

Properties of Polymers as a Nanoscale Material for Fibers in Leather

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Abstract: Hyperbranched polymers, an innovative class of nano-polymers, could enhance the properties of fibers owing to their unique structures. In this study, the ester compound (HPAE) of 3-(bis(2-hydroxyethyl)amino)propionic acid and pentaerythritol was treated with undecylenic acid to obtain novel hyperbranched multiterminal alkenyl polymers (HPAE-UAs). The sizes of the HPAE-UAs could be controlled conveniently from 400 to 1300 nm by adjusting the capped fraction of the hydroxyl groups with undecylenic acids. The molecular structures of HPAE-UAs were characterized by means of FT-IR and ¹H-NMR. Then, the effect of the HPAE-UAs on the structures, thermal, and mechanical properties of the wet blue leather were investigated. TEM and SEM demonstrated that the spacing between fibers was enlarged. The thermogravimetric analysis showed that the residual volume of leather could reach up to 30.3 % at about 500 °C. Furthermore, the shrinkage temperature increased to 89.4 °C. It was found that the HPAE-UAs used in leather could improve the thermal performance, physical and mechanical properties. All of these results indicate that HPAE-UAs can be used as a fatliquor with retanning in leather process.

Keywords: Hyperbranched multiterminal alkenyl polymers, Synthesis, Characterization, Crosslinking, Fibers

Introduction

Fatliquoring, a process of coating the surface of leather fibers with a thin layer of oil, is one of the key operations in leather manufacturing [1]. Leather, as a collagen structure material, usually requires the addition of fatliquoring agents that can improve its tensile strength, stitch-tear resistance, abrasive resistance, water-repellent properties, and resistance toward chemical actions [2]. However, the primary purpose of fatliquoring is to reduce the friction between collagen fibers and improve the softness of leather with the aid of fatliquor for the lubrication of leather collagen fibers.

However, most present fatliquors among the fibers are those with linear structure or linear fatliquors with fewer branches. Because of this relatively simple structure, it is hard to produce fatliquor with high efficiency, multi-function, and strong combination. In addition, almost all the retan agents used in leather industry are linear molecular structures which have the disadvantages of single structure, few functional group species, and low activity. What is worse, the absence of all-round three-dimensional combination in fibers results in a poor retanning property.

Hyperbranched polymer is a kind of three-dimensional macromolecular polymer with multiterminal base and higher degree of branching. Compared with dendrimers polymers, hyperbranched polymers have received considerable research attention and have been regarded as a new type of raw material owing to relatively easy preparation, special properties, and potential application prospects. Furthermore, the hyperbranched polymers have multi functional groups, and

they would easily modify substrates. Therefore, it is widely used in the field of liquid crystal display (LCD), functional materials, life sciences, cosmetics, paint, etc [3-8]. Then, the alkenyl group easily reacts with other reagents, yielding alkenylated products. Meanwhile, the collagen fibers contain many functional groups such as hydroxyl, carboxyl, amidogen, and so on. So the alkenyl has strong crosslinking function with collagen fibers.

Although hyperbranched polymer is widely used, their application in fibers of leather as a fatliquor has rarely been studied [9-11]. In this study, HPAE-UAs were synthesized through the reaction of HPAE and undecylenic acid. It was then used between fibers of leather in the process of fatliquoring. The hyperbranched structure, containing the alkenyl group, could enter the fibers, leading to crosslinking between collagen fibers and hyperbranched polymers. Here, when applied to fibers of leather fatliquoring process, hyperbranched multiterminal alkenyl polymers (HPAE-UAs) have been explored and the interaction between HPAE-UAs and collagen fibers has also been investigated.

Experimental

Materials

Methyl acrylate, pentaerythrite, diethanolamine, and undecylenic acid (UA) were purchased from Sigma Aldrich (Shanghai) Trading Co., Ltd. *p*-toluene sulfonic acid (99 %) was from Tianjin Kemiou Chemical Reagent Co., Ltd. Industrial fatliquoring agent (neatfoot oil) was purchased from Shanghai Grain and International Trade Co., Ltd. Acid skin and wet blue goatskin were obtained from Shaanxi Li-Qiang Leather Factory. All these reagents were used without

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further purification.

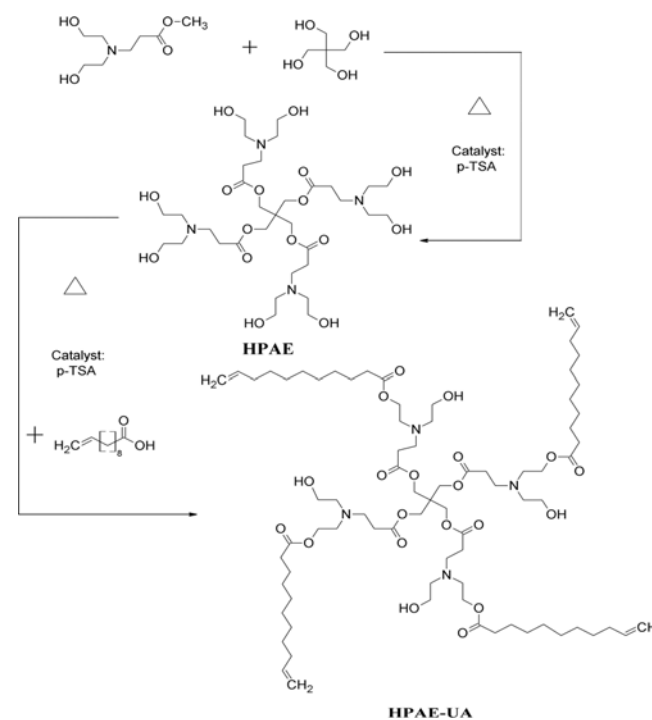
Synthesis of N,N-Hydroxyethyl 2-3 Amino Propionic Acid Pentaerythritol Ester (HPAE)

The N,N-dihydroxy methyl ethyl-3-amino propionic acid was synthesized according to the procedure from our earlier report [12]. Briefly, in a 250 ml three-neck cylindrical glass reactor equipped with mechanical stirrer, Pentaerythritol (13.6 g, 0.1 mmol), N,N-dihydroxy methyl ethyl-3-amino propionic acid (76.4 g, 0.4 mol) and p-toluene sulfonic acid (0.45 g, 0.5 % of the total mass) were added into a reactor and heated to about 120 °C, during which methanol was removed and was reacted for 6 h.

An orange oily (head product) was obtained. It was then cooled, washed by CH₂Cl₂ and filtered in vacuum. The p-toluene sulfonic acid and unreacted pentaerythritol were removed from it. The solvent CH₂Cl₂ was removed through decompression rotary evaporation. Finally, the product of HPAE was obtained after the process was repeated three times.

Synthesis of Hyperbranched Multiterminal Alkenyl Polymers (HPAE-UAs)

HPAE-UAs were synthesized by esterification of HPAE with UAs and p-toluene sulfonic acid as the catalyst. The numbers of consumed hydroxyl groups in HPAE are 12.3 %, 23.7 %, 35.2 %, and 45.4 % respectively and the corresponding specimens are named as HPAE-UA_{0.123}, HPAE-UA_{0.237},



Scheme 1. Detailed scheme for synthesis of HPAE-UA_{0.454}.

HPAE-UA_{0.352}, and HPAE-UA_{0.454}. As a typical example of HPAE-UA_{0.454}, the molar ratio was 1:4 of HPAE and UA. The synthetic route of HPAE-UA_{0.454} is shown in Scheme 1. The flask was immersed in oil-bath at 60 °C, kept thermostatic mixing reaction for 4 h. Then an orange oily was obtained. The unreacted HPAE, UA, and p-toluene sulfonic acid in the mixture were removed by means of vacuum suction filter. An orange oily, a multiterminal alkenyl polymer (HPAE-UA) was obtained by vacuum rotary evaporation with tetrahydrofuran, CH₂Cl₂, de-ionized water, and acetone for obtaining. HPAE-UA_{0.123}, HPAE-UA_{0.237}, and HPAE-UA_{0.352} were synthesized likewise.

The Application of HPAE-UAs in Leather

HPAE-UA as a fatliquor was applied to the process for the goat wet blue. The specific operation process is shown in Table S1. Thermal characterizations and physical mechanical properties among the fibers in leather were tested.

Instrumentation and Characterization

The Fourier transform infrared (FT-IR) spectra were recorded using a Bruker-IFS-88 FT-IR spectrometer with KBr pellets [13,14]. Hydrogen-nuclear magnetic resonance (¹H-NMR) measurements were conducted using an ADVANCE 400 MHz nuclear magnetic resonance instrument from Cerman BRUKER Company and D₂O was used as solvent. Mastersizer 2000 laser particle size analyzer was used to measure the size and distribution of HPAE-UA emulsion (PDI) and the light scattering measurements were performed at 25±0.1 °C and at θ=90° scattering angle. The emulsions were diluted by a factor of 10000, respectively. Potentiometric titration was performed using a Metrohm all purposes 905 Titrino apparatus equipped with a combined 804 Ti Stand and 800 Dosina.

The leather samples were prepared by staining method with Nile blue sulfate salt. The samples were acquired from the leathers and cut into small flakes by frozen sections technology. After dried at room temperature, the samples were disposed by metal spraying. The slices of samples were measured with KH-7700 three-dimensional digital microscope made by HIROX Company. The JSM-7100F field emission scanning electron microscopy (SEM) made by Japanese Electronics was used to measure the size and distribution of the inner fiber bundles of the finished leather. The transmission electron microscopy (TEM) images were obtained using an FEI Tecnai G2 F20 S-TWIN microscope operated at 120 kV. The ATR-FT-IR spectra of the studied leather were detected by a Spectrum 400 FT-IR spectrometer (Bruker Inc. VERTE70) with an ATR attachment (resolution 0.5 cm⁻¹, 32 scans, wavelength range 190-3100 cm⁻¹). The TGA Q500 thermogravimetric analyzer made by American TA Company was used to measure the *T_g* of leather, with the heating rate at 10 °C/min and the room temperature at ~600 °C.

Results and Discussion

Characterization of HPAE and HPAE-UA

The FT-IR spectra of HPAE and HPAE-UA_{0.454} were depicted in Figure S1. It can be seen that the peaks of carbonyl (C=O) and ester bond (C=O-O-C) obviously increased at 1729 and 1192 cm⁻¹ [15]. What's more, in the 734 cm⁻¹, a new bending vibration absorption peak on the olefin (=C-H) appeared. The result shows that the grafting UA onto HPAE gave rise to HPAE-UA.

The molecular structures of UA, HPAE, and HPAE-UA_{0.454} were further analyzed using ¹H-NMR. Figure 1 depicts the ¹H-NMR spectra of UA, HPAE, and HPAE-UA_{0.454}. In the ¹H-NMR spectra of UA (1a), the characteristic absorption peaks of the alkenyl (CH₂=CH-) were clearly found [16], particularly peak a (CH₂=) at 5.83 ppm, peak b (CH=) at 4.98 ppm, peak c (=CH-) at 5.42 ppm. Peak g (O=C-CH₂-) was the methylene connected to the carbonyl at 2.37 ppm. Peak d (=CH-CH₂-) was the methylene connected to alkenyl at 2.05 ppm. Peak f (-CH₂-) and e (-CH₂-) were the methylene far from alkenyl at 1.65 and 1.37 ppm [17]. In the ¹H-NMR spectra of HPAE (1b), peak h (-OH) appeared at 3.67 ppm, peak n (-O-CH₂-) at 3.58 ppm, peak i (HO-CH₂-C-) at 3.41 ppm, peak k&j (-C-CH₂-N-) at 2.99 ppm, and peak m (-C-CH₂-C=O) at 2.37 ppm [18]. From Figure 1(c), it was noted that the proton peak of long-chain in the final product HPAE-UA_{0.454} moved to the low field, but the peak of nucleus in HPAE moved to the high field. Those indicate that ester bond generated between HPAE and UA yielding to a certain shielding effect, which accounts for the successful condensation between the two materials. In brief, the above ¹H-NMR and FT-IR results clearly demonstrated that HPAE-UAs were synthesized successfully.

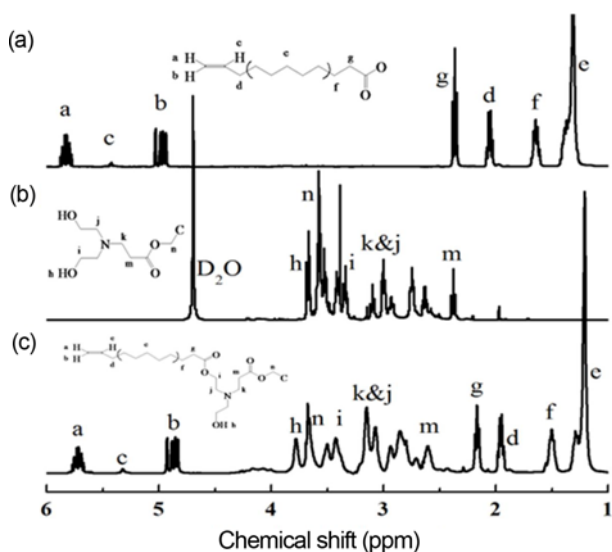


Figure 1. ¹H-NMR spectrum of UA (a), HPAE (b), and HPAE-UA_{0.454} (c).

The molecular structures of HPAE-UAs with different grafting rates were further analyzed using ¹H-NMR (Figure 2). From Figure 2, it can be observed that the proton peaks on the grafting chain increased with the number of grafting. What's more, the movement of some peaks to low field varied, suggesting that the content of ester bond generated by HPAE and UAs determines the strength of shielding effect.

The grafting ratio (*J*) of different HPAE-UAs products can be calculated by comparing the integral of peak a (*S_a*) with that of peak b (*S_b*), and the expression is shown in the formula [19].

$$J = S_a / 2 : S_b / 10 = 5S_a / S_b$$

The obtained *J* values of HPAE-UAs products were 12.3 %, 23.7 %, 35.2 %, and 45.4 %, respectively, indicating a successful condensation between the two materials. The content of hydroxyl in the synthetic product HPAE-UAs were titrated by potentiometric titrator (Table 1). It can be seen that the experimental values were slightly bigger than the theoretical values, mainly due to the fact that the synthesized hyperbranched polymer wasn't in a spherical structure as expected. As a result, the reaction turned to be incomplete. Simultaneously, in the actual process, some hydroxy hid in the molecule and failed to participate in reaction. Consequently the theoretical content of hydroxyl

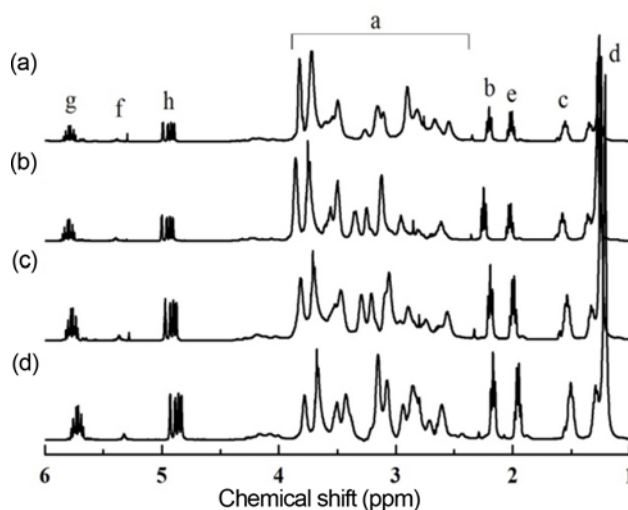


Figure 2. ¹H-NMR spectrum of HPAE-UAs: HPAE-UA_{0.123} (a), HPAE-UA_{0.237} (b), HPAE-UA_{0.352} (c), and HPAE-UA_{0.454} (d).

Table 1. The hydroxyl content in HPAE-UAs

Number	1 [#]	2 [#]	3 [#]	4 [#]
Molar ratio of HPAE and UA	1:1	1:2	1:3	1:4
Theoretical value (mmol/g)	8.05	5.79	4.16	2.92
Measured value (mmol/g) ^a	9.01	6.45	4.97	3.72

^aDetermined by ¹H-NMR.

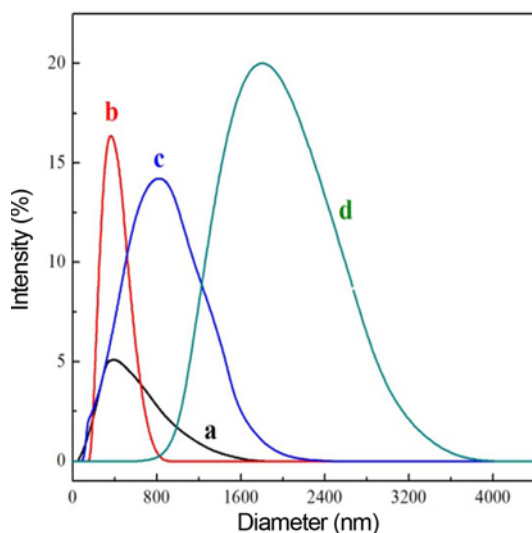


Figure 3. Typical intensity-weighted size distributions of HPAE-UA: HPAE-UA_{0.123} (a), HPAE-UA_{0.237} (b), HPAE-UA_{0.352} (c), and HPAE-UA_{0.454} (d) in water.

was smaller than that of experimental.

Generally, polymers with higher degree of polymerization have large sizes when dissolved into solvents [20]. In the fatliquoring process, the size of emulsion particles plays an important role in the product's entering fibers in leather. Here, DLS stands for the characterization of emulsion particle sizes, which were measured by laser particle size analyzer. As is shown in Figure 3, the average particle sizes of HPAE-UA_{0.123}, HPAE-UA_{0.237}, HPAE-UA_{0.352}, and HPAE-UA_{0.454} appeared to be 450 nm, 420 nm, 820 nm, and 1790 nm respectively, and were narrowly distributed. The emulsion appeared no stratification for 24 h, suggesting their good stability. The DLS images indicated that the emulsion of HPAE-UAs could enter the fibers and be employed in the leather process.

Characterization of HPAE-UAs between Fibers

In Figure 4, the final leathers were placed in the shade to dry, then the structures before and after fatliquoring were characterized by ATR-FT-IR. It is noticed that the following peaks obviously enhanced with the increase of *J*: the stretching band of O-H and N-H at 3316 cm⁻¹, C-H stretching vibration at 2927 cm⁻¹, C=C stretching vibration at 1645 cm⁻¹, the stretching vibration of C-H in alkene at 3078 cm⁻¹, the asymmetry and symmetrical bending vibration of C-H at 1455 cm⁻¹ and 1333 cm⁻¹, the stretching vibration of C-O in saturated ester at 1240 cm⁻¹, the plane bending vibration of C-H in alkene at 910 cm⁻¹ [21,22]. The above absorption peaks happened to be the characteristic peaks of HPAE-UAs, suggesting that HPAE-UAs had been added to the leather samples. In addition, the bond of C=O moved from 1745 cm⁻¹ to 1710 cm⁻¹ after application and the bond of C-O in the saturated esters also moved from 1115 cm⁻¹ to 1070

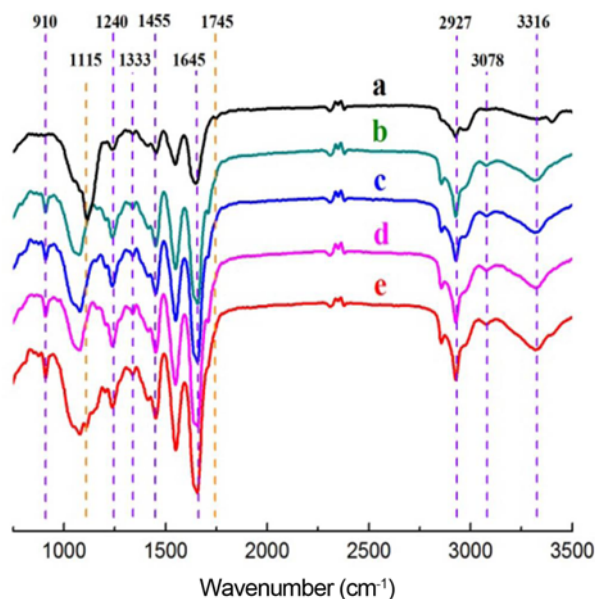


Figure 4. FT-IR spectrum of wet-blue leather (a), the final leathers: HPAE-UA_{0.123} (b), HPAE-UA_{0.237} (c), HPAE-UA_{0.352} (d), and HPAE-UA_{0.454} (e).

cm⁻¹, indicating that strong molecular inter-atomic forces were formed or chemical reaction between HPAE-UAs in the final leathers and collagen occurred [23].

The TEM and SEM images of wet-blue leather and the final leathers are shown in Figure 5 and Figure 6 respectively. In Figure 5, compared with wet-blue leather, the fiber bundles of final leathers appeared looser [25]. Moreover, the SEM images show that the fiber of wet-blue was arranged more closely, and there were some gaps between the fibers of final leathers. This proved that HPAE-UAs had been filled between the leather fibers, and had a certain loose effect on fiber. This is because the long-chains in HPAE-UAs had hydrophobic effect, which weakened or covered the forces between the side chain of polarity and the main chain on the fiber chain, resulting in nonpolar regions between the molecule chains. Simultaneously, it widened the space between the fiber molecular chains. Figure 5 and Figure 6 show a strongest crosslinking of HPAE-UAs and collagen fibers.

The thermal properties play an important role in the properties of leather. Figure 7 is the *T_g* diagram of the wet-blue and the final leather. When the temperature of the wet-blue leather rose to 230 °C, it began to lose weight. At 300 °C, the rate of weightlessness began to increase sharply. At 500 °C, the weightlessness leveled off and the remnant of wet-blue leather dropped to 13.1 %. The weight loss occurred at 120 °C, but the degradation rate became low after fatliquoring. When temperature reached 270 °C, the rate of weightlessness began to increase sharply. The weightlessness also leveled off when the temperature increased to 500 °C. The remnant

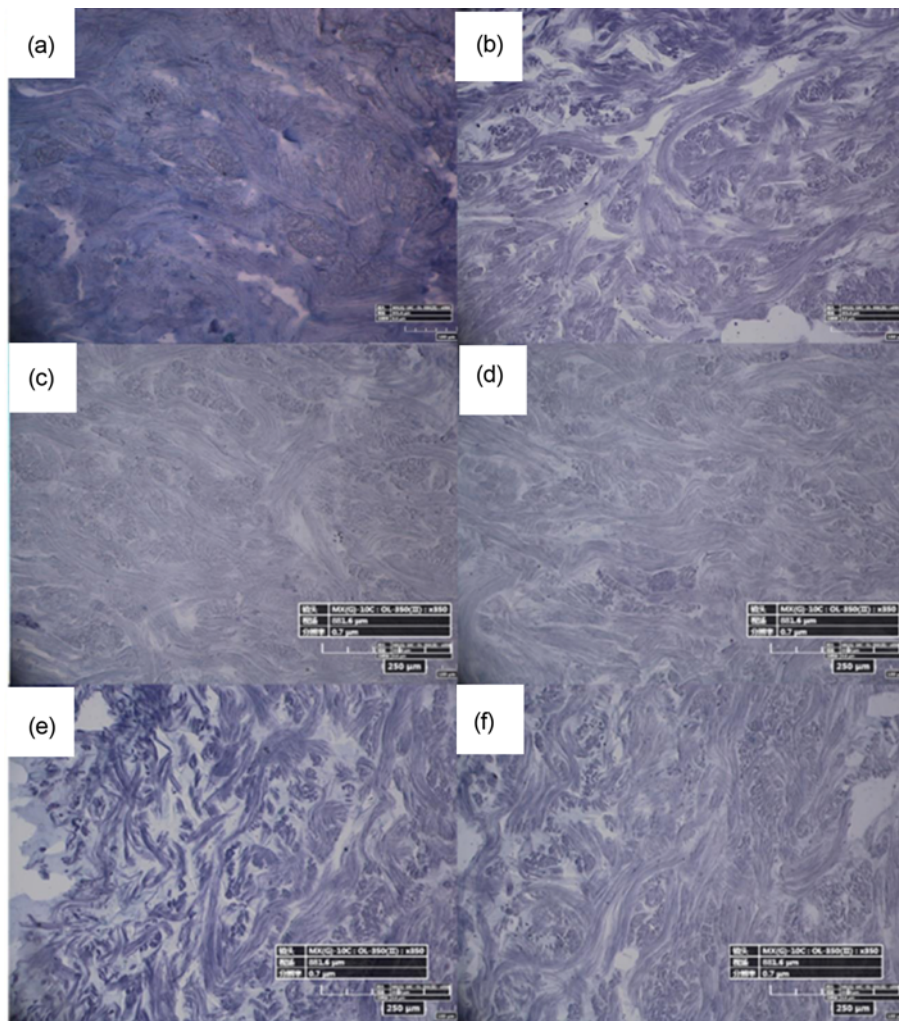


Figure 5. TEM images of wet-blue leather (a) and the leather after fatliquoring: industrial fatliquor (b), HPAE-UA_{0.123} (c), HPAE-UA_{0.237} (d), HPAE-UA_{0.352} (e), and HPAE-UA_{0.454} (f).

of the final leather with industrial fatliquor, HPAE-UA_{0.123}, HPAE-UA_{0.237}, HPAE-UA_{0.352}, and HPAE-UA_{0.454} increased to 16.7 %, 21.7 %, 23.0 %, 30.3 %, and 24.9 %, respectively. At the same temperature, the rate of weightlessness of final leather was smaller than that of wet-blue, suggesting that crosslink between HPAE-UAs and the leather fiber occurred in the interior of leather, enhancing the stability of the final leathers. Figure 7(b), 7(c), 7(d), 7(e), and 7(f) show that, within 150-270 °C, the rate of weightlessness increased first and then leveled off, probably due to the free HPAE-UAs. Based on the analysis of Figure 7(b), 7(c), 7(d), 7(e), and 7(f), it can be concluded that, when HPAE-UAs were used as fatliquor applied in leather, the residuals of final leather increased in various degrees in comparison to leather with the industrial fatliquor. The results fully prove the fact that HPAE-UAs crosslinked with collagen after being filled into leather. Thus, thermodynamic and mechanical performances of final leather were improved. Moreover, when HPAE-

UA_{0.352} was used as fatliquor, the remnant remained the highest, indicating that the crosslinking of HPAE-UA_{0.352} and leather collagen fibers was the strongest.

The T_s diagram of the final leather is presented in Figure 8. The T_s of leathers were improved to a certain degree with the application of HPAE-UAs as a fatliquor in fatliquoring process of wet-blue (goatskin). However, when HPAE-UA_{0.352} was used as fatliquoring leathers, T_s increased significantly, rising to 89.4 °C. Compared with the leather used in industrial fatliquor, its T_s increased 8.05 °C. The results reveal that the HPAE-UAs have a certain degree of retanning effect. This is maybe the reason that HPAE-UAs with hydroxyl and alkenyl, and the electronegative groups could bind with chromium complex ligand. So, the HPAE-UAs can be crosslinked with collagen fibers side chain.

Physical and mechanical properties are very important properties of leather and are known to depend on the arrangement of the collagen fibers within the material [24].

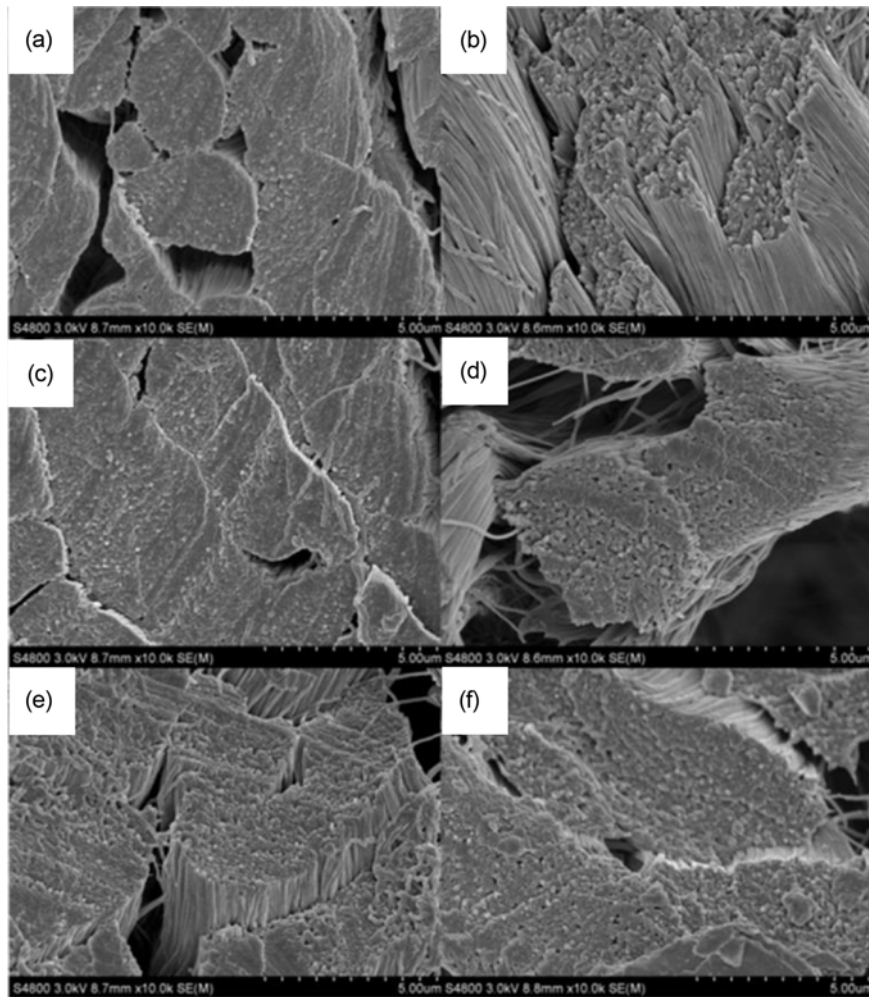


Figure 6. SEM images of wet-blue leather (a) and the leather after fatliquoring: industrial fatliquor (b), HPAE-UA_{0.123} (c), HPAE-UA_{0.237} (d), HPAE-UA_{0.352} (e), and HPAE-UA_{0.454} (f).

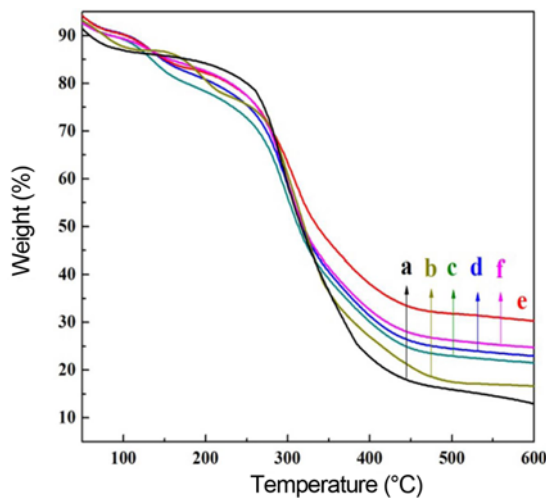


Figure 7. T_g diagram of the wet-blue leather (a), the leather after fatliquoring: industrial fatliquor (b), HPAE-UA_{0.123} (c), HPAE-UA_{0.237} (d), HPAE-UA_{0.352} (e), and HPAE-UA_{0.454} (f).

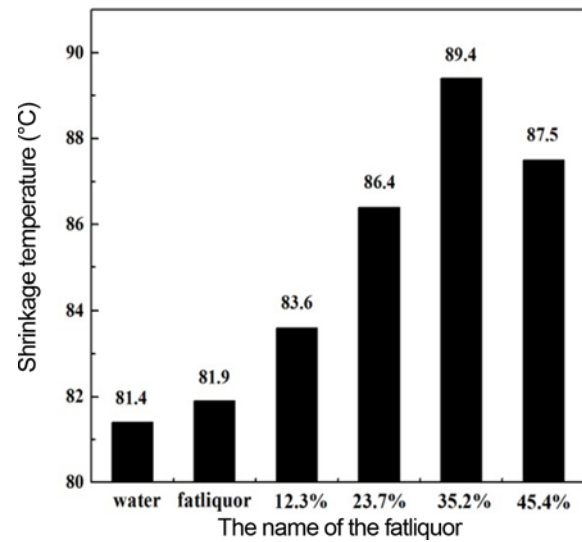


Figure 8. T_s histogram of wet-blue leather and the leather after fatliquoring.

Table 2 shows the change of physical and mechanical properties of fibers in the final leather. According to the result, the physical and mechanical properties of final leathers had also been improved when HPAE-UAs were used as a fatliquor in leather. When HPAE-UA_{0.352} entered the fibers, the physical and mechanical properties of final leathers improved significantly: the tensile strengths increased 33.77 MPa, the tear strengths became 78.18 N/mm, and elongation increased 35.75 %. When HPAE-UA_{0.352} was used as fatliquor, its physical and mechanical properties of final leather appeared to be a little lower than that of industrial fatliquor. But the fatliquoring effect varied

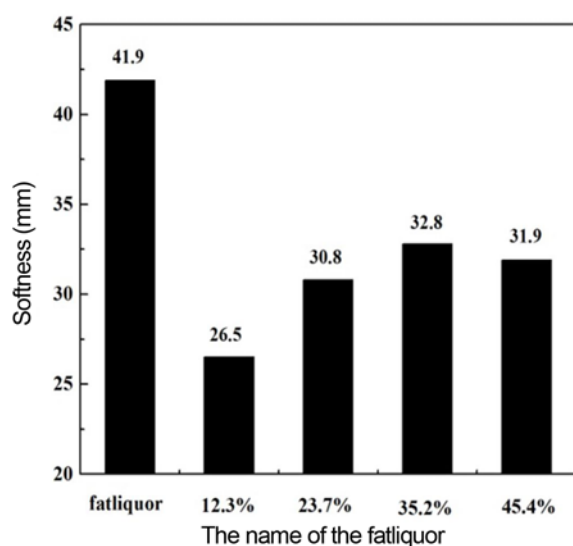


Figure 9. Softness histogram of the final leather.

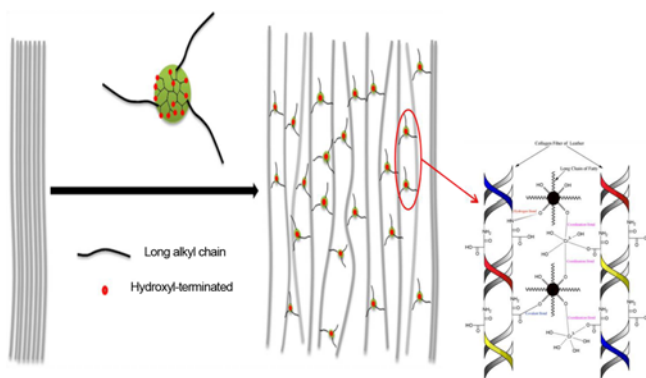


Figure 10. Schematic diagram of fiber crosslinking in final leather.

Table 2. Effect of final leather physical and mechanical properties

Number	1 [#]	2 [#]	3 [#]	4 [#]	5 [#]
Fatliquor	Industrial fatliquor	HPAE-UA _{0.123}	HPAE-UA _{0.237}	HPAE-UA _{0.352}	HPAE-UA _{0.454}
Tensile (MPa)	39.79	24.17	27.49	33.77	30.40
Tear strength (N·mm ⁻¹)	85.36	57.06	59.27	78.18	67.43
Elongation (%)	39.91	24.13	30.68	35.75	32.53

slightly.

Figure 9 shows the softness histogram of the final leather. Evidently, the final leather with HPAE-UA_{0.352} as fatliquor was softer. However, the HPAE-UAs are softer than the industrial fatliquor because industrial fatliquors are multi-component mixtures and contain greases, which could enhance the lubricity between fibers in leather.

Figure 10 shows the schematic diagram of fiber crosslinking in final leather when HPAE-UAs were used as fatliquor. As is known, the structures of polymers at all levels of interaction determine the characteristic of polymers. The HPAE-UAs have large numbers of active functional groups, such as hydroxyl groups on the surface of polymers. So the hydrogen bond with the carboxyl and amine groups play a major role accompanied by Van der Waals forces to crosslink the fibers. Furthermore, Cr³⁺ and hydroxyl groups can form the coordination bond with each other. From above data, we can see that the hyperbranched multiterminal alkenyl polymers can enhance the properties of fibers in leather. So, the hyperbranched multiterminal alkenyl polymers can be the novel nanoscale material to be applied in fibers.

Conclusion

A series of alkenyl polymers (HPAE-UAs) with different grafting ratios were synthesized through the reaction between HPAE and UAs. Its molecular structures were characterized by ¹H-NMR and FI-IR. The results show that the synthesis was carried out as designed. The application of HPAE-UAs emulsion show a significant improvement of handle as well as the thermodynamic performance and physical and mechanical properties of fibers. Moreover, HPAE-UA_{0.352} as fatliquor was applied in the leather, and all the performance reached the maximum. The results reveal that the probability of using HPAE-UAs can crosslink with fibers of leather significantly, and can be a new type of retan-fatliquor in leather fatliquoring process.

Acknowledgments

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