Study on the Combination Tanning Property of Amino-Terminated $PAMAM_8$ Dendritic Compound and THPS

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Abstract: With diethylamine and methyl acrylate as the raw materials, The second generation of polyamideamine dendritic compound (shortened as $PAMAM_8$) with 8 amioes is synthesized by divergence method. Their structures are characterized as well. We have combined $PAMAM_8$ and THPS, and have tanned the collagen fibres of the hide. The experimental result shows that the effect of the combination tanning is superior to that of the single tanning with THPS. The optimum technological conditions are that the dosage of THPS is 2% (based on the hide quality) and the dosage of the amino-terminated $PAMAM_8$ dendritic compound is 0.8%. Compared with single THPS tanning, the shrinkage temperature (Ts) of the crust leather increases by 6℃, the content of free formaldehyde in the leather sample decreases by more than 50% and the tensile strength and tear strength increases by 15% and 9% respectively. In addition, in the subsequent treatment of dyeing and fatliquoring, the combination tanning can improve the absorption of crust leather for a dyestuff and fatliquoring agent.

Key words: dendritic compound; $PAMAM_8$; THPS ; tannage ; leather

1 Introduction

At present tanning agents employed in leather industry are based mainly on chromium-containing tanning agents, which are much better than other inorganic tanning agents, synthetic tanning agents and vegetable tanning agents in terms of the comprehensive performance of the leather tanned by them. Nevertheless, as the increasing environmental problems brought by chrome tanning method and the strategy for chromium resources, chrome tanning method has already faced serious challenges. Nowadays people are seeking natural products, and advocating the preparation of leather products from green chemicals. Therefore, it becomes an important task of chemists in leather industry to research and develop clean and green tanning agents to replace chromium-containing tanning agents at present.

Tetrakis (hydroxymethyl) phosphonium salt, commonly used as the flame-retardant in fabrics and bactericide in oilfield water treatment systems and cooling water treatment systems, is a kind of organic compounds which is found to be able to tan leather long ago. It consists mainly of tetrakis (hydroxymethyl) phosphonium chloride (THPC) and tetrakis (hydroxymethyl) phosphonium sulfate (THPS).[1-3] Organic phosphonium salts have been used as the tanning agents to prepare leather abroad since 1960s, and certain progress has been achieved on the basis of it. However, such a method did not bring enough attention at that time. In recent years, as the improvement in the research and development of chromium-free tanning method, the unique performance of organic phosphonium salts as a kind of tanning agent has attracted more and more attention of leather-making people, and the investigation on it becomes a hot topic in the study of chromium-free tanning materials. It is especially significant and

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valuable for the re-recognization of organic phosphonium salts' tanning capability.[4] Organic phosphonium salts have similar mechanism of tanning leather collagen fiber to aldehydes do. During the leather tannage process, formaldehyde will be released, which leads to a certain amount of free formaldehyde left in the leather, and thus, such organic phosphonium salts' applications in leather processing industry have been restricted. In the present paper, the second generation polyamide-typed dendrimer (Poly(amide amine), abbreviated as $PAMAM_8$), which contains 8 amino groups on the periphery, has been synthesized by Divergent Synthesis Method based on ethylenediamine and methyl acrylate, and then it was combined with THPS to tan leather collagen fiber. We have discussed the influence of this amino group-terminated polyamide-typed dendrimer on the process of tanning leather by THPS, and the dendrimer's capability of capturing free formaldehyde left in crust fiber, and attempted to study and establish a clean technology and method of tanning collagen fiber by THPS. The potential application of this dendrimer in leather processing field has been examined both theoretically and practically.

2 Experimental

2.1 Materials and equipment

2.1.1 Materials

Raw materials ethylenediamine and methyl acrylate have a purity level of AR, and were purified before use. All of the reagents used in the experiments such as toluene, anhydrous methanol, and so on, are of AR, and were purchased from Beijing Dongfang Longshun Chemical Synthetic Technology Development Center. THPS (75%, Tianjin Sunrise Science and Trade Co., Ltd.) is an industrial product. Pickling goatskin was provided by Leather Engineering Center of Shaanxi University of Science and Technology.

2.1.2 Equipment

85-2 Thermostat Magnetic Stirrer, Henan Gongyi City Yuhua Instrument Co., Ltd.; Rotary Evaporato SB-2000, Shanghai Ailang Instruments Co., Ltd.; Circulating Water Vacuum Pump SHE-D(III), Henan Gongyi City Yuhua Instrument Co., Ltd.; V70 infrared spectrum (IR) Instrument, Bruker; AV400 nuclear magnetic resonance (NMR) instrument, Bruker; MJD-A300 Desktop Organic Glass Drum for temperature controlling experiment, Wuxi Xinda Light Industry Machinery CO., Ltd; MSW-YD4 Apparatus for Determination of Shrinkage Temperature of Leather, Yangguang Dianzi Technology Institute of Shaanxi University of Science and Technology.

2.2 Methodology

2.2.1 Synthesis of amino group terminated dendrimer $PAMAM_8$[6]

The raw material ethylenediamine was used as the core and allowed to react with methyl acrylate in anhydrous methanol at -5–0ºC. The system was then warmed up to room temperature and yielded the addition product with 4 methyl acrylate molecules attached at the end. After that, this product was aminolyzed by excessive ethylenediamine to get amidated tetraamino-terminated product. The excessive ethylenediamine can be removed by azeotropic distillation with toluene and methanol (9:1). Then the above-mentioned procedure was repeated again to yield the second generation polyamide-typed dendrimer with 8 amino groups at the end (abbreviated as $PAMAM_8$). The pH of the product was adjusted by hydrochloric acid to 6–7, and water was added to ensure a water content of 50%. The appearance of the final product is light yellow liquid.

2.2.2 Technology of leather tannage and application

A piece of 20×20 cm^2 of pickling goatskin (pH = 2.0–3.0) was weighed and placed in the drum for the

experiment. The procedure is as follows:

Weighing samples:

The weight percentages of materials below are based on the weight which increases the weight of pickling skin by 100%.

Immersing sample in acid again:

Water (25ºC) 100%;

Sodium chloride 8%, rotated for 30 min; pH of the bath solution was adjusted to 2.0–3.0 by formic acid, and then the system was rotated for 30 min again.

Tannage:

THPS 0.5% (0.8%, 1%, 2%, 3%), rotated for 120 min;

$PAMAM_8$ 0% (0.2%, 0.5%, 0.8%, 1.0%, 1.2%), rotated for 4 h;

Sodium bicarbonate 0.5%–1%, used to adjust the pH of the bath solution to 6.0–6.2 in several times, rotated for 120 min. The system stayed for 12 h, and then left the drum and stayed outside. Then we carried out the shrinkage temperature (Ts) measurement and the determination of free formaldehyde content in the crust sample.

Weighing samples:

The weight percentages are based on the weight of crust sample used below.

Dyeing and fatliquoring:

Water (25ºC) 150%;

Dye 1.5% rotated for 30 min;

Fatliquoring agent;

Formic acid 1.5%–2.0%, added twice with a time interval of 15 min, to adjust the pH of the bath solution to 3.5–4.0; rotated for 30 min. The sample was washed with water, taken out of the drum, hung and dried, and hit until it became soft. The color and grain of the leather were evaluated, and the performance such as mechanical properties of the crust sample was tested.

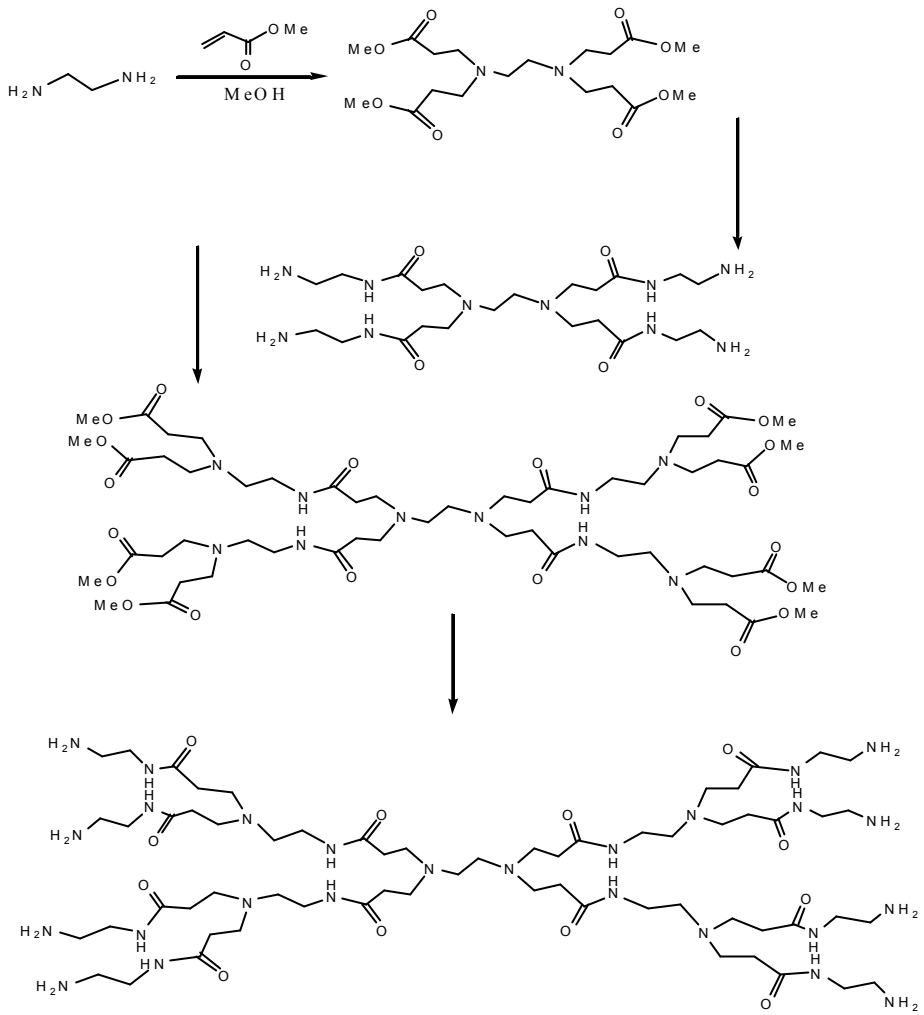
2.2.3 Analysis of crust sample

The determination of free formaldehyde content in the crust was in accordance with the reference[7]. The shrinkage temperature (Ts), tensile strength and tear strength of the crust sample were measured according to the testing method defined in GB 4589. The color and grain of the crust were evaluated by eyes.

3 Results and discussion

3.1 Synthetic route and characterization of structure of amino group-terminated dendrimer $PAMAM_8$

The synthetic route of amino-terminated dendrimer $PAMAM_8$ is as follows:



The spectra of amino-terminated dendrimer $PAMAM_8$ is as follows:

$({}^{a}CH_2{}^{a}CH_2)[N({}^{b}CH_2{}^{c}CH_2{}^{d}CO{}^{e}NH{}^{f}CH_2{}^{g}CH_2N({}^{h}CH_2{}^{i}CH_2{}^{j}CO{}^{k}NH{}^{l}CH_2{}^{m}CH_2{}^{n}NH_2)_2)_2]_2$

IR ν_{max}/cm^{-1}: 1750 (C=O), 3400 (NH);

^{1}H-NRM(400MHz,$CDCl_3$) δ_H: 8.03 (12H, m, e, k), 3.31-3.15 (24H, m, f, l), 2.65 (8H, t, g), 2.61-2.51(52H, m, a, b, c, h, i), 2.45 (16H, t, n), 2.25 (16H, m, m);

^{13}C-NMR (100MHz,$CDCl_3$) δ_C: 178.21 (d), 174.48 (j), 52.13 (f), 49.15 (l), 46.21 (g), 45.11 (a), 43.18 (b), 42.11 (c), 38.21(h), 35.51(i).

3.2 Influence of the amount of THPS on Ts and free formaldehyde content in crust

Figs. 1 and 2 show the influence of the amount of THPS employed in the experiment on Ts of the crust and the free formaldehyde content in the crust, respectively. The crust was produced according to the method described in Section 2.2.2 with different amount of THPS and without $PAMAM_8$.

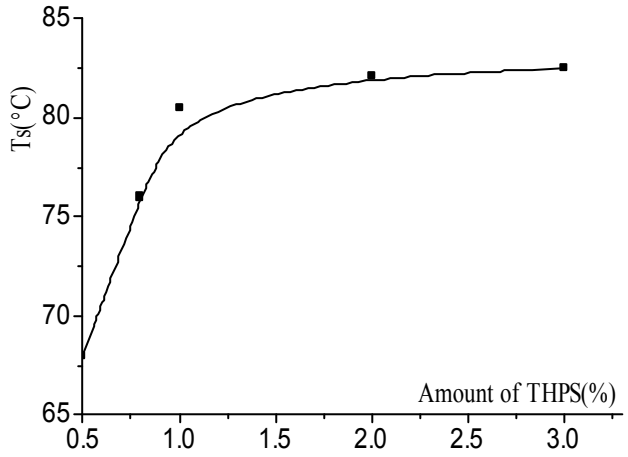


Fig.1 Effect of the amount of THPS on the Ts of crust

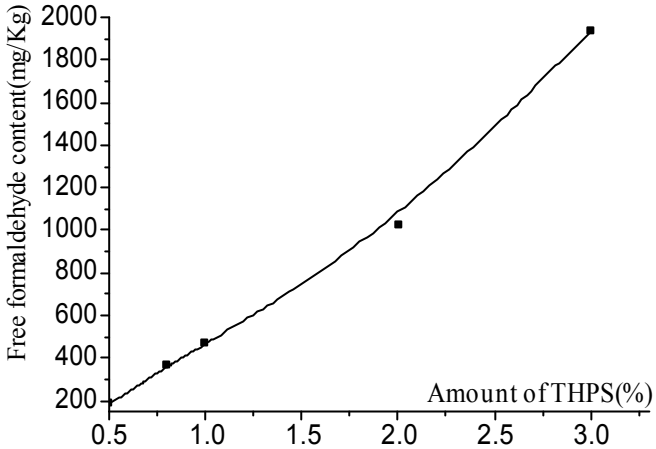


Fig.2 Effect of THPS' amount on the free formaldehyde content in the crust

It can be seen from Fig. 1 that when the amount of THPS is less than 1.0%, the shrinkage temperature of the crust goes up fast as the increase in the amount of THPS employed in the experiment; but when the amount of THPS exceeds 1.0%, the shrinkage temperature gradually approaches a constant value. Therefore, under such experimental conditions, the optimal amount of THPS is around 2.0% in terms of the shrinkage temperature of the crust. A higher consumption of THPS makes little contribution to the promotion of the shrinkage temperature of the crust.

It can be found from Fig. 2 that the free formaldehyde content in the crust also rises as the increase in the amount of THPS. Therefore, when using quite a large amount of THPS, one has to add some materials capable of capturing formaldehyde on the later stage, or carry out the post-processing on the crust (eg., to oxidize the crust with hydrogen peroxide, sodium perborate or sodium percarbonate), to obtain the crust with a low content of free formaldehyde in accordance with environmental protection requirements.

3.3 Impacts of sequence of adding THPS and $PAMAM_8$ on combination tannage

THPS mainly crosslinks with amino groups in collagen; it also reacts with hydroxyl groups and peptide residue.[8] Through the utilization of crosslinking reaction between THPS and amino groups, one can add amino-terminated dendrimer $PAMAM_8$ during THPS tannage process to form the crosslinking structure among collagen fiber, THPS and $PAMAM_8$, and to enhance THPS' effect of tanning collagen fiber. At the same time, $PAMAM_8$'s capability of capturing free formaldehyde can be employed to reduce

the content of free formaldehyde in the crust tanned by THPS.

The amount of THPS and $PAMAM_8$ was fixed at 2.0% and 0.8%, respectively. The tanning experiment was carried out according to the method described in Section 2.2.2 by adding THPS and $PAMAM_8$ in different sequences. In each sequence, the pH of the bath solution was adjusted gradually. The influence of the pH of the bath solution and the sequence of adding raw materials on Ts of the tanned crust is shown in Fig. 3; their influence on the content of free formaldehyde in the leather is listed in Table 1.

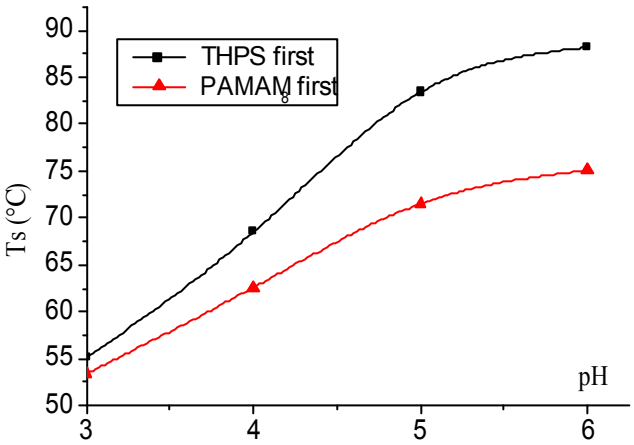


Fig.3 Effect of pH on the Ts of crust

It is learned from Fig. 3 that Ts of the combination tannage crust increases with pH in both sequences, and the sequence of adding THPS and PAMAM8 has larger impact on Ts of the crust. In the case of adding THPS first, the effect of combination tannage is much better, and Ts of the crust has a larger improvement. The reason is that THPS competes with $PAMAM_8$ for the crosslinking reaction with collagen fiber, which leads to the fact that Ts of the combination tannage crust produced by adding THPS first is obviously higher than Ts of the crust produced by adding THPS later. Furthermore, such a competitive reaction becomes more obvious as the increase of the pH. Therefore, at a larger pH, the Ts difference between the tanned crusts produced in two sequences of adding raw materials becomes larger.

Tab.1 Effect of charging sequences on the free formaldehyde content in the crust

tannage	THPS	THPS + $PAMAM_8$	$PAMAM_8$ + THPS
Content of free formaldehyde（mg/Kg）	1025.4	492.7	502.4

On the later stage of the tannage, alkali was added to the bath solution to bring the pH up to about 6.0. The sample was allowed to stay overnight; after that the crust was dried, and then the content of free formaldehyde in the crust was determined. It can be seen from Table 1 that comparing with THPS tannage alone, the $PAMAM_8$ and THPS combination tannage can yield a crust with a much lower (by more than 50%) content of free formaldehyde, which is attributed to the capability of $PAMAM_8$ molecule's amino end groups of capturing free formaldehyde in the crust sample. Nevertheless, the sequence of adding $PAMAM_8$ and THPS has little influence on the content of free formaldehyde in the combination tannage crust, which is mainly due to the fixed total number of reactive amino groups in collagen fiber and $PAMAM_8$ molecules. Consequently, no matter what the consequence of adding $PAMAM_8$ and THPS is, the amount of THPS consumed during the tannage is similar, and thus, the

consumption of by-product formaldehyde is similar.

3.5 Impact of $PAMAM_8$ consumption on combination tannage

On the basis of fixed amount of THPS (2.0%) and varied amount of $PAMAM_8$, the tannage experiment was carried out according to the procedure described in Section 2.2.2 to investigate the influence of $PAMAM_8$ consumption on the tanning effect of the crust. It can be seen from Table 2 that the consumption of $PAMAM_8$ has certain influence on Ts of the tanned crust, the content of free formaldehyde and physical mechanical properties of the crust. As the increase in the consumption of $PAMAM_8$, Ts goes up by a certain extent, so do the tensile strength and tear strength. In other words, the introduction of $PAMAM_8$ can strengthen the effect of THPS tannage. The reason can be ascribed to the formation of network structure among collagen fiber, THPS and $PAMAM_8$. At a consumption of 0.8%, $PAMAM_8$ has the most significant effect of strengthening THPS tannage: Ts increases by about 6ºC; tensile strength and tear strength are improved by 15% and 9%, respectively. Due to the competition between THPS and $PAMAM_8$ for the crosslinking reaction with collagen fiber, when the amount of $PAMAM_8$ exceeds 0.8%, the crosslinking reaction between THPS and collagen fiber is depressed, which caused the decrease of Ts, tensile strength and tear strength of the tanned crust. However, the increase in the consumption of $PAMAM_8$ means the introduction of additional reaction amino groups; the content of free formaldehyde in the crust comes down.

Tab.2 Effect of $PAMAM_8$' amount on the tanning properties of crust

Amount of $PAMAM_8$	0%	0.2%	0.5%	0.8%	1.0%	1.2%
Ts of crust(°C)	82.1	84.1	86.9	88.2	80.2	69.5
Tensile strength（N/mm²）	9.30	9.6	9.8	10.7	8.9	7.6
Tear strength（N/mm）	17.6	17.9	18.3	19.2	17.4	15.1
Content of free formaldehyde（mg/Kg）	1025.40	856.7	701.9	492.7	410.9	342.8

3.6 Influence of THPS and $PAMAM_8$ combination tannage on dyeing and fatliquoring properties of crust

Numerous amino end groups in the dendrimer $PAMAM_8$ will form a certain amount of amino backbone when combined with leather, which can also improve the dyeing and fatliquoring properties of the crust. It can be seen from the experimental results (shown in Table 3) that comparing with the addition of THPS along, the addition of THPS followed by $PAMAM_8$ during the combination tannage can significantly improve the crust's absorption rate of dye and fatliquoring agents. The bath solution has a light color, and is quite transparent; the crust grain is fine, and has a bright color; the crust surface has a dark color. The above-mentioned experimental results can be explained by the amino end groups of $PAMAM_8$ molecules and tertiary amino groups of ethylenediamine molecule backbone. After formic acid is added to the system on the later stage of dyeing and fatliquoring, as the decrease of the pH of the bath solution, these groups change from dormant cationic to cationic, and are able to react violently with anionic dye and fatliquoring agents. Finally they promote crust's absorption of dye and fatliquoring agents.

Tab.3 Effect of combination of THPS and $PAMAM_8$ on the dyeing and fatliquoring properties

Tannage	Dye uptake(%)	Shade of crust surface	Clarity of effluent after fatli

			quoring
THPS(2%)	89	dark	A little cloud
THPS(2%)+ $PAMAM_8$(0.8%)	95	darker	clear

4 Conclusions

(1) The second generation polyamide-typed dendrimer (abbreviated as $PAMAM_8$) with 8 amino groups on the periphery can be prepared from ethylenediamine and methyl acrylate according to Divergent Synthesis Method. $PAMAM_8$ and THPS were combined to tan raw hide collagen fiber, and it was found that $PAMAM_8$ strengthened THPS' tanning effects obviously.

(2) During $PAMAM_8$ and THPS combination tannage, the tanning effect brought by adding THPS first is far superior to that brought by adding $PAMAM_8$ first. The optimal technology conditions are: THPS 2% (with respect to the weight of raw hide), amino group-terminated dendrimer $PAMAM_8$ 0.8%.

(3) Compared with the crust tanned by THPS alone, the crust, which was prepared by $PAMAM_8$ and THPS combination tannage at the optimal technology conditions, has a shrinkage temperature (Ts) increased by 6℃ and the content of free formaldehyde reduced by more than 50%; its absorption rate of dye and fatliquoring agents is obviously improved during dyeing and fatliquoring; its bath solution has a light color, and its surface has a dark color; its dry sample has tensile strength and tear strength increased by 15% and 9%, respectively.

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