

Synthesis and Properties of Hydroxyl-terminated Hyperbranched Poly Isocyanurate-ester Retanning Agents

by

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Abstract

AB₂ monomer was synthesized by Michael addition of diethanolamine (DEA) and methyl acrylate (MA). Then the hydroxyl-terminated hyperbranched poly isocyanurate-ester with different generations (HPICEs) which were named as HPICE-I, HPICE-II and HPICE-III, were prepared respectively via three-(2-hydroxyethyl) isocyanurate (THEIC) and AB₂ monomer in which THEIC was used as the core and AB₂ monomer as the branching unit. The structure and mass of HPICEs were characterized by Fourier Transform Infrared Spectra (FT-IR), nuclear magnetic resonance hydrogen spectra (¹H-NMR) and gel permeation chromatography (GPC). HPICEs were applied in the retanning process of wet blue leather. The results show that when the dosage of HPICEs retanning agent is 3% (basing on the weight of wet blue leather), the properties of leather retanned with HPICE-III are the best compared with those retanned with HPICE-I and HPICE-II. The thickening percentage of the back and belly were 14.88% and 20.54%, respectively. Compared with that of leather retanned with RST, a kind of acrylic retanning agent widely used in the market, the tearing strength, tensile strength and cracking strength of the leather retanned with HPICE-III are increased by 53.31%, 65.69% and 85.28% respectively. All the leather samples retanned by HPICEs exhibited better dry rub fastness but worse wet rub fastness than that retanned by RST. In addition, the samples present better surface properties as well.

Introduction

Retanning plays an important role in the production of light leather, and is known as "Golden Touch" in the leather industry. It can not only further supplement tanning, improve the fullness and softness of leather, tighten the grain of leather, but also can enhance the hydrothermal stability, level-dyeing property and wear resistance of leather. Meanwhile, the retanning process is

helpful to subsequent finishing operations.¹ Therefore, the quality of the retanning materials is a significant factor to determine the effect of retanning.² Nowadays, the domestic leather production generally attaches importance to the retanning technology, so as to improve the performance and appearance of leather, as well as the commercial value of leather products. In a conventional leather retanning process, retanning materials used include both inorganic salt like basic chromium salt, zirconium salt and aluminum salt and organic materials such as vegetable tanning agent, synthetic tanning agent, resin retanning agent and aldehyde tanning agent. At present, the syntan containing chrome is more often used as the retanning agent. But vinyl monomer/polymer tanning agent is more popular and widely used with its high reactivity. Although aromatic synthetic tanning agent which is commonly used in China tends to be declining, it is still widely used in foreign tanneries. The demand is not less than the acrylic resin retanning agent. Domestic Aldehyde tanning agent used in leather production include glutaraldehyde, modified glutaraldehyde and other aliphatic aldehyde.³ Therefore, it is necessary to develop a novel environmentally friendly retanning agent so as to reduce environmental pollution and improve the properties of leather.^{4,5}

In recent years, more and more attention has been paid to hyperbranched polymers due to their easy synthesis, unique properties and potential application prospects.⁶⁻¹¹ The hyperbranched polymer is a kind of multibranched polymer with highly irregular and three-dimensional spherical structure.¹² Compared with ordinary polymers, hyperbranched polymers have good solubility, low viscosity, especially high reactivity with more terminal functional groups.¹³⁻¹⁵ The terminal groups of hyperbranched polymers (such as hydroxyl, amino, carboxyl, etc.) can combine with the groups on collagen fiber macromolecules to form firm chemical bonds and a multipoint crosslinking structure.¹⁶ Thus, it can be a tanning agent or retanning agent to endow the leather with special tanning effects¹⁷⁻¹⁹ such as better fullness, softness and dyeing

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uniformity. According to Wang Xuechuan et al²⁰ by employing hyperbranched polymer in retanning process of chrome tanned leather the tensile strength and tearing strength of leather were improved. Qiang Taotao et al²¹ synthesized a chrome-free tanning agent based on hyperbranched polymers with terminal carboxyl groups and aluminum sulfate. The agent proved to possess excellent retanning effect, therefore, the problem of poor washability and low shrinkage temperature of the tanned leather with only Aluminum sulfate was solved.

In this paper, the hydroxyl-terminated hyperbranched poly isocyanurate-ester with different generations (HPICEs) was prepared by a one-step method. The HPICEs were employed in the retanning process of wet blue leather of sheepskin to investigate their resultant performances.

Experimental

Materials

Diethanolamine (DEA) and P-toluene sulfonic acid (P-TSA) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Methyl acrylate (MA) was purchased from Tianjin Chemical Reagent Factory. Anhydrous methanol and N,N-dimethylformamide (DMF) were provided by Tianjin Tianli Chemical Reagent Co., Ltd. Three-(2-hydroxyethyl) isocyanurate (THEIC) was obtained from Tokyo Chemical Industry Co., Ltd. Wet blue leathers were supplied by Hebei Dongming Leather Co., Ltd. Desaitan RST (Solid content is 13%) was obtained from Sichuan Tingjiang New Materials Co., Ltd.

Instruments

The VERTE70 Fourier-transform infrared spectrometer was provided by Bruker Co., Germany. The ADVANCEIII400MHz NMR spectrometer was provided by German Brook Company. The GSD-350 drum was produced by Wuxi Xinda Light Industry Machinery Co., Ltd. The MH-YDI digital leather thickness measuring instrument was produced by Shaanxi University of Science and Technology, China. The Y571D rubbing color fastness tester was produced by Wenzhou Fangyuan Instrument Co., Ltd. The XK-8012 leather tensile strength testing machine was produced by Kunshan Xiangke Detection Instrument Co., Ltd.

Synthesis of HPICE

DEA (0.1mol) and anhydrous methanol (10mL) were added into a three-neck flask (250mL), and stirred until DEA was completely dissolved at room temperature. MA (0.2mol) was added dropwise for 15-20min. The reaction was carried out at 35°C for 4h, then the excess methanol and MA were removed in vacuum. A colorless transparent AB₂ monomer was obtained after extraction with ether. THEIC (0.05mol) was completely dissolved in DMF solution (5g) in a three-neck flask, and 1.5% p-toluene

sulfonic acid (basing on the total weight of AB₂ monomer and THEIC) was added. After the temperature was raised to 110-120°C, AB₂ monomer was added dropwise within 30~40min. The reaction was carried out at 115°C for 4h. The product was precipitated by using a rotary evaporator at -0.08Mpa and 100°C until bubbles disappeared. Then, a light yellow viscous liquid was obtained. The crude HPICE was dissolved in acetone, re-precipitated with dichloromethane, extracted and washed with diethyl ether. The operation was repeated 3 times, and then the upper liquid was treated in a rotary evaporator with vacuum distillation to remove solvent. According to different molar ratios of AB₂ monomer and THEIC which were 3:1, 9:1 and 21:1, the hydroxyl-terminated hyperbranched poly isocyanurate-ester with different generations (HPICE-I, HPICE-II and HPICE-III) were prepared. The synthesis equations of HPICE-I are shown in Figure 1.

Solid Content Testing

The solid content of HPICE was examined according to the national standard (GB1725-2007).²² The total mass is W₁ after adding certain amount of sample into a watch glass whose mass is W₀. Then the sample and watch glass were kept under constant temperature in drying oven for specified time. The dry weight

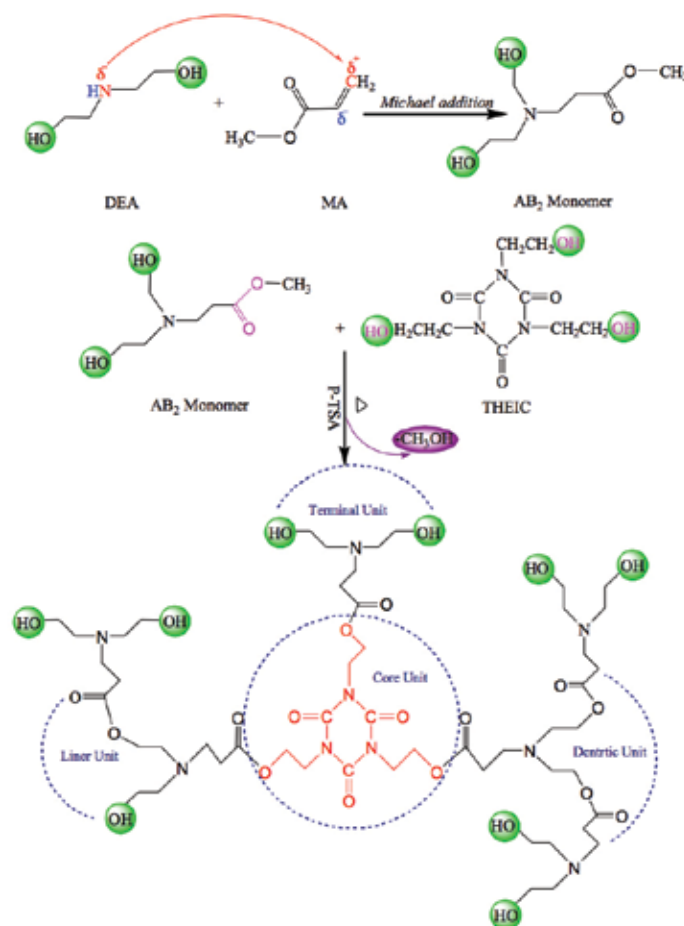


Figure 1. The synthesis equation of HPICE-I.

was noted down after the sample was removed and cooled to room temperature. This process was repeated until the mass change less than 0.01g, the constant mass was W_2 , solid content was calculated according to the above results.

Solubility Testing

A certain amount of product and solvent were added into reaction flask equipped with stirrer, then kept stirred for 5-10 min at room temperature, filtered after standing for 24h. The solubility of products was tested by the weighing method, the results will be converted to grams of product can be dissolved in per 10mL solvent. More than 1g HPICE can be dissolved in 10mL solvent as soluble, 0.1~0.99g products can be dissolved in 10mL solvent as slightly soluble and only less than 0.1g products can be dissolved in 10mL solvent as insoluble.

The pH Testing

A proper amount of HPICE was taken to examine its pH by using pH Meter.

Fourier Transform Infrared Spectroscopy (FT-IR)

A Fourier Transform Infrared Spectrometer (VECTOR-22, BRUKER Company, Germany) was used to characterize the THEIC and HPICES. The scanning frequency range was 4000–400 cm^{-1} .

Nuclear Magnetic Resonance Hydrogen Spectra ($^1\text{H-NMR}$)

HPICE was dissolved in D_2O and then its NMR spectra were acquired on an ADVANCEIII 400 MHz NMR spectrometer.

Gel Permeation Chromatography (GPC)I

Polystyrene (PS) was taken as an internal standard and the sample solution was measured in gel permeation chromatograph polystyrene.

Table I
Retanning Procedure of wet-blue sheepskin.

Process	Materials	Dosage/%	Temperature/ $^{\circ}\text{C}$	Time/min	pH	Remarks
rewetting	water	200	40			
	degreasing agent DN	1.5		40		
washing	water	200	40	10		
neutralizing	water	150	40			
	neutralizing agent NT	1				
	sodium bicarbonate	0.8				dilution 1:20
	sodium formate	1		90	5.5-5.8	checking incision
washing	water	200	40	10		
retanning	water	150	40			
	retanning agent	3		120		comparative test
washing	water	200	40	10		
fatliquoring and dyeing	water	100	55			
	fatliquor LQ-5	18		60		
	black dyestuff	2.5		30		
	formic acid	1.5		3*10 + 30	3.5-4.0	

drying

Remarks: the dosage of materials was based on the weight of shaved wet-blue leather.

Retanning Procedure

In the process, the sampling was symmetrical along the backbone. HPICEs and RST were used to retan wet-blue sheepskin. The changes in thickness and mechanical properties before and after retanned were tested. The retanning process is shown in Table I.

RST is an acrylic resin tanning agent. It has a significant thickening percentage to leather, strong combination with collagen fiber and excellent selective filling effect. Therefore, RST was used to compare with our retanning agents to determine the application properties of HPICEs.

Test of Thickening Percentage

The thickness of leather before and after being retanned was measured(QB/T2709-2005).²³ 5 points were tested respectively, and the result was the average value of five points.

Table II
The physical properties of HPICEs.

Indicators	HPICE-I	HPICE-II	HPICE-III
appearance	light yellow viscous liquid	light yellow viscous liquid	light yellow viscous liquid
solid content (%)	81.1±2.0	79.9±2.0	77.9±2.0
pH	7~8	7~8	7~8

Table III
The solubility of HPICEs.

Solubility	HPICE-I	HPICE-II	HPICE-III
water	soluble	soluble	soluble
methanol	soluble	soluble	soluble
DMF	soluble	soluble	soluble
chloroform	slightly soluble	slightly soluble	soluble
THF	insoluble	slightly soluble	soluble
ether	insoluble	insoluble	insoluble
cyclohexane	insoluble	insoluble	insoluble
benzene	insoluble	insoluble	insoluble

Test of Tensile Strength, Tearing Strength and Cracking Strength

According to the Chinese standard for garment leather (QB/T2710-2005, QB/T2711-2005 and QB/T2712-2005), the tensile strength and tearing strength of leather retanned by HPICEs and RST were tested.²³

Test of Dry and Wet Rub Fastness

The dry and wet rub fastness of leathers retanned by HPICEs and RST were tested by standard method of light industry.²³

Organoleptic Properties of Retanned Leathers

The organoleptic properties of leathers retanned by HPICEs and RST were tested by standard method of light industry.²³

Results and Discussion

HPICEs Characterization

Solubility

Table III shows that hyperbranched polymers present high solubility owing to their highly branched structure and the terminal structure. The high polar ends of the hydroxyl terminated hyperbranched polymers can make good solubility. So, they can be dissolved in high polar solvents such as water, alcohol, N, N-dimethylformamide (DMF), N, N-dimethyl acetamide (DMA), etc.

FT-IR Analysis

FT-IR spectroscopy is a method for identifying the structure of a substance by the characteristic absorption peaks of the functional groups. The infrared spectrum of the raw material THEIC and AB₂ monomer are shown in Figure 2. The infrared spectra of HPICEs are shown in Figure 3.

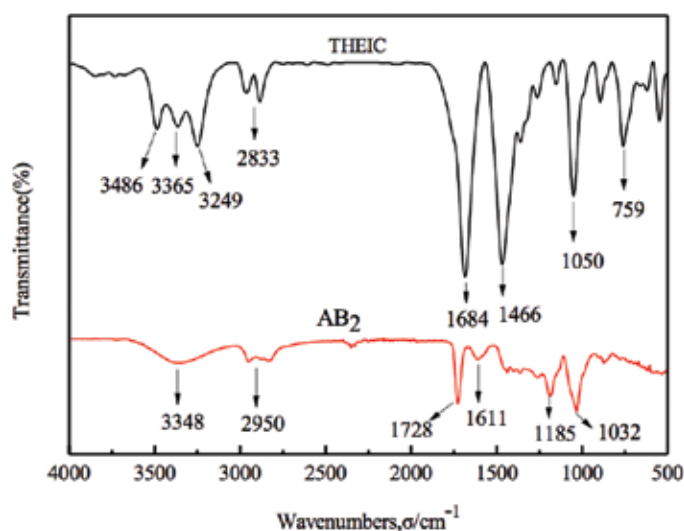


Figure 2. FT-IR spectra of THEIC and AB² monomer.

As shown in Figure 2 and Figure 3, a characteristic absorption sharp peak of hydroxyl on THEIC is found at 3365 cm^{-1} and a broad band of hydroxyl on HPICEs in the region of 3367 cm^{-1} , indicating that the content of hydroxyl is increasing in the structure of HPICEs. The formation of the broad band is attributed to the hydrogen bonding of multiple hydroxyl groups.²⁴ The strong and sharp peak at 1466 cm^{-1} in the THEIC spectrum corresponds to that at 1455 cm^{-1} in the HPICEs spectra, which belongs to the characteristic absorption peak of acylamino. The sharp peaks at 1684 cm^{-1} in THEIC spectrum and 1683 cm^{-1} in HPICEs spectra are the stretching vibration of carbonyl in acylamino, while the peak at 1612 cm^{-1} in HPICEs spectra is the stretching vibration of carbonyl in ester group. The absorption peak of 1050 cm^{-1} belongs to the vibration of C-N bond and the vibration of C-H group appeared at 2950 cm^{-1} in AB_2 monomer spectrum and in the region of 2833 cm^{-1} in HPICEs and THEIC spectra,²⁵ indicating that the reaction is carried out according to the expected route.

As shown in Figure 3, the degree of carbonyl in the acylamino movement to low field is increasing with the increase of generations of HPICEs. This is because electron withdrawing groups such as ester groups in structure of products are increasing and the charges from the oxygen atom move to the double bond due to the strong electron withdrawing effect of the ester groups, thus the property of double bond of C=O increased and the absorption frequency decreased.

¹H-NMR Analysis

Figure 4 shows ¹H-NMR spectra of hydrogen exchange between HPICEs and D₂O.

As shown in Figure 4, ¹H NMR (400 MHz, D₂O, δ): a solvent peak of D₂O appears at 4.70 ppm, 2.35 (t, H, —OH), 3.63 (m,

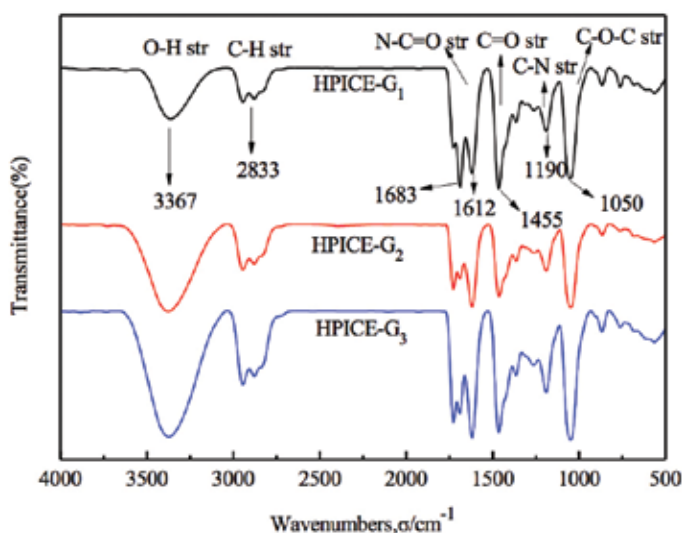


Figure 3. FT-IR spectra of HPICEs.

12H, OH—CH₂—), 2.55 (t, 6H, OH—CH₂—CH₂—), 3.28 (t, 6H, —OOC—CH₂—CH₂—), 2.75 (t, 6H, —OOC—CH₂—), 3.66 (t, 6H, —N—CH₂—CH₂—O—), 3.51 (t, 6H, —N—CH₂—). It can be concluded from above that HPICEs are prepared through the transesterification reaction of AB₂ monomer and THEIC in accordance with the expected design route. Compared HPICE-I, HPICE-II and HPICE-III, we can find that the peaks of hydrogen atoms in the different environments of the products gradually become broader and broader though the increase of the generations in ¹H-NMR.

GPC Analysis

As shown in Figure 5, (a), (b) and (c) are the GPC maps of HPICE-I, HPICE-II and HPICE-III. It can be seen from Table IV that the theoretical relative molecular masses of HPICE-I, HPICE-II and HPICE-III are 738, 1691 and 3599, respectively. The tested molecular masses are 630, 1393 and 3108, respectively. The tested molecular masses are lower than the theoretical relative molecular masses, which is caused by the method of determination of relative molecular mass for hyperbranched polymer. Linear polymers known molecular weight are often used as the polydispersity index of the sample, but the structure of linear and HPICEs are significantly different. Thus, GPC determination of the relative molecular mass is lower than the theoretical molecular mass.²⁶ The polydispersity index of relative molecular masses of HPICE-I, HPICE-II and HPICE-III are 1.04, 1.05 and 1.07. Analyzed GPC maps in Figure 5 can be seen that peaks of HPICE-I and HPICE-II are sharp and curve of GPC spectrum is single, indicating there are a few small molecules in HPICE-I and HPICE-II and the reaction system is uniform. The GPC spectrum curve of HPICE-III becomes wide, the

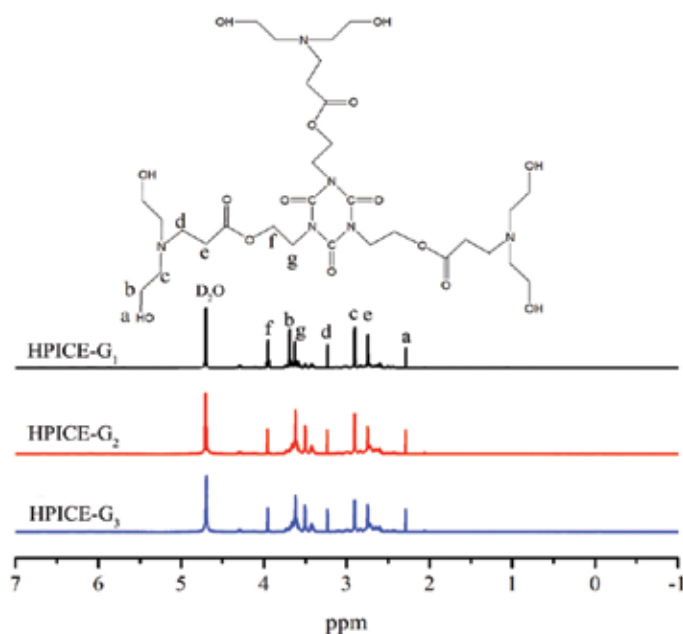


Figure 4. ¹H-NMR spectra of HPICEs.

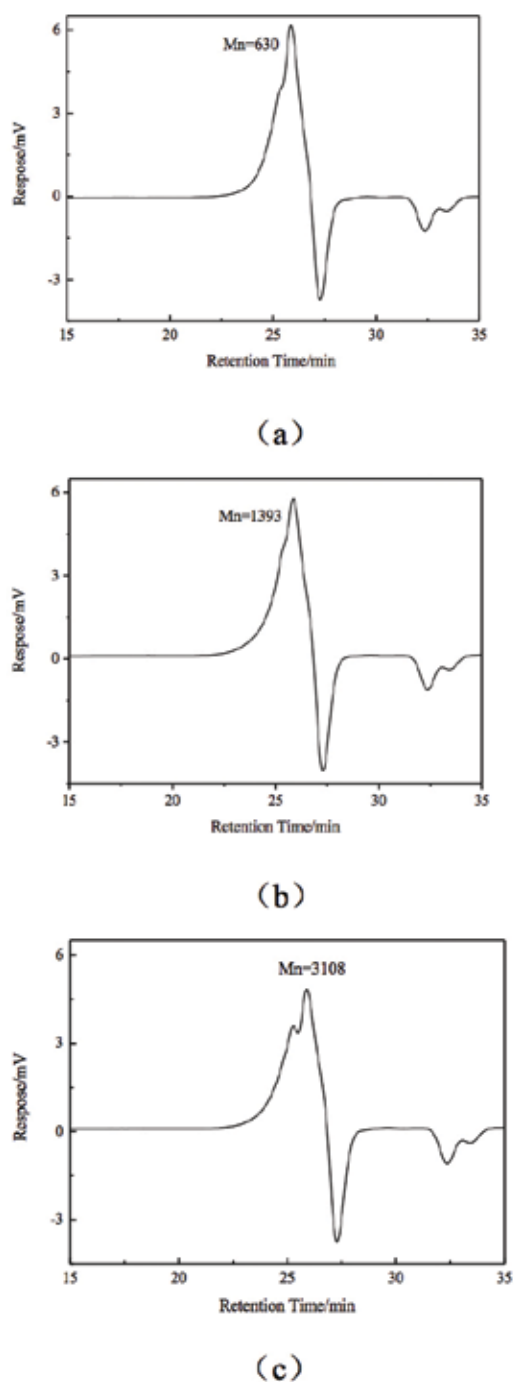


Figure 5. GPC spectra of HPICEs.

polydispersity index becomes larger and the peak of GPC spectrum is not single, indicating the side reactions in HPICE-III reaction system are more. The reaction system is complex and may contain HPICE-II and other by-products, mainly due to the grafting reaction is randomly carried out.

For leather, pore distance among the fibers is fixed, which determines the molecular size of tanning agent. If the tanning agent molecule is smaller, it is difficult to form an effective combination with collagen. On the contrary, if the relative molecular weight of tanning agent is larger, it is difficult to penetrate into leather. Relative molecular weight of vegetable tanning agent commonly used is generally 500~3000. If less than 500, ideal tanning effect can not be achieved. If more than 3000, the effect of combination with fiber will be poor. Figure 6 is a distribution model of the relative molecular weight of different tanning agent in leather fibers. According to the molecular weight of the synthetic tanning agent and the vegetable tanning agent, the relative molecular weight of HPICEs prove to be moderate, so it will not affect the application in leather processing.

Result of Thickening Percentage

HPICEs and RST were used in the retanning process of wet-blue sheepskin. The results are shown in Table V.

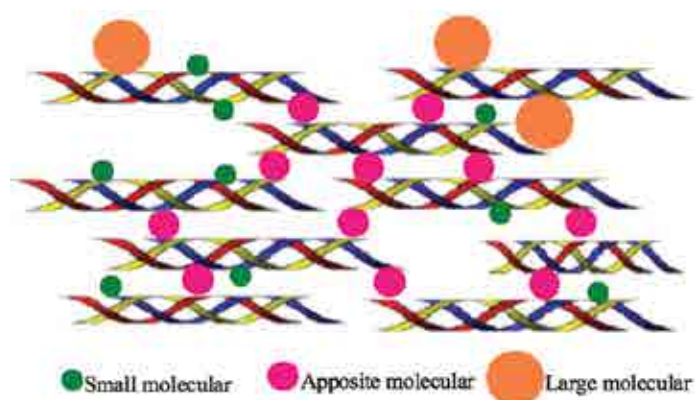


Figure 6. The distribution model of the relative molecular weight of different tanning agent in leather fibers.

Table IV
The relative molecular weight of HPICEs.

HPICEs	Theoretical value	Mn	Mw	Mp	Mz	Mz+1	Polydispersity
HPICE-I	738	630	656	598	684	715	1.04
HPICE-II	1691	1393	1469	1292	1562	1671	1.05
HPICE-III	3599	3108	3331	2766	3601	3918	1.07

As shown in Table V, the thickening percentage of the belly of leather retanned with HPICE-III was more remarkable compared with that of leather retanned by HPICE-I and HPICE-II. The thickening percentage in back and belly of leather retanned with HPICE-III was 14.88% and 20.54%, respectively due to the larger molecular mass of HPICE-III and existence of large number of hydroxyl groups in HPICE-III structure. These hydroxyl groups can replace other groups and combine with the chromium ion ligands to form new complex. For chrome-tanned leather, the most likely ligands of chromium ion are sulfate and hydroxyl, etc. Their coordination ability with trivalent chromium ion was as follows:²⁷ water molecule < sulfate ion < sulfite ion < hydroxyl < carboxyl in collagen fiber. The hydroxyl in HPICE can replace sulfate, water molecule, etc. HPICE-III has high molecular mass and contains more hydroxyl, so the retanning agent is more helpful for the thickening effect of leather. The thickening effect of leather retanned by HPICE-III is slightly lower than that of leather retanned by RST. The reason is that the active groups on the molecular chain of HPICE are hydroxyl groups, but the active groups on RST are carboxyl groups which can complex with Cr^{3+} well. Also, filling is predominantly decided by the molecular weight of retanning agent. The

molecular weight of RST is larger than that of HPICE-III, so RST shows better filling performance.

Results of Tensile Strength, Tearing Strength and Cracking Strength

As shown in Table VI, the tensile strength effect of retanned leather for HPICE-I was not obvious, which is due to the lower relative molecular mass of HPICE-I cannot form more effective crosslinking between collagen fibers. The mechanical properties of the leather retanned with HPICE-III are better than that of leather retanned by RST. The tensile strength, tearing strength and cracking strength were increased by 53.31%, 65.69% and 85.28% compared with the leather retanned by RST. The reason may be that the hyperbranched polymer has special branched structure and contains many active functional groups. It can form both hydrogen bonds with collagen fiber and effective crosslinking structure after it enters into the collagen fiber. The schematic diagram is shown in Figure 7, it is a conceptual cross-linking that may effectively restrain the deformation of collagen fiber under axial tension and improve the tearing strength and tensile strength of the leather. And the moisture content may be another important reason that is beneficial for strength. Because

Table V
The thickening percentage of leathers retanned with HPICEs and RST.

Types of retanning agent	Thickening Percentage (back) /%	Thickening Percentage (belly) /%
RST	26.47	30.29
HPICE-I	6.84	10.51
HPICE-II	11.62	15.08
HPICE-III	14.88	20.54

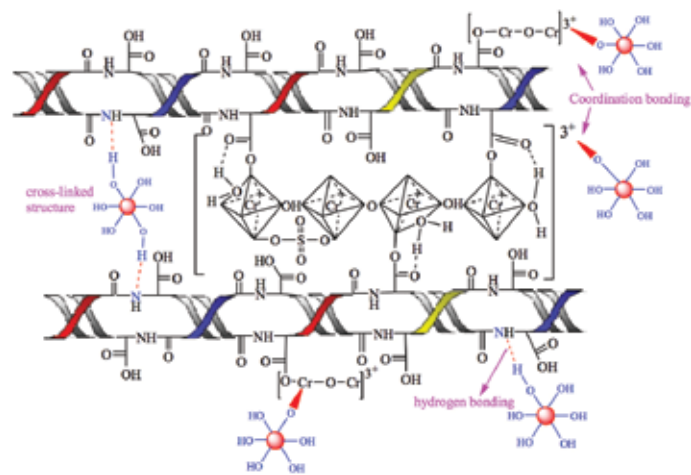


Figure 7. The bonding forms of HPICE with chrome-tanned leather.

Table VI
The tensile strength and tearing strength of leather retanned with HPICEs and RST.

Types of retanning agent	Tensile strength/ MPa	Tearing strength/ N·mm ⁻¹	Cracking strength/ N·mm ⁻¹
RST	12.98	32.99	231.03
HPICE-I	13.11	46.67	334.56
HPICE-II	17.53	50.38	367.72
HPICE-III	19.90	54.66	428.05

Table VII
The dry and wet rub fastness of retanned leathers by RST and HPICEs.

Types of retanning agent	dry rub fastness	wet rub fastness
RST	2-3	2-3
HPICE-I	3	2
HPICE-II	3	2
HPICE-III	3	2

of the multi-hydroxyl structure in HPICEs, the moisture of leather is higher with HPICE leather than that with RST. HPICE-III has high molecular mass and contains more hydroxyl, more hydrogen bonds, so effective crosslinking structure with collagen fiber are formed. Thus, the mechanical properties of leather retanned by HPICE-III became excellent relative to the others.

Results of Dry and Wet Rub Fastness

As shown in Table VII, the dry rub fastness of leathers retanned with HPICEs was better, but the wet-rub fastness was slightly lower than that of leather retanned by RST. Because the hydroxyl groups in HPICE molecules can form hydrogen bond with the amino groups on the collagen fiber. Along with the increase of the hydroxyl in HPICE-I, HPICE-II and HPICE-III, more and more hydrogen bonds with amino groups on the collagen fiber are formed. Therefore, the adsorption of collagen fiber to dyestuffs decreases. Meanwhile, it is easy to be rubbed off with a wet cloth. Also, leather retanned with HPICEs is hydrophilic and loves water in the wet rub test. Thus, the wet-rub fastness of leather retanned with HPICEs was slightly lower than that of leather retanned with RST.

Optimization of the Dosage of HPICE-III

The retanning process was carried out under different dosage of HPICE-III which increased from 2% to 6%. The properties of retanned leather were presented in Table VIII

As shown in Table VIII, when the dosage of HPICE-III was 3.0%, the thickening percentage reached to the maximum value (10.01%), so did the tensile strength and tearing strength reaching 3.0%. The reason is that when the penetration of HPICE-III into the chrome-tanned leather reaches balance, its combination with collagen fiber also gets balance correspondingly. When more than 3% of HPICE-III was added, the thickening percentage, tensile strength and tearing strength began to decrease. The reason is that excessive HPICE-III cannot penetrate into the collagen fiber and it may have a negative effect on the balance that has been reached leading to the poor combination with collagen fiber. Thus, the optimum dosage of HPICE-III was 3.0%.

Organoleptic Properties

The organoleptic properties of retanned leathers are given in Table IX.

From Table IX, it is observed that both the RST retanned leather and HPICEs retanned leather exhibited the organoleptic properties with good softness, fullness, tightness and smoothness. But the latter has the lowest fullness. This is because RST has greater molecular weight than HPICEs when the solution pH is 5.5-5.8. Therefore, it can fill the grain.

Table VIII

Properties of leathers retanned by HPICE-III with different dosages.

The dosage of HPICE-III/%	2	3	4	5	6
Thickening percentage/%	8.11	10.01	6.90	4.31	4.92
Tensile strength/MPa	12.11	14.01	10.90	8.31	8.92
tear strength /N·mm ⁻¹	45.85	47.49	39.82	44.24	35.70

Table IX

The organoleptic properties of retanned leathers.

Properties	HPICE-I	HPICE-II	HPICE-III	RST
softness	8	8	8	8
fullness	7.5	7.5	8	9
grain tightness	8	8	8	8
grain smoothness	9	9	9	9

Remarks: Larger number = better properties; the best property is 10.

Conclusions

The hydroxyl-terminated hyperbranched poly isocyanurate-ester with different structure/composition/molecular weights (HPICES) were prepared by one-step method, in which diethanolamine (DEA) and methyl acrylate (MA) were used as raw materials. The structure of HPICE-I was characterized by Fourier Transform Infrared Spectra (FT-IR) and nuclear magnetic resonance spectra (¹H-NMR). HPICES as retanning agents were employed in the retanning process of wet blue leather. The results show that when the dosage of HPICE-III retanning agent is 3%, the properties of its leather are the best compared with that of leather retanned by HPICE-I and HPICE-II. The thickening percentage of the back and belly are 14.9% and 20.5%, respectively. Meanwhile, compared with that of leather retanned with RST, the tearing strength, tensile strength and cracking strength of the leather retanned with HPICE-III are increased by 53.3%, 65.7% and 85.3% respectively due to the valuable effect of higher moisture and effective crosslinking structure with collagen fiber. All the leather samples retanned by HPICES exhibited better dry rub fastness but poorer wet rub fastness than that retanned by RST. In addition, the samples presented better surface properties as well. Meanwhile, the interaction between HPICES and collagen fiber was visually analyzed. The results show that HPICES retanning agent can be a retanning agent and may possibly reduce the pollution caused by chrome tanning agent in tannery effluent.

Acknowledgments

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