAMAM-Si 2G enhanced the interaction with fibers, giving rise to the decrease of thermal degradation rate. On the contrary, commercial fatliquor increased the distance and reduced fiction, resulting in the increase of thermal degradation rate. The polysiloxane chain was filled among fibers to reduce their interaction. The

polysiloxane chain content of PAMAM-Si 1G was higher than that of PAMAM-Si 2G, and the active group number was lowered. Therefore, at the beginning of second stage, the increased fiber gap reduced fiction and enhanced degradation rate, but the combination reduced degradation rate later.

### 3.7 Binding form

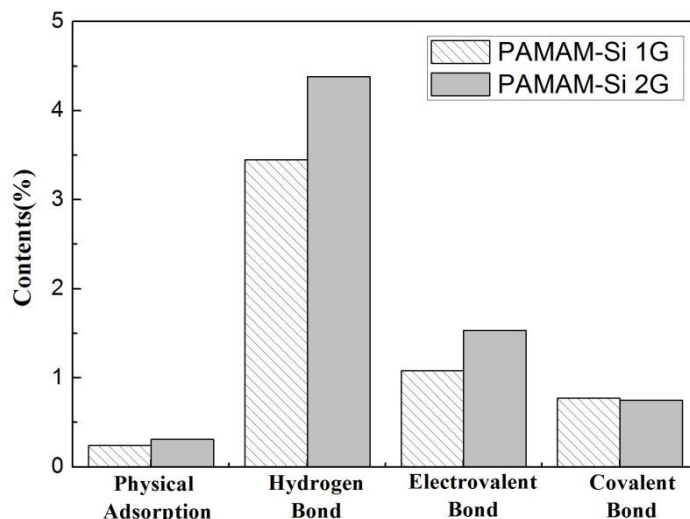


Fig. 6. Binding form of PAMAM-Si 1G and PAMAM-Si 2G with leather.

Water washing can remove the physical adsorption on the leather; acetone liquid washing can remove combination with collagen fiber by hydrogen bond; dilute alkali washing can remove substances by electrovalent bond; the remaining amount after dilute alkali washing can be considered to be material combined with collagen fiber base on the form of covalent bond. The bank is standard.

Sample after water washing, the combination of PAMAM-Si 1G fell by 0.24 %, the combination of PAMAM-Si 2G fell by 0.31 %; After acetone liquid washing, PAMAM-Si 1G fell by 3.45 % and PAMAM-Si 2G by 4.38 %; After dilute alkali washing, PAMAM-Si 1G fell by 1.08 % and PAMAM-Si 2G by 1.53 %; After the above treatment, PAMAM-Si 1G reduced to 0.77 %, PAMAM-Si 2G to 0.75 %, indicating that the binding form between PAMAM-Si and collagen fiber was mainly hydrogen bond, electrovalent bond and a certain amount of physical adsorption and covalent bond. Hydrogen bond was the combination among PAMAM-Si peripheral amino and hydroxyl, amino and carboxyl of leather. The electrovalent bond was generated by the partial amino with a positive charge ( $\text{NH}^{3+}$ ) and ionized carboxyl with negative charge ( $\text{COO}^-$ ) in experimental condition. And a few amino was reacted with hydroxyl group or carboxyl group of collagen fibers to make covalent bond. Fig. 6 shows that the amount of hydrogen bond and electrovalent bond between PAMAM-Si 2G and leather was significantly more than that of PAMAM-Si 1G. The combined group was mainly amino in PAMAM-Si. PAMAM-Si 2G has larger molecule structure and more amino groups than PAMAM-Si 1G, which was helpful to combine leather tightly and enhance interaction. The interaction mechanism of PAMAM-Si and collagen fiber was shown in Fig. 7.

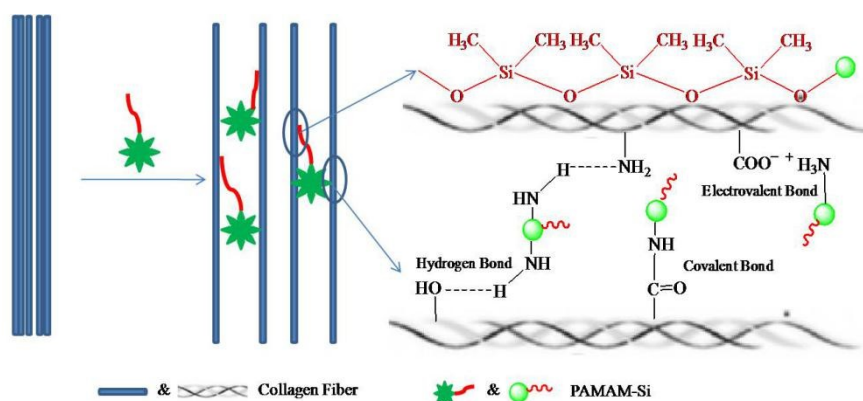


Fig. 7. Schematic illustration of PAMAM-Si in the collagen fiber.

#### 4 Conclusions

The dendritic-linear polymer PAMAM-Si was prepared with 1G and 2G PAMAM and SEPDMs obtained by hydrosilylation reaction. The molecular structure of PAMAM-Si was characterized by FT-IR and  $^1\text{H-NMR}$ . According to the investigation of emulsion properties, PAMAM-Si were weak alkali products, with high stability against acids, alkalies and chromium salts. The particle size of PAMAM-Si 1G was 35.8 nm, and PAMAM-Si 2G was 26.7 nm.

When PAMAM-Si was applied to fatliquoring process, the softness, fullness, physical and mechanical properties and healthiness of fatliquored leather were significantly improved. The silicon content of PAMAM-Si 1G was higher than that of PAMAM-Si 2G, so the softness of leather with PAMAM-Si 1G was superior to that of PAMAM-Si 2G. However, there are more active groups in PAMAM-Si 2G. Therefore, when it was combined with PAMAM-Si 2G, the interaction of fibers became stronger and shrinkage temperature and physical and mechanical properties of crust changed more obviously.

PAMAM-Si can permeate into the skin and distribute between the collagen fibers, increase the distance and disorder, but not destroy the molecular structure of collagen. There are interaction with PAMAM-Si and collagen fiber. It improved the thermal properties of the fiber. The binding form of PAMAM-Si and collagen fiber was mainly hydrogen bond, electrovalent bond as well as a certain amount of physical adsorption and covalent bond. Hydrogen bond was the combination among the peripheral amino of PAMAM-Si and hydroxyl, amino and carboxyl of leather. The electrovalent bond was generated by the partial amino with a positive charge ( $\text{NH}^{3+}$ ) and ionized carboxyl with negative charge ( $\text{COO}^-$ ) in experimental condition. And a few amino were reacted with hydroxyl group or carboxyl group of collagen fibers to make covalent bond.

#### References

- Jayanthi, D.; Victor, J. S.; Chellan, R.; Chellappa, M.: (2019). Green processing: minimising harmful substances in leather making, *Environ Sci Pollut Res*, 26(7), 6782-6790, 2019
- Rahman, M. S.; Islam, M. R.; Mondol, O.; Rahman, M. S.; Sabrin, F.; Zohora, U. Screening of Protease Producing Bacteria from Tannery Wastes of Leather Processing Industries at Hazaribag, Bangladesh. *JUJBS*, 7(1), 23-34, 2018
- Rosu, L.; Varganici, C. D.; Crudu, A. M.; Rosu, D.; Bele, A.: Ecofriendly wet-white leather vs. conventional tanned wet-blue leather. a photochemical approach, *J Clean Prod*, 117(10), 708-720; 2017
- Errasti, M.E.; Caffini, N.O.; López, L.M.I.: Proteolytic extracts of three Bromeliaceae species as eco-compatible tools for leather industry, *Environ Sci Pollut Res*, 25(22), 21459–21466, 2018
- Ramalingam, S.; Sreeram, K. J.; Rao, J. R.: Hybrid composites: amalgamation of proteins with polymeric phenols as a multifunctional material for leather processing, *RSC Advances*, 5(42), 33221-33232, 2015

6. Abul, H. M.; Abdul, M. M.; Mehedi, H.: Leaf paste aided goat skin preservation: significant chloride reduction in tannery, *J. Environ. Chem. Eng.*, 6(4), 4423-4428, 2018
7. Sun, X.; Jin, Y.; Lai, S.; Pan, J.; Du, W.; Shi, L.: Desirable retanning system for aldehyde-tanned leather to reduce the formaldehyde content and improve the physical-mechanical properties, *J Clean Prod*, 175(20), 199-206, 2018
8. Jan, A.; Krzysztof, M.; Katarzyna, M.; Agnieszka, T.: Research on application of flax and soya oil for leather fatliquoring, *Journal of Cleaner Production*, 65(15), 583-589, 2014
9. Sivakumara, V.; Rao, P.G.; Ramabrahama, B.V.; Swaminathana, G.: Power ultrasound in fatliquor preparation based on vegetable oil for leather application, *Journal of Cleaner Production*, 16(4), 549-553, 2008
10. Leticia M. S.; Mariliz, G.: Reusing of a hide waste for leather fatliquoring, *J Clean Prod*, 15(1), 12-16, 2007
11. Du, J.; Shi, L.; Peng, B.: Amphiphilic acrylate copolymer fatliquor for ecological leather: influence of molecular weight on performances, *J Appl Polym Sci*, 133(20), 43440, 2016
12. Lv, B.; Gao, J. J.; Ma, J. Z.; Gao, D. G.; Wang, H. D.; Huang, X. W.: Nanocomposite based on erucic acid modified montmorillonite/sulfited rapeseed oil: Preparation and application in leather, *Appl Clay Sci*, 121, 36-45, 2016
13. Bao L.H.; Lan Y. J.; Zhang S. F.: Aliphatic anionic polyurethane microemulsion leather filling-retanning agent, *Journal of the Society of Leather technologists and Chemists*, 91(2), 73-80, 2007
14. Nashy, El-Shahat H. A.; Essa, Mohamed M.; Hussain, Ahmed I.: Synthesis and application of methyl methacrylate/butyl acrylate copolymer nanoemulsions as efficient retanning and lubricating agents for chrome-tanned leather, *Journal of applied polymer science*, 124(4), 3293-3301, 2012
15. Zhu, W. P.; Gao, J.; Sun, S. P.; Zhang, S.; Chung, T. S.: Poly (amidoamine) dendrimer (pamam) grafted on thin film composite (tfc) nanofiltration (nf) hollow fiber membranes for heavy metal removal, *J Membrane Sci*, 487, 117-126, 2015
16. Wang, X. C.; Sun, S. W.; Wang, H. J.; Guo, X. X.: Synthesis and characterization of polysiloxane grafted polyamide-amine surfactants, *J Surfactants Deterge*, 20(2), 1-8, 2017
17. Qiang, T. T.; Bu, Q. Q.; Huang, Z. F.; Wang, X. C.: Synthesis and characterization of hyperbranched linear surfactants, *J Surfact Deterg*, 17(2), 215-221, 2014
18. Ibrahim, A. A.; Youssef, M. S. A.; Nashy, E. H. A.: Using of hyperbranched poly (amidoamine) as pretanning agent for leather, *International Journal of Journal of Polymer Science*, (5), 690-695, 2013
19. Li, B.; Li, J. X.; Li, L. X.: Synthesis and application of a novel functional material as leather flame retardant, *J Am Leather Chem As*, 109(7), 239-245, 2014
20. Tang C, Liu W.: Syntheses of novel photosensitive polysiloxanes and their effects on properties of UV-cured epoxy methacrylate coatings, *J Coat Technol Res*, 7(5), 651-658, 2010
21. Jia, L.; Ma, J, Z.; Gao, D. G.; William R.T.; Sun, L. Y.: A star-shaped POSS-containing polymer for cleaner leather processing, *J Hazard Mater*, 361(5), 305-311, 2019
22. Shi, X. Y.; Lesniak, W.; Islam, M. T.: Comprehensive characterization of surface-functionalized poly (amidoamine) dendrimers with acetamide, hydroxyl, and carboxyl groups, *Colloid Surface A*, 272(1), 139-150, 2006
23. GB/T 6369-2008, Surface active agents-determination of emulsifying power-colorimetric method [S]. Beijing: China Standard Press, 2008.
24. Maxwell C A, Wess T J, Kennedy C J.: X-ray diffraction study into the effects of liming on the structure of collagen, *Biomacromolecules* 7(8):2321-6, 2006
25. Yang, Q.Y.; Qin, S.F.; Chen, J.F.; Ni, W.; Xu, Q.: Supercritical Carbon Dioxide-assisted Loosening Preparation of Dry Leather, *Applied polymer*, 113(6), 4015-4022, 2009
26. Gao, X.; Zhou, J. F.; Huang, X.: Facile synthesis of mesoporous sulfated Ce/TiO<sub>2</sub> nanofiber solid superacid with nanocrystalline frameworks by using collagen fibers as a biotemplate and its application in Esterification, *RSC Advances*, 4(8), 4010-4019, 2014
27. Zoltán, S.; Zsuzsanna, C.; Elena, B.; Cristina, C.; Claudiu, S.; Eszter B.; Rajnaia, J.; Lucretia, M.; Emma, J.: Thermal characterization of new, artificially aged and historical leather and parchment, *Journal of Analytical and Applied Pyrolysis*, 115, 419-427, 2015
28. Marcillaa, A.; Garcíaa, A. N.; Leóna, M.; Martínezb, P.; Bañónb, E.: Study of the influence of NaOH treatment on the pyrolysis of different leather tanned using thermogravimetric analysis and Py/GC-MS system, *Journal of Analytical and Applied Pyrolysis*, 92(1), 194-201, 2011