

Preparation and Application of Hyperbranched Poly(amine-ester) with Functional Acylhydrazine Groups as Formaldehyde Scavenger

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Abstract: In this study we investigated the preparation and application of a new hyperbranched polymer as formaldehyde scavenger. Hyperbranched poly (amine-ester) was synthesized with N-ethoxyl-3-amino-N, N-dimethyl propionate and succinic anhydride via one-step manner. The monomer N-ethoxyl-3-amino-N, N-dimethyl propionate was synthesized by Michael addition of ethanolamine and methyl acrylate. Then a new formaldehyde scavenger (FSA) was obtained by hydrazinolysis of hyperbranched poly (amine-ester). Their structures were characterized by FTIR and ¹H NMR. The characteristics and formaldehyde scavenging effects of this product have been investigated. It has been found that this new formaldehyde scavenger has excellent performance of capturing free-formaldehyde in leather and can also improve the physical and mechanical properties of treated leather.

Key words: hyperbranched polymer; acylhydrazine; formaldehyde scavenger; leather

1 Introduction

Hyperbranched polymers (HBPs) are three dimensional highly branched macromolecules with numerous functional groups. In recent years, HBPs have received increasing attention because of their unique structures and properties such as high solubility, low viscosity, and abundance of terminal groups. These features make HBPs potentially applicable as drug-delivery agents, catalysis, micelle mimics, nanoscale building blocks to artificial cells, and so on^[1-3]. Hyperbranched polymers could be synthesized very efficiently on a large-scale through a one-step polycondensation process of AB_x type monomers^[4]. The simplicity of their direct preparation methods enables their production on a large scale at a much more reasonable cost than the cost of ordinary dendrimers. Therefore, increasing efforts are turned to the synthesis and functional modification of hyperbranched polymers. However, so far, few attempts have been made to use hyperbranched polymers as additives in leather and fur industry^[5].

Formaldehyde has been applied in leather industry widely as tanning agent or fixation agent, formaldehyde is also a main raw material of some leather chemicals such as amino resin and synthetic tanning agent. The free-formaldehyde will be inevitably left in the leather when we are using formaldehyde or resins containing formaldehyde in leather-making process. Now it was a common consider that formaldehyde is carcinogenic chemical. The content of free formaldehyde in leather and fur production have been strictly limited in many countries^[6]. However, due to its good properties and low price, formaldehyde can not be substituted at present, so it is necessary and urgent to seek a formaldehyde scavenger with outstanding performance in order to lessen the content of formaldehyde in leather and fur products.

The conventional treatment method to decrease and minimize formaldehyde content in leather is the

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addition of formaldehyde scavengers which are based on some compounds like ammonia, ammonium salts, organic amine and so on. Cheng^[7] investigated the reaction capacity of 18 kinds of small molecular compounds on formaldehyde, and found some small molecular compounds such as sodium bisulfite, sodium sulfite have good capacity to capture free-formaldehyde in leather. Considering small molecular compounds is easy to be washed off in leather processing, it had better choose polymer formaldehyde scavenger in leather-making in order to reduce formaldehyde emissions during storage and service of leather products.

Qiang X.H^[8] prepared the dendri-PAMAM formaldehyde capture agent, which has well capacity for capturing free-formaldehyde in leather and can improve the absorption rate of dye and fatliquoring agent when its dosage is 2%. Zhou Y.X^[9] synthesized polyamino amphiphilic polymer by the copolymerization reaction of acylamide and other vinyl monomer under certain condition and then Hofmann degradation. This polymer could capture about 30% free-formaldehyde in leather and have no side effect on leather properties.

Although hydrazine hydrate has excellent capacity of capturing free-formaldehyde, it can not be used directly because of its toxicity. The intent of this study was to prepare a new polymer formaldehyde scavenger based on hydrazine hydrate. Firstly, the monomer N-ethoxyl-3-amino-N, N-dimethyl propionate was synthesized by Michael addition of ethanolamine and methyl acrylate. Secondly, different generations of hyperbranched poly (amine-ester) with terminal ester groups were synthesized respectively by N-ethoxyl-3-amino-N, N-dimethyl propionate via one-step manner, during which succinic acid anhydride was used as core molecules. Then hyperbranched poly(amine-ester) with functional acylhydrazine groups (FSA) was prepared by hydrazinolysis of obtained hyperbranched poly (amine-ester) and used as a formaldehyde scavenger in leather processing. Its performance of capturing free-formaldehyde and effect on physical and mechanical properties of treated leather were discussed.

2 Experimental

2.1 Materials

Succinic Anhydride, ethanolamine, p-toluene sulfonic acid (p-TsOH), Methanol, methyl acrylate (MA), hydrazine hydrate were purchased from the Shanghai Chemical Company. Methanol, methyl acrylate (MA) were distilled just prior to use. All chemicals used were analytical grade. Deionized water was used throughout.

2.2 Preparation of N-ethoxyl-3-amino-N, N-dimethyl propionate

N-ethoxyl-3-amino-N, N-dimethyl propionate was prepared according to Scheme 1. In a flask equipped with a stirrer, thermometer, and reflux condenser, 1 mol freshly methyl acrylate was reacted with 1mol ethanolamine in methanol under a nitrogen atmosphere at 25 °C for 24 hrs. Then the flask was connected with a revolving-distillation apparatus. Under reduced pressure, the residual MA and methanol were removed from the reaction system. The reaction product was colorless transparency oily liquid.

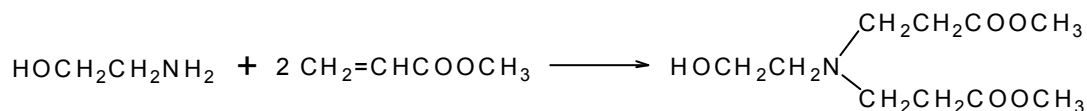
2.3 Preparation of ester-terminated hyperbranched poly(amine-ester)

Ester-terminated hyperbranched poly(amine-ester) were synthesized via a one-step manner in the melt at 120 °C using succinic anhydride (as a molecular core) and N-ethoxyl-3-amino-N, N-dimethyl propionate (as an AB₂ monomer) with p-TsOH as the catalyst. Different generations of hyperbranched poly(amine-ester) were prepared by changing the ratio of molecular core and monomer. The synthesis route was shown in Scheme 2.

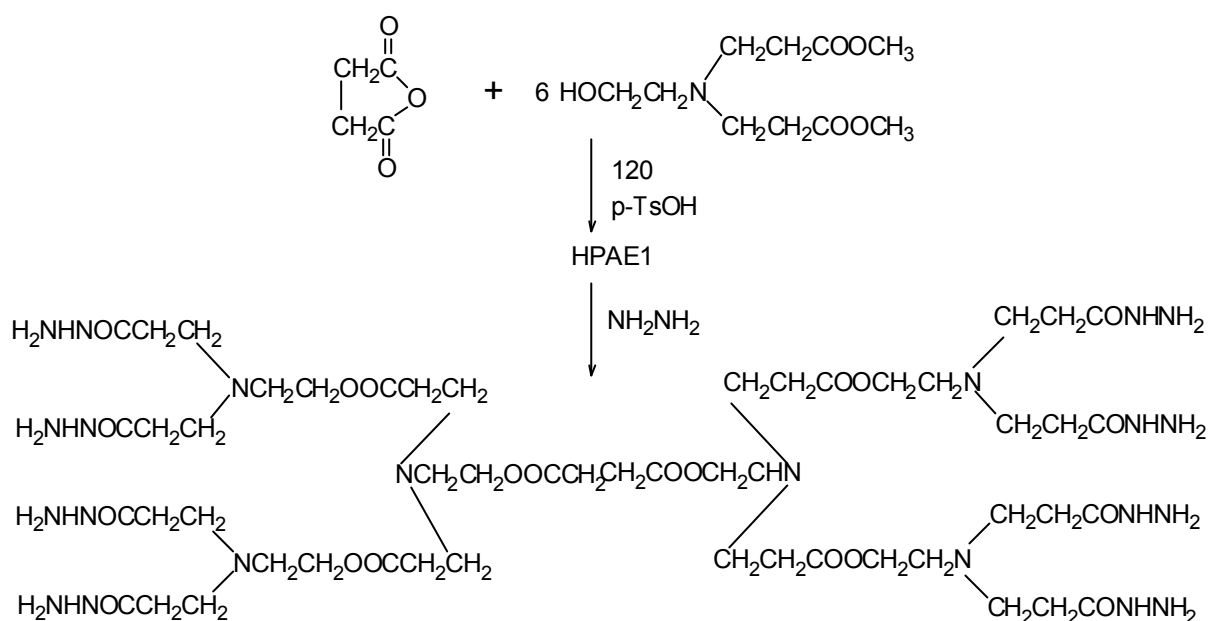
2.4 Preparation of formaldehydescavenger FSA

The preparation and structure of FSA is also given in Scheme 2. A typical example is given as follows:

261.2 g of the third generation of hyperbranched poly (amine-ester) and 120.1g of hydrazine hydrate were placed in a flask. The mixture was kept at 70 °C for seven hours with stirring. Then under reduced pressure, the residual hydrazine hydrate was removed from the reaction system. A thick yellow liquid was obtained.



Scheme 1 Synthesis route of N-ethoxyl-3-amino-N, N-dimethyl propionate



Scheme 2 Synthesis route of hyperbranched poly(amine-ester) with acylhydrazine groups

2.5 Characterization

2.5.1 FTIR Analysis

The FTIR spectra were measured with a Bruker Tensor 27 spectrometer in the region 400cm⁻¹~4000cm⁻¹ by smear method.

2.5.2 ¹H NMR Analysis

¹H NMR spectra were recorded on an AVANCE-400MHz spectrometer in CDCl₃.

2.6 Application formulations of FSA

The experimental material was shaved chrome tanned pig skin (thickness was about 0.5~0.6 mm). The process was carried out in drums. The wet-blue was cut along the backbone into two parts. The right half was processed according to a standard process. The left half of the leather was treated similarly and the experimental products were employed. The retanning and fatliquoring materials were kindly provided by a local tannery. The formulation used is presented in Tab.1. In Tab.1, formaldehyde as retanning agent was used directly, or two commercial amino resin retanning agent were used, which contain about 4000 ppm free-formaldehyde.

2.7 Sample analysis

2.7.1 The content of free-formaldehyde

The content of free-formaldehyde in leather was measured according to reference. Distilled water as extract solvent and acetylacetone as developing reagent, the method can be seen in GB/T 19941-2005 .

$$\text{Capture ratio (\%)} = (W_1 - W_2) / W_1 \times 100\%$$

Where: W_1 -the content of free formaldehyde in blank leather (mg/kg)

W_2 -the content of free formaldehyde in leather after captured (mg/kg)

2.7.2 Thickness Increment Ratio

The thickness increment ratio(Δd) was determined using a thickness measurement apparatus.

$$\Delta d = (d_2 - d_1) / d_1 \times 100\%$$

In which, d_1 is average thickness of leather sample before treatment.

d_2 is average thickness of leather sample after treatment.

2.7.3 Mechanical Properties

The tensile strength, and Unit Elongation Ratio were determined on a tensile testing machine according to the standard for pigskin garment leather.

2.7.4 The color and grain grade

The color and grain grade was evaluated through sense.

Tab. 1 Retanning and fatliquoring formulation of blue pigskin garment leather

Operation	Products	T(°C)	Quantity(%)	Time(min)	Control
Washing	Water	35	400	60	
	detergent		0.5%		
Drain					
Neutralizing	Water	35	200	60	
	NH ₄ HCO ₃		1.0		
	NaHCO ₃		0.5		check pH 5.5,cross-section blue to BCG
Washing	water	35	200		
Retaning	water	35	150		
	dicyandiamide-formaldehyde resin		2		
	mela mine-formaldehyde resin		3	120	
	Or				
	Formaldehyde(3 7%)		2	120	
Drain					
Filling	Water	35	150		
	FSA series ^a		X ^b	60	
Washing	Water	35		30	
Dyeing and	Water	50	150		
Fatliquoring	Dyestuff(black)		2	60	
	Fatliquor agent		18	60	
	HCOOH		1.5	30	Check pH 3.8~4.0
					Drains ,washing, dry.

a: omitted in the control test

b: based on solid

3 Results and discussion

3.1 Structure Analysis

Fig.1 demonstrates the typical FTIR spectra of N-ethoxyl-3-amino-N, N-dimethyl propionate. The bands are identified as follows: the band at 3397cm^{-1} is attributed to —OH stretching peak, the bands at 2953cm^{-1} and 2882cm^{-1} are due to —CH_3 and —CH_2 symmetric and asymmetric stretching vibration. The band at 1733cm^{-1} is characteristic absorption of —C=O . The bands at 1440cm^{-1} and 1364cm^{-1} are attributed to bending vibration of —CH_3 and —CH_2 groups, and the bands at 1200cm^{-1} and 1035cm^{-1} to the C-N and C-O stretching vibration. The absorption of C=C at 1600cm^{-1} has disappeared.

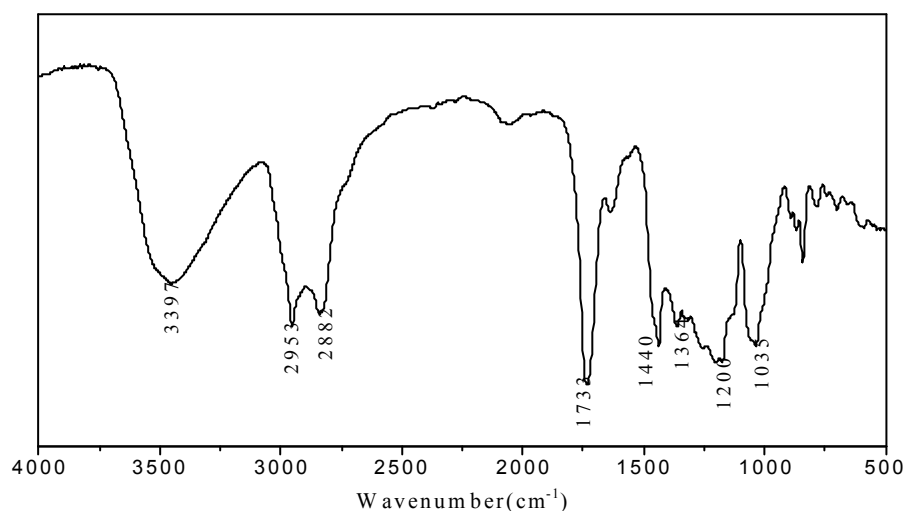


Fig.1 FTIR spectrum of N-ethoxyl-3-amino-N, N-dimethyl propionate

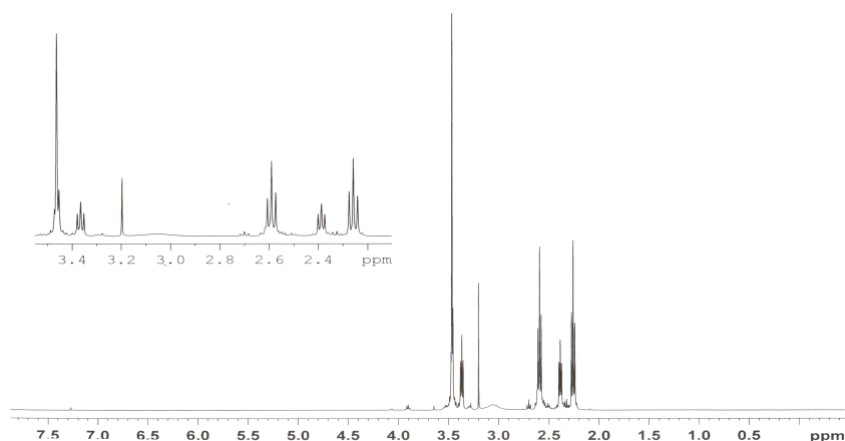


Fig.2 ^1H NMR spectrum of N-ethoxyl-3-amino-N, N-dimethyl propionate

Fig.2 shows ^1H NMR spectrum of N-ethoxyl-3-amino-N, N-dimethyl propionate. $\delta(\text{C}\underline{\text{H}}\text{OOC})$ was 3.44 , $\delta(\text{OOC}\text{C}\underline{\text{H}}_2\text{CH}_2)$ was 2.26 , $\delta(\text{OOC}\text{CH}_2\text{C}\underline{\text{H}}_2)$ was 2.59 , $\delta(\text{NCH}_2\text{CH}_2\text{O}\underline{\text{H}})$ was 3.20 , $\delta(\text{NCH}_2\text{C}\underline{\text{H}}_2\text{OH})$ was 3.35 , $\delta(\text{NC}\underline{\text{H}}_2\text{CH}_2\text{OH})$ was 2.37 . The absorption peak of vinyl hydrogen was not found, which indicated the Michael addition of ethanolamine and methyl acrylate was completed successfully.

Fig.3 shows the FTIR spectrum of the second generation of hyperbranched poly (amine-ester), which is similar with that of N-ethoxyl-3-amino-N, N-dimethyl propionate. The bands at 1739cm^{-1} , 2947

cm^{-1} and 2850 cm^{-1} are strengthened obviously. Fig. 4 shows ^1H NMR spectrum of the second generation of hyperbranched poly (amine-ester), the absorption peak at $\delta 3.20$ of $(-\text{NCH}_2\text{CH}_2\text{O}-)$ has disappeared, which shows that polymeric reaction has happened.

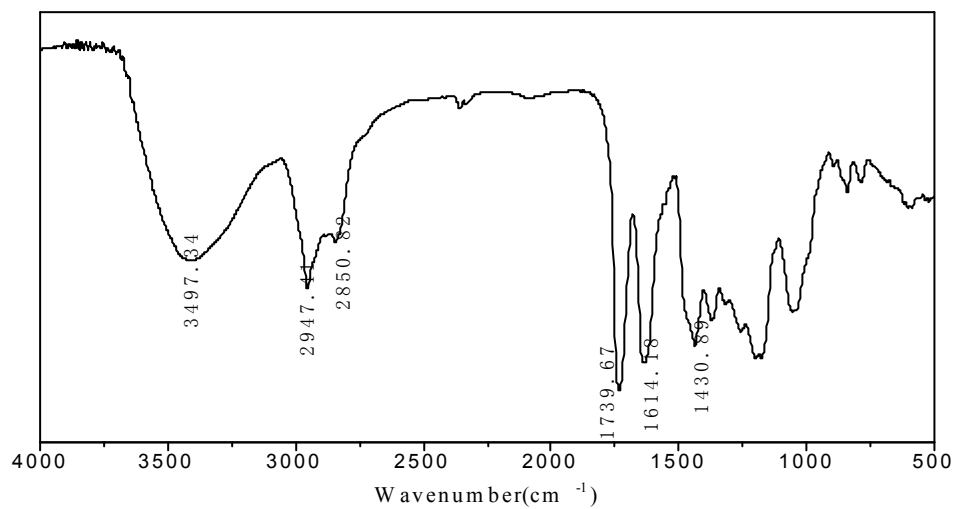


Fig.3 FTIR spectrum of the second generation of hyperbranched poly (amine-ester)

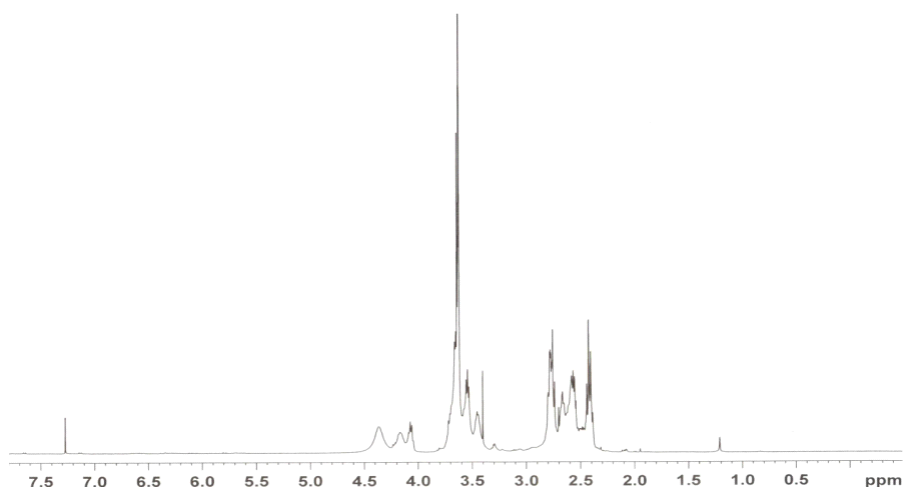


Fig.4 ^1H NMR spectrum of the second generation of hyperbranched poly (amine-ester)

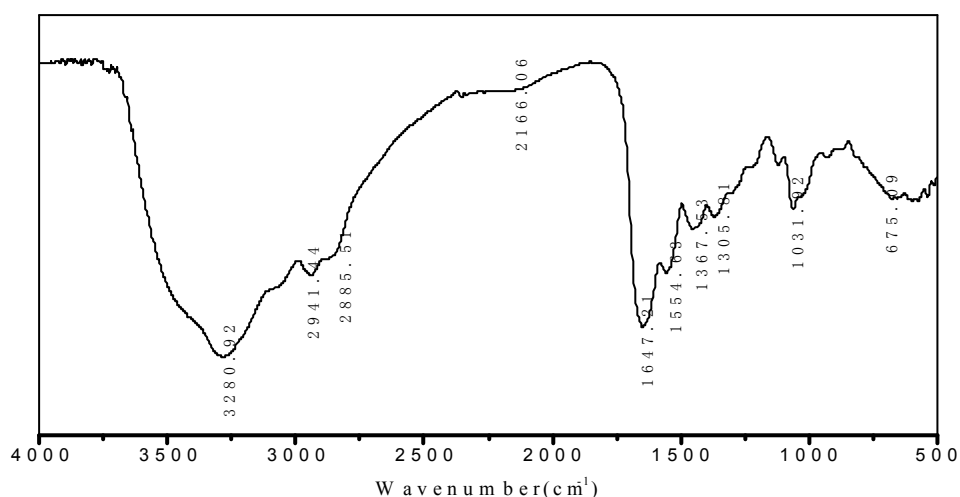


Fig.5 FTIR spectrum of FSA

Fig. 5 is FTIR spectrum of the formaldehyde scavenger FSA. The bands are identified as follows: the band at 3280.92cm^{-1} is attributed to N-H stretching vibration in $-\text{NH}-\text{NH}_2$ group. The bands at 2941.44cm^{-1} and 2885.51cm^{-1} are due to stretching vibration of methyl and methylene. Comparing with Fig.3, the absorption of ester carbonyl at 1739.67cm^{-1} disappeared, while the absorption of CO-NH at 1647.21cm^{-1} appears, which indicates that the hydrazinolysis reaction of hyperbranched poly (amine-ester) has happened.

3.2 Effect of FSA on the content of free-formaldehyde in leather

Tab.2 shows that the capacity of capturing formaldehyde of FSA as a function of different generation at the same dosage. The results indicate that with the addition of FSA, the content of free formaldehyde in the leather decreased significantly. The capacity of capturing formaldehyde of FSA increased with the increase of their generation. When the generation of FSA increases, the content of acylhydrazine in polymer molecular also increases. An increase in the content of acylhydrazine can lead to more functional group, which tend to react with free formaldehyde.

Tab.2 Effect of the different generations of FSA on capacity of capturing formaldehyde

Sample	The content of formaldehyde (mg/L)	The content of formaldehyde (mg/kg)	The capture rate of formaldehyde (%)
Blank	0.351	161.01	0
the second generation	0.229	106.02	34.15
the third generation	0.180	81.82	49.18
the fourth generation	0.156	71.42	55.64

Tab.3 Effect of the dosage of FSA on performance of capturing formaldehyde in leather treated by formaldehyde retanning agent

The Dosage of FSA(%)	The content of formaldehyde (mg/ L)	The content of formaldehyde(mg/kg)	The capture rate of formaldehyde (%)
0	0.585	585	—
0.5	0.463	463	20.85
1	0.349	349	40.34
2	0.176	176	69.91
3	0.164	164	71.96

Tab.4 Effect of the dosage of FSA on performance of capturing formaldehyde in leather treated by amino resin retanning agent

The Dosage of FSA(%)	The content of formaldehyde (mg/ L)	The content of formaldehyde(mg/kg)	The capture rate of formaldehyde (%)
0	0.4321	192.3	—
0.5	0.3589	178.1	7.38
1	0.3101	143.7	25.27
2	0.2451	110.5	42.54
3	0.2126	89.95	53.22

Tab.3 and Tab.4 show that the capacity of capturing formaldehyde of FSA as a function of different dosage. The content of free-formaldehyde in leather is closely related to the chemicals employed in leather making. When the formaldehyde (37%) was used directly as a retanning agent, the content of free-formaldehyde in leather is about 585 ppm, while ordinary amino resin was used as retanning agent, the content of free-formaldehyde is about 192 ppm. The experimental results indicate that with the increase of FSA dosage, the content of free-formaldehyde in the leather decreased gradually. When the amount of FSA is above 2.0%, the reduction of the content of free-formaldehyde was not remarkable. When the dosage of FSA is 3%, the content of free formaldehyde in the leather can decrease to below 200 ppm and below 100 ppm respectively.

3.3 Effect of FSA on physical and mechanical properties of leather treated

The physical testing results of the treated leather are tabulated in Tab.5. It is evident from Tab.5 that the molecular weight of polymer has effect on the physical and mechanical properties of treated leather. The tensile strength of treated leather increased obviously with the generation of polymer, the tearing

strength and thickness increment of treated leather increased slightly with the generation of polymer, while unit load elongation of treated leather decreased slightly with the generation of polymer. In addition, the crust leather had clear grain, deep color of surface. With the addition of FSA, the absorption rate of dyestuff and fatliquoring agent raised obviously. This may be because the abundant amine groups in FSA can help the treated leather to absorb more anionic materials.

Tab.5 Physical and mechanical properties of chromed leather treated by FSA series

Sample	Thickness	Tensile Strength	Unit Load	Tearing Strength
	Increment (%)	(N/mm ²)	Elongation (%)	(N/mm)
Control	0	18.29	68.79	69.05
the second generation	1.3	25.54	66.03	69.37
the third generation	1.4	28.47	63.89	72.54
the fourth generation	1.8	29.72	61.16	75.29

4 Conclusions

Hyperbranched poly (amine-ester) with functional acylhydrazine groups (FSA) can be used as a novel formaldehyde scavenger in leather industry. The synthesis route of FSA is as follows: hyperbranched poly (amine-ester) was synthesized with N-ethoxyl-3-amino-N, N-dimethyl propionate and succinic anhydride via one-step manner. The monomer N-ethoxyl-3-amino-N, N-dimethyl propionate was synthesized by Michael addition of ethanolamine and methyl acrylate. Then FSA was prepared by the hydrazinolysis reaction of hyperbranched poly (amine-ester). Their structures were confirmed and characterized by FTIR and ¹H NMR. FSA would have a dual function of absorbing formaldehyde and filling leather. FSA can obviously reduce the content of free-formaldehyde in leather. The generation of FSA is closely related to its capturing ability. When the amount of FSA was 3%, it can absorb more than 50% free-formaldehyde in leather. FSA also has effect on the physical and mechanical properties of treated leather. It can remarkably increase the tensile strength of treated leather, and help the treated leather to absorb anionic dyestuff and fatliquor agent.

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