Paper D5

Synthesis and application of amphiphilic hyperbranched-liner fatliquor

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Abstract: A novel macromolecular amphiphilic hyperbranched-liner polymer was designed and synthesized in which oleic acid was as the hydrophobic group, and terminal hydroxyl hyperbranched polymer was as the hydrophilic group, at 110^{0}C with the vacuum was 0.08MPa in the rotary evaporator. A series of properties, such as saponification value, emulsibility, emulsion stability and so on, was determined. The emulsion particle size distribution was characterized by laser particle size analyzer. In application experiment, the softness, fullness, oily feeling and the absorption of the greased waste water was evaluated. Compared with the leather oiled by LQ-5 and L-3, the leather, greased by hyperbranched-liner polymer and the mixture of the hyperbranched-liner polymer with neutral oil and surfactants, showed excellent physical & mechanical properties and softness. The results showed that, when certain amount of hydroxyls were replaced by hydrophobic groups, the fatliquoring effect of hyperbranched-liner polymer and its complex with other neutral oil or surfactants were excellent.

Key words: hyperbranched-liner polymer; application; complex fatliquor

1 Introduction

Fatliquor, which affects the quality of softness, fullness and flex resistance, is one of the most important chemicals in leather production. Nowadays, most fatliquors are modified oil, which contained sulfation, phosphorylation, sulfonation, esterification, amidation, quaternary ammonium products, and other synthesized polymer or liner micromolecule. Hyperbranched polymer is a kind of multibranched polymer and has many particular characteristics, such as low viscosity, excellent solubility, multiterminal groups and three-dimensional structure, so it is paid more attention in macromolecule. There is no report on the exclusive application of hyperbranched-liner polymer in leather fatliquoring process. Chen[3] synthesized a hyperbranched polymer which was used in leather industry as retanning agent and fatliquor. The terminal carboxyl groups can combine with Cr^{3+} on the collagen fiber. However, some terminal groups are modified by acrylic acid and the hydrophobicity of long chain acrylic acid polymer can lubricate collagen fiber. So the hyperbranched polymer shows excellent retanning and greasing effect. There are particular cavity and multiterminal groups in hyperbranched-liner polymer fatliquor, so it can package micromolecule and form single molecular micelles in solution. It is beneficial for hyperbranched-liner polymer to emulsify and disperse in solution. All of these indicate that hyperbranched-liner polymer will present excellent application effect in leather greasing. In this paper, an amphiphilic hyperbranched-liner polymer through oleic acid modified hyperbranched polymer with terminal hydroxyl was synthesized, which would help to increase combination so that to enhance the greasing effect. The hyperbranched-liner polymer and its complex with other neutral oil or surfactant were used in fatliquoring process. And the size distribution of emulsion fatliquor and greasing effect were studied, such as physical & mechanical properties, softness and fullness of leather. Meantime, the result was compared with other commercial fatliquor.

2 Experimental section

2.1 Materials

Methyl acrylate (MA) (distilled before use), diethanolamine (DEA), p-toluenesulfonic acid (p-TSA), diethyl malonate (DEM), and trimethylol propane (TMP) were provided by Tianjin No.1 Chemical Reagent Factory (Tianjin, China). The fatliquor L-3 (commercial reagent) was supplied by Tingjiang New Materials Co., Ltd. Oleic acid (AR) was purchased from BASF Chemical Co., Ltd. Tianjin, Bubulum, fatty alcohol-polyoxyethylene ether (AEO-9), castor oil, bean oil, L-3and LQ-5 were supplied by Tingjiang New Materials Co., Ltd.

2.2 Preparation of hyperbranched polymer with terminal hydrophilic groups

Hyperbranched polymer with hydroxyl groups was synthesized by melt polycondensation technique in accordance with the former work as the document[5], in which AB_2-type monomer was charged to TMP kept in a four-neck round bottom flask placed over oil bath and equipped with a thermometer, mechanical stirrer, nitrogen inlet and Dean-Stark apparatus. The reaction mixture was slowly heated to 120^0C. After complete melting of the reactants, the temperature was maintained between 110~120°C with a continuous nitrogen flow for about 4~5h. 2% *p*-TSA (basing on the total weight of monomer and TMP), was as the catalyst of the transesterification reaction, was added. Similarly, using the same apparatus, the second and the third generation terminal hydrophilic hyperbranched polymers were prepared by adding the required amount of monomer and TMP at one time. The preparation principle as followed:

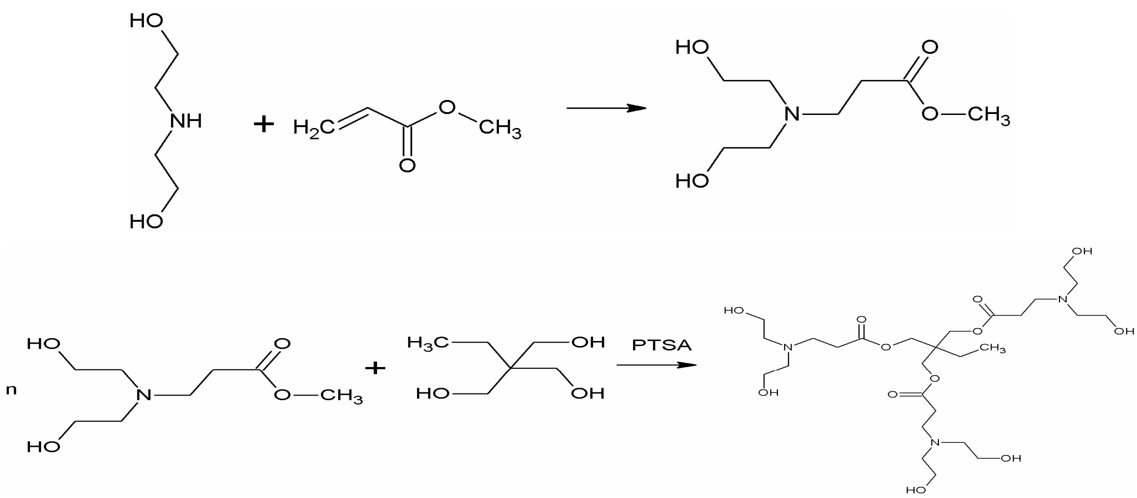

Figure 1 progress of synthesized hyperbranched polymer with hydroxyl groups

2.3 Preparation of hyperbranched-liner polymer fatliquor

In a flask equipped with a magnetic stirring, oleic acid and terminal hydroxyl hyperbranched polymer, prepared in 2.2, were complexed. The molar ratio of terminal hydroxyl hyperbranched polymer and oleic acid was 6:1 (HPB-1), 6:2(HPB-2), 6:3(HPB-3), 6:4(HPB-4), 6:5(HPB-5), 6:6(HPB-6), respectively. The vacuum was 0.08MPa, temperature was 110^{0}C and the reaction was kept for 3h. HPB-6 has not contained hydroxyl, because all of hydroxyl had replaced by the oleic acid through esterfication.

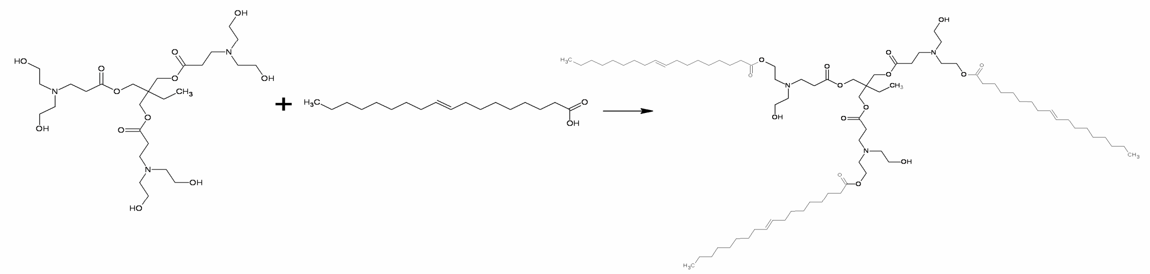

Figure 2 The reaction scheme for HPB-3

2.4 Application experiment

The hyperbranched-liner polymer was mixed with bubulum, AEO-9, castor oil and bean oil according to certain mass ratio, and then some kinds of complex fatliquor, with the solid content was 50%, were obtained. They were used in fatliquoring of pig skins and compared with commercial products L-3 and LQ-5. L-3 is an anionic and multifunctional fatliquor which is prepared by sulfited reaction of modified natural oil. LQ-5 is one of synthesized macromolecule hydrocarbon fatliquor and has excellent electrolyte resistance performance, so it is widely used in large-scale tanneries along the coast of China. The pickled pig skin was sampled in symmetrical position and it was as raw material to produce garments leather. The softness, fullness, oily feeling and absorption of waste water after greased were determined to evaluate the application properties of fatliquor. All indexes were appraised by experts in the same condition. (Full marks were 10, the higher of score the better of softness, fullness, oily feeling and absorption of greased waste water). The technics was as the follows.

2.5 Characterization

Fourier transform infrared spectroscopy (FTIR) was recorded on a VECTOR-22 fourier transform infrared spectrophotometer (Germany). ^{1}H-NMR spectra were recorded on a AVANVE-400 MHz using DMSO-d6 according to a method described by Malstro¨m et al[14]. The emulsion stability and saponification value of hyperbranched-liner polymer were determined according to the document [7],[8]. The size and size distribution of particle were obtained from Malvern laser particle size analyzer (master sizer 2000). The leather greased by different fatliquor was evaluated its softness, fullness, oily feeling and absorption of greased waste water by experts at the same condition. The physical and mechanical properties, such as tensile strength, tear strength, bursting strength, elongation, were measured according to the reference [11].

Table 1 Greasing process of pigskin garment leather

Process	amount/%	Chemicals	T/^{0}C	time/min	pH	Remarks
Re-pickling	100.0	water	20			
	7.0	salt				
	1.5	formic acid		10		
Add skin				60	2.5	
tanning	8.0	Tankrom SB		120		
	1.0	Sodium bicarbonate		4*30+60	4.0	overnight
				30	3.5	Measure Ts
	0.6	Sodium bicarbonate		2*30	4.0	
Rinse	300.0	Water	40			
	1.5	Degreasing agent				
	0.3	Oxalic acid		40	4.0	
Re-tanning	100.0	Water	40			
	3.0	Tankrom FS		120		Measure pH
	0.6	Sodium bicarbonate		2*30	5.0	
Washing	300.0	Water	45	10		
Greasing	100.0	Water				
	16.0	Fatliquor *	45	60		
	0.5	Oxalic acid		45	3.5	

*Remarks: Fatliquor were self-prepared amphiphilic hyperbranched-liner polymer, L-3 and LQ-5; the weight of acid skin was increased 50%.

3 Results and Discussion

3.1 FTIR spectrum analysis

As shown in Fig.3 measured by VECTOR-22 Fourier transform infrared spectrophotometer, the strong absorption band observed at 1445cm^{-1} and 990cm^{-1} in MA was associated with C=C stretching vibration. This band disappeared in the spectrum of its monomer, which indicated that most C=C had been consumed in addition reaction. The absorptions at 1440cm^{-1} and 1363cm^{-1} assigned to bending vibration absorption peaks of OH indicated that the characteristic absorption peaks at 3386cm^{-1} belonged to the OH stretching vibration and not to NH. The absorption at 1734cm^{-1} was assigned to C=O in the ester units ($COOCH_3$). All these spectral data proved that AB_2-type monomer had been formed in the addition reaction.

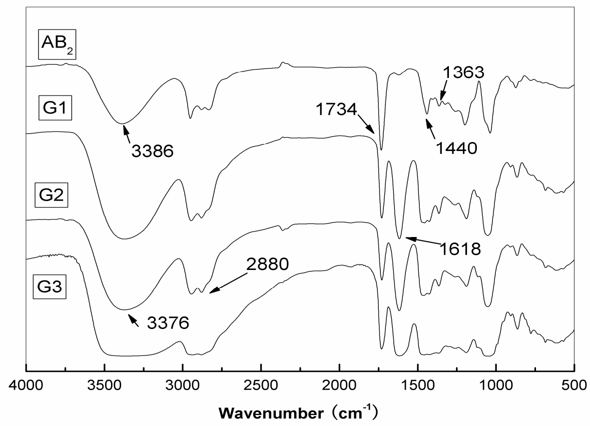

Figure 3 The IR spectrums of hyperbranched polymer with terminal hydroxyl (G1, G2 and G3) and AB_2 type monomer (AB_2)

It can be seen that FTIR spectrums of hyperbranched polymer with terminal hydrophilic groups and monomer were similar. The functional groups of different generations of polymer were basically consistent. But the absorption peaks of OH at 3376cm^{-1}, C-H at 2880cm^{-1} and C-N at 1618cm^{-1} significantly became strong.

3.2 FTIR spectrum of hyperbranched-liner polymer fatliquor

Figure 4 showed the spectrum, recorded on Verte 70 form American Brook Company, of hyperbranched-liner polymer fatliquor, the strong absorption band observed at 3458cm^{-1} and 1379 cm^{-1} was associated with -OH stretching vibration. The absorption of 2928 cm^{-1} was associated with $-CH_2$ and $-CH_3$ stretching vibration. The stretching vibration of ester appeared at 1741cm^{-1}. In 1654 cm^{-1}, it presented the stretching vibration of C=C, which demonstrated that oleic acid was successfully grafted in hyperbranched polymer.

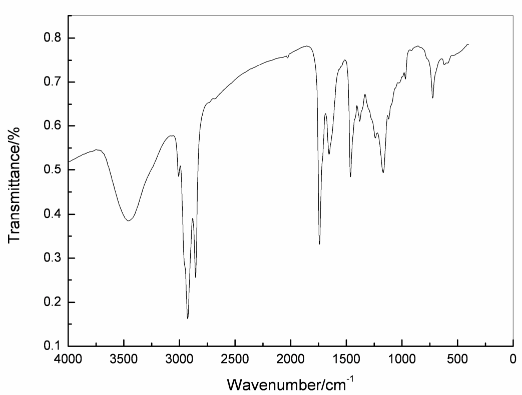

Figure 4 FTIR spectrum of hyperbranched-liner polymer fatliquor

3.3 1H-NMR spectrum of hyperbranched-liner polymer fatliquor

As shown in figure 5, chemical shift signal at 2.5ppm assigned to dimethyl sulfoxide-D6', the peak on

1.24ppm assigned to methylene of hydrophobic group in oleic acid. The signal on 3.35ppm belonged to methylene in hyperbranched polymer. The multiple signals at 0.85ppm assigned to methyl which came from TPM. Signals on 1.97ppm and 2.18ppm belonged to methylene in $-NCH_2CH_2$ and $-OOCCH_2CH_2$. The Multiple peaks at 5.3ppm assigned to C=C resulting from reaction of oleic acid with hyperbranched polymer, which demonstrated that oleic acid had reacted with hydroxyl in hyperbranched polymer.

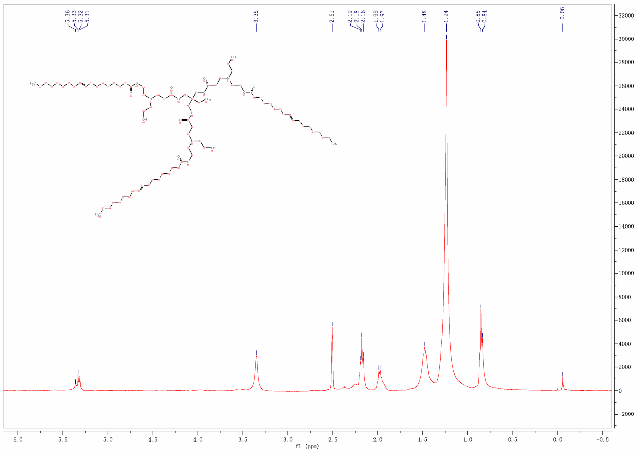

Figure 5 ^{1}H-NMR spectrum of hyperbranched-liner polymer fatliquor

3.4 Physical and chemical properties and emulsion stability

The physical & chemical properties of HPB-4 was tested and shown in table 2. We could see that all the physical & chemical properties were in the range of suitable classes. And the emulsion stability about different mass ratio of hyperbranched-liner polymer with neutral oil and AEO-9 were researched. The result showed that when the mass ratio of AEO-9 with HPB-5 was 1:9, 3:17, 1:5, and the mass ratio of AEO-9 with HPB-6 was 1:9, 3:17, 1:5, the emulsion presented stratified. However, as the mass ratio was 1:19, the hyperbranched-liner with bubulum, bean oil, castor oil, and AEO-9 did not present stratified.

Table 2 physical and chemical properties and emulsion stability of HPB-4

Parameter	Result
Appearance	Orange-red transparent oily liquid
pH	6.1-6.8
Water and volatile matter/%	<4.5%
saponification value /mg(KOH)*g-1	172
Relative density/g*cm3	0.937
Refractive index	1.461
Emulsion stability	1:9 emulsion>24h no stratified

3.5 Emulsion particle size analysis

As shown in figure 6, 7, 8, we could see that the emulsion particle size distribution of HPB-2 was larger than that of HPB-3. The reason was that the hydrophilic groups of HPB-2 were more than that of HPB-3; it would form a hydration layer in particle surface which resulted HPB-2's emulsion particle size was larger than that of HPB-3. The hydrophilic and hydrophobic properties of HPB-3 were better than that of HPB-2, the distribution of emulsion particle size was narrow and the average particle size of emulsion was smaller than that of HPB-2. The average particle size of HPB-3 and HPB-4 had little difference, which was according to the consequence of the effect in greasing. Figure 7 and 8 showed that as the hydrophobic groups increased, the average particle size increased. The reason was that too many hydrophobic groups would hinder from the fatliquor dispersing, as s result, the average particle size was larger. It was difficult for larger particle size to unevenly distribute in leather fibers. The result was identical to the result of greasing. From figure 9, we could see that the average particle size of the mixture of HPB-5 and AEO-9 was smaller than that of HPB-5, which indicated that the mixture could more well dispersed in collagen fiber than HPB-5. The reason was AEO-9 could help HPB-5 distribute in water, which was beneficial for the mixture to infiltrate into collagen fiber that concerned with softness of leather.

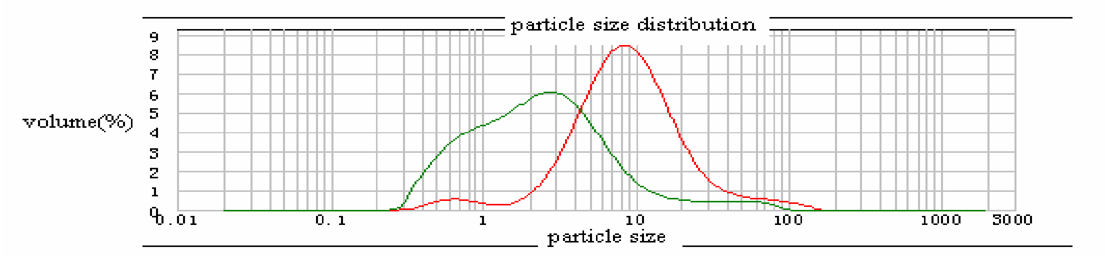

Figure 6 The distribution of emulsion particle size(μm) for HPB-2 and HPB-3

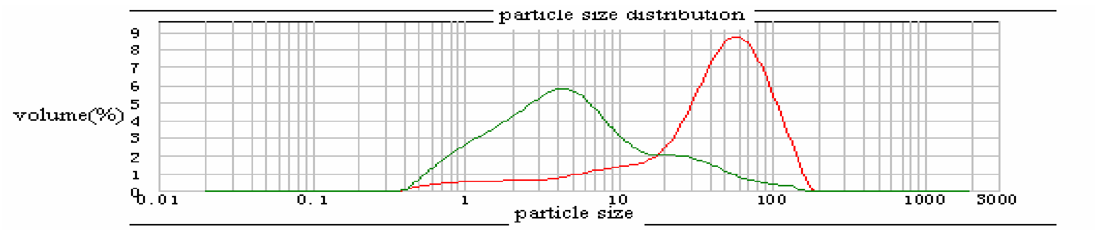

Figure 7 The distribution of emulsion particle size(μm) for HPB-4 and HPB-5

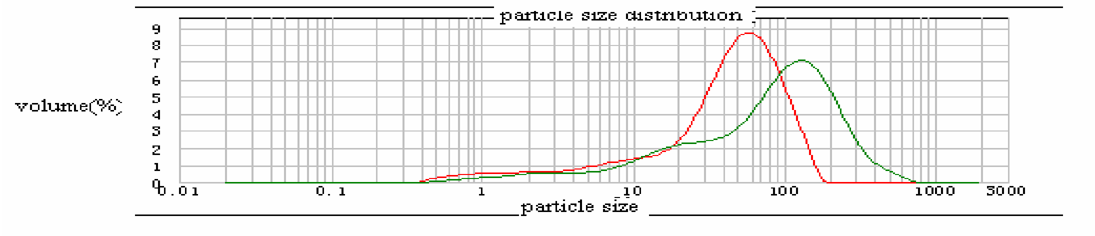

Figure 8 The distribution of emulsion particle size(μm) for HPB-5 and HPB-6

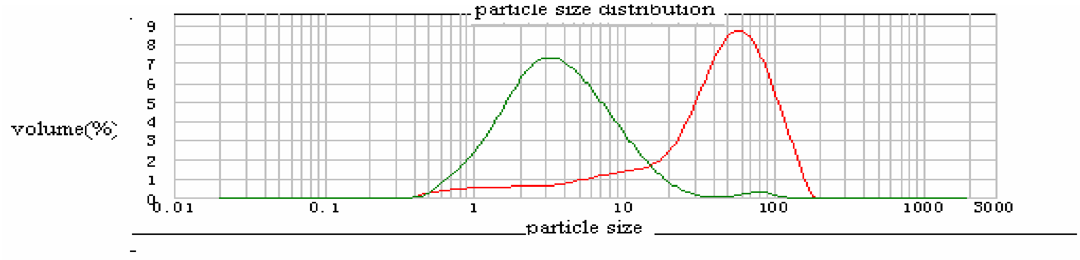

Figure 9 The distribution of emulsion particle size(μm) for HPB-5 and the mixture of HPB-5 and AEO-9

3.6 Performance testing after leather greased

3.6.1 Properties of leather oiled by hyperbranched-liner polymer

As shown in table 3, the leather oiled by HPB-3 and HPB-4 had perfect softness, fullness and high absorption of waste water. The reason might be that HPB-1 contained many hydrophilic groups that could not combine with leather; as a result, it was unhelpful to improve softness. However, HPB-5 and HPB-6 contained many hydrophobic groups so that it could unevenly distribute in water, which were adverse to enhance softness. As the hydrophobic groups increased, the softness of leather increased and then decreased, and the oily feeling increased unremittingly, which demonstrated that it was significant to control the hydrophilic and hydrophobic properties.

Table 3 The properties of leather oiled by hyperbranched-liner polymer

Fatliquor (solid content was 50%)	Softness	Fullness	Oily feeling	Absorption of greased fatliquor
HPB-1	3	5	5	9
HPB-2	5	7	7	8
HPB-3	10	10	8	9
HPB-4	10	8	7	8
HPB-5	7	8	8	5
HPB-6	6	8	8	5

3.6.2 Performance of leather oiled by mixture of hyperbranched-liner and neutral oil

Because neutral oil could improve oily feeling of leather, the bubulum, bean oil and castor oil were mixed with hyperbranched-liner polymer in different mass ratio. As shown in table 4, the fatliquoring effect of the mixture of HPB-2 and bubulum was the best, and other complex fatliquor were unsatisfactory in greasing. The reason might be that the bubulum consisted of oleic acid and triolein which was helpful for compatible with HPB-2. It was beneficial for fatliquor to penetrate into collagen fiber so that to enhance softness of leather. As the increase of amount of bubulum, the softness of leather decreased. The reason was that emulsification of macromolecular bubulum was poor; as a result, it was difficult for bubulum to penetrate into collagen fiber and caused softness and absorption of waste water decreased.

Table 4 effect of greasing by mixture of hyperbranched-liner polymer and neutral oil

Fatliquor (solid content was 50%)	Softness	Fullness	Oily feeling	Absorption of greased fatliquor
Mixture of 95%HPB-2 and 5% bean oil	6	8	5	9
Mixture of 95%HPB-2 and 5% bubulum	9	8	8	9
Mixture of 95%HPB-2 and 5% castor oil	4	8	5	9
Mixture of 90%HPB-2 and 10% bubulum	6	7	7	7
Mixture of 90%HPB-2 and 10% castor oil	5	8	4	6
Mixture of 90%HPB-2 and 10% bean oil	7	8	8	8

3.6.3 Performance of leather oiled by mixture of different hyperbranched-liner with bubulum and AEO-9

Because the content of hydrophobic groups, HLB value and emulsification property of HPB were different, HPB with different hydrophobic groups' content was mixed with bubulum, AEO-9. Then they were used to fatliquor. As shown in Table 5, the softness, oily feeling and fullness of leather oiled by the mixture of HPB-4 with bubulum, HPB-5 with AEO-9 and HPB-6 with AEO-9, were excellent. But the absorption of waste water was lower, which indicated that the absorption ratio of fatliquor were incomplete. The mixture of HPB-4 and bubulum could increase the oily feeling.

3.6.4 Comparison results of the mixture of HPB-5 and AEO-9 with commercial products

Based on above results, the fatliquoring effect of HPB-4, the mixture of HPB-5 and AEO-9(the mass ratio was 19:1), the mixture of HPB-4 and bubulum (the mass ratio was 19:1) and the mixture of HPB-2 and bubulum(the mass ratio was 19:1) were the best, so they were compared with some commercial products. The results were shown in table 7. Compared to commercial products, the softness, fullness and color of leather oiled by HPB-4 were excellent, but the leather grain was dried and oily feeling was not strong. Moreover, the leather oiled by the mixture of HPB-5 and AEO-9 presented on good softness, oily feeling, fullness and absorption of waste water. It indicated that its application effect in leather fatliquoring was best.

3.7 Physical and mechanical properties of leather

As shown in table 8, the tensile strength of leather oiled by HPB-4 and the mixture of HPB-5 and AEO-9 was higher than that of LQ-5. But tear strength and elongation were lower. The bursting strength of leather oiled by the kinds of fatliquor has little change, which indicated that the hyperbranched-liner polymer and its mixture with other surfactant could be applied in fatliquoring process.

Table 5 The properties of leather oiled by the mixture of hyperbranched-liner polymer and bubulum or AEO-9

Fatliquor (solid content was50%)	Softness	Fullness	Oily feeling	Absorption of greased fatliquor
Mixture of 95%HPB-1 and 5% bubulum	5	9	8	9
Mixture of 95%HPB-2 and 5% bubulum	5	6	8	9
Mixture of 95%HPB-3 and 5% bubulum	8	6	7	9
Mixture of 95%HPB-4 and 5% bubulum	10	8	7	10
Mixture of 95%HPB-5 and 5% AEO-9	10	8	8	4
Mixture of 95%HPB-6 and 5% AEO-9	10	8	9	6

Table 7 compare commercial commodity with hyperbranched-liner polymer

Fatliquor (solid content was50%)	Softness	Fullness	Oily feeling	Absorption of greased fatliquor
HPB-4	10	9	9	8
LQ-5	10	10	9	4
L-3	10	10	10	10
Mixture of 95%HPB-5 and 5% AEO-9	10	10	9	8

Table 8 Physical and mechanical properties of leather

Fatliquor	Tensile strength(N/mm^2)	Tear strength(N/mm)	Bursting strength(N/mm)	Elongation/%
HPB-4	118.49	26.15	22.1	43.1
95%HPB-5 and 5% AEO-9	81.06	30.34	24.3	39.78
LQ-5	79.48	36.84	24.4	51.92

4 Conclusions

Hyperbranched-liner polymer was synthesized by hyperbranched polymer with terminal hydroxyl groups and oleic acid, and characterized by FTIR and NMR. The result of FTIR and NMR indicated that hyperbranched polymer with terminal hydroxyl was prepared and oleic acid was successfully grafted on terminal hydroxyl hyperbranched polymer. Application result indicated that if HLB value of hyperbranched-liner polymer fatliquor was suitable, whatever it was used solely or blending with other surfactants and neutral oil, it would exhibit excellent properties in softness, fullness, oily feeling and other physical and chemical properties of leather. As the mass ratio of HPB-2 and bubulum was 19:1, the stability of emulsion and properties of greasing were excellent. The properties of leather oiled by HPB-4 and the mixture of HPB-5 and AEO-9 showed excellent, such as softness, fullness, oily feeling and absorption of waste water. Compared with LQ-5 and L-3, there were some advantage on the absorption of waste water and tensile strength. Therefore hyperbranched-liner polymer would be applied in fatliquoring and there was good prospection.

Acknowledgments

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