The Relationship Between the Structure of Hyper-branched Polymer and its Effect on High Exhaust Chrome in Reduced Chrome Tanning

by

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Abstract

Hyper-branched polymer (HBP) has been widely used as pretanning, tanning auxiliary and retanning agent in chrome tanning industry. However the effect of the structure of HBP including the degree of branching (DB) and molecular weight (Mw), on chrome tanning has seldom been studied. In this study a series of carboxyl-terminated hyper-branched oligomer (HBP) with different DB and Mw have been prepared and characterized by GPC and ^{1}H-NMR for determining their molecular weight and its distribution, as well the DB. The effect of DB and Mw on the chrome uptake and shrinkage temperature (Ts) of hide was investigated. Experimental results showed that the chrome uptake was affected by both DB and Mw of developed HBP. HBP that possesses high DB and the Mw closed to 2000 Da, has endowed the obtained leather with higher Ts and chrome uptake. Moreover, the leather tanned with 3% chrome and 1.5% HBP possesses similar properties to the traditional tanning process using 6-8% chrome. Therefore, the carboxyl-terminated HBP presents a potential application as a tanning auxiliary in reduced chrome tanning due to it's improving the absorption of chrome.

Introduction

Tanning is the conversion of animal hides and skins into useful articles. Although several types of metallic salts have been employed for tanning of leather, chromium salts are still considered as the most important tanning agents used for all types hides or leather. Generally, chromium salts are involved in more than 80% of the tanning industry worldwide,[1] Between all the tanning methods, chrome tanning methods which endow leather unparalleled properties are still very popular in the leather industry worldwide. With increasing concerns for the environment, a number of researchers have developed various chromium management technologies,[2, 3] including chromium recovery and reuse, i.e. direct chrome liquor recycling.[4] In fact, it is nearly impossible to recover all chromium from the post tanning effluents due to technical difficulty and costs.[5] High exhaust chrome tanning and tanning salts are some examples of recent developments in this area. Therefore, developing reduced chrome tanning with high absorption of chrome has become the key direction of further leather industry development.

For the most part, several tanning auxiliaries are available on the market, such as glyoxylic acid,[6] gallic acid,[3] oxazolidines,[7] and nanocomposites.[8, 9] However, the usage of these mentioned tanning auxiliaries materials need to reach high values to improve chrome uptake. Accordingly, hyper-branched polymers, having novel structures, unique properties, and potential application prospects, have attracted more attentions of researchers in the recent years. Compared with linear polymers, hyper-branched polymers have a large number of active groups, which can form many stable chemical bonds and multisite crosslinked structures. Therefore, studying reduced chrome tanning based on hyper-branched polymers is very meaningful.

Previous studies have shown that hyper-branched polymers can be used in the leather industry as pre-tanning agents,[10,11] retaning agents,[12,13] and chrome tanning auxiliaries.[14] Polyamidoamine hyper-branched polymer (HPAM) has been used in pretanning of the depickled hides to enhance the chrome uptake during the tanning process.[15] Qiang[16] confirmed terminal carboxyl groups of the hyper-branched polymer (HPAE-C) have excellent retanning effect and overcomes the poor washables and low shrinkage temperature of the aluminum tanning agent. Ibrahim[11] used hyper-branched polyamidoamine in a chrome-tanning process, which significantly improved the chrome fixation and exhaustion. Our previous work[17] has also illustrated that compared with linear polyacrylic acid, hyper-branched polyacrylic acid reduces the content of residual Cr(III) in waste by 28.5%, and the leather quality is also improved.

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However, current research is often limited to focus on a single hyper-branched polymer and there is little systematical relationship discussion between hyper-branched polymer structural factors and its coordination capability in leather-making. This paper aims at studying the influence of hyper-branched polymer structure on chrome uptake and shrinkage temperature. In this paper, carboxyl-terminated hyper-branched polyester is synthesized by multifunctional-monomer copolymerization with "AB_3+C_3" system. Citric acid (AB_3 monomer) has been used in the preparation of functionalized dendrimers. In order to enhance the degree of branched and reactivity of hydroxyl group, polyfunctional core monomer trimethylolpropane (TMP) is added in the condensation polymerization system.[18-20] The degree of branching and molecular weight of hyper-branched polymer are controlled by adjusting the ratio of monomers and reaction time. It is also hoped to provide a theoretical basis for use of hyper-branched polymers in reduced chrome tanning.

Materials and Methods

Chemicals and Materials

Citric acid [analytical reagent (AR)], trimethylolpropane [(TMP) (AR)], p-toluenesulfonic acid (AR), and potassium hydroxide (AR), were purchased from Aladdin Chemical Reagent Corporation (shanghai, China). Polyacrylic acid(biochemical reagent BR, Mw=2516) was purchased from Sigma-Aldrich Co., Ltd. and used as received. The chemicals such as sodium chloride, acetic acid, basic chromium sulphate, and formic acid, used in the chrome tanning operations were those normally used in the leather industry.

Table I
The reaction time and monomer mole ratio for synthesis of HBP-x.

Sample	Monomer molar ratio CA: TMP
HBP-1	2.5:1(45 min)
HBP-2	2.5:1(60 min)
HBP-3	3.0:1(45 min)
HBP-4	3.0:1(60 min)
HBP-5	3.5:1(45 min)
HBP-6	3.5:1(60 min)
HBP-7	4.0:1(60 min)

Carboxyl-terminated hyper-branched oligomer was prepared as depicted in foregoing; the schematic was shown in Figure 1.

Synthesis of the Carboxyl-terminated Hyper-branched Oligomer

Carboxyl-terminated hyper-branched oligomer, HBP-x(x=1,2…7) was synthesized by reacting citric acid (CA) with core molecular TMP. In a traditional reaction process, a 250mL four-necked flask, equipped with a mechanical stirrer and thermometer in a thermostatic oil bath, a mixture of CA and TMP with certain mole ratio and catalyst *p*-toluenesulfonic acid (0.2wt% of the total monomers) was added. In order to avoid gelling, CA was added to the reaction system gradually.[21, 22] After the reaction system was completed, it was kept oil bath at 120°C and vacuum was maintained at 0.07 MPa for given time. Thereafter, it was removed from oil bath and cooled down in a drying cabinet at room temperature. A yellow color resinous material HBP-x was obtained.

The reaction time and monomer mole ratio of different products are shown in Table I.

Chrome Tanning

Figure 2 illustrates the traditional and novel chrome tanning process in 250 mL flask on a shaker of 80cm (length)×50cm(width)×40cm(height). Pickled tanning, and basification processed wet-salted pigskins. Briefly, the pickled pigskin was soaked in 8%wt sodium chloride, then the pH was adjusted to 3.0 by 5%wt sulfuric acid and formic acid at 25°C. Secondly, the pickled skins were treated with chrome powder of 8%wt (on weight of skin) for the conventional trial. But for the novel chrome tanning trial, another 1.5wt% of HBP (on weight of skin) was added. After ascertaining the penetration of chromium by examining the cross-section, the pH of the tanning bath raised to 4.0 by using 10 wt% of $NaHCO_3$ solution. Thereafter setting the temperature of the shaker to 45°C for another 4h, the shaker was rested overnight and shaken for another 1h in the next day.

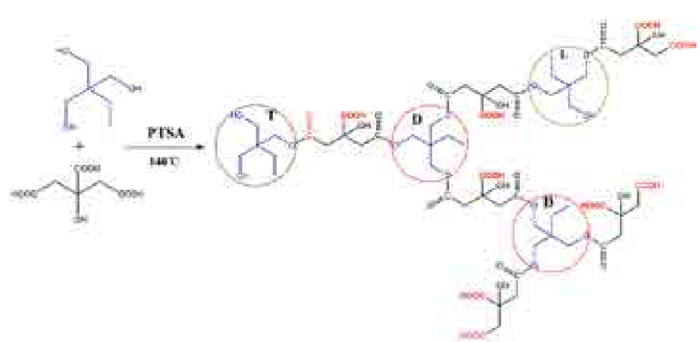


Figure 1. Schematic illustration for HBP-x with citric acid (CA) and trimethylolpropane (TMP).

Instruments and Measurements

Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) was carried out with a Waters 515 pump and a Waters 2410 refractive-index detector equipped with an OH pak KB-803 HQ column at (20.0±0.1)°C. The polyethylene glycol was used as the weight-average molecular weight (Mw) standard, and 0.2 mol/L $NaNO_3$ was the eluent.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was carried out with a DSC Q20 V23.12 Build 103 instrument in the range from 50 to 170°C with a scanning rate of 10°C /min under a nitrogen atmosphere.

FT-IR spectra

FT-IR spectra of HBP-x was recorded using KBr pellets in a Nicolet MX-1E FTIR spectrometer (Nicolet, Japan) between 4000 and 400 cm^{-1}.

^1H NMR

The ^1H NMR (AM 300 MHz Nuclear Magnetic Resonance, Bruker USA) of HBP-x was recorded with D_2O and DMSO-d_6 as mixed solvent.

The Acid Value

The acid value of HBP-x was measured with a 0.10 mol/L KOH standard solution titrated in the presence of phenolphthalein.

Shrinkage Temperature

The shrinkage temperature of leather was determined by using the standard IULTCS (International Union of Leather Technologists and Chemists Societies) method.[23] The leather sample was suspended vertically in water and glycerin, and the rate of heating was maintained at 2 ± 0.2°C/min. When the leather shrinks to one-third of its original length, this temperature was taken as the shrinkage temperature.[24]

The physical testing has been examined using the standard IULTCS methods.[23] The mechanical properties of chromium tanned leathers were analyzed by an electronic universal testing machine (UTM2102, Shenzhen Suns Technology Stock Co., Ltd.). The mechanical properties were compared after conditioning the leather for 48 h at 20 ± 2°C with a relative humidity of 65 ± 2%.

Chrome Uptake

The upper solution were collected by centrifugation, digestion and analysis for the chrome concentration using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Optima 2100DV, Perkin Elmer, USA)

$$\text{chrome uptake}=\frac{\text{initial chrome-chrome in effluent}}{\text{initial chrome}}\times 100\% \quad (1)$$

Results and discussion

Characterization of HBP-x

The characterizations of HBP-x were accomplished by a combination of FTIR, ^1H NMR and GPC. Following, we take the HBP-1 as the example.

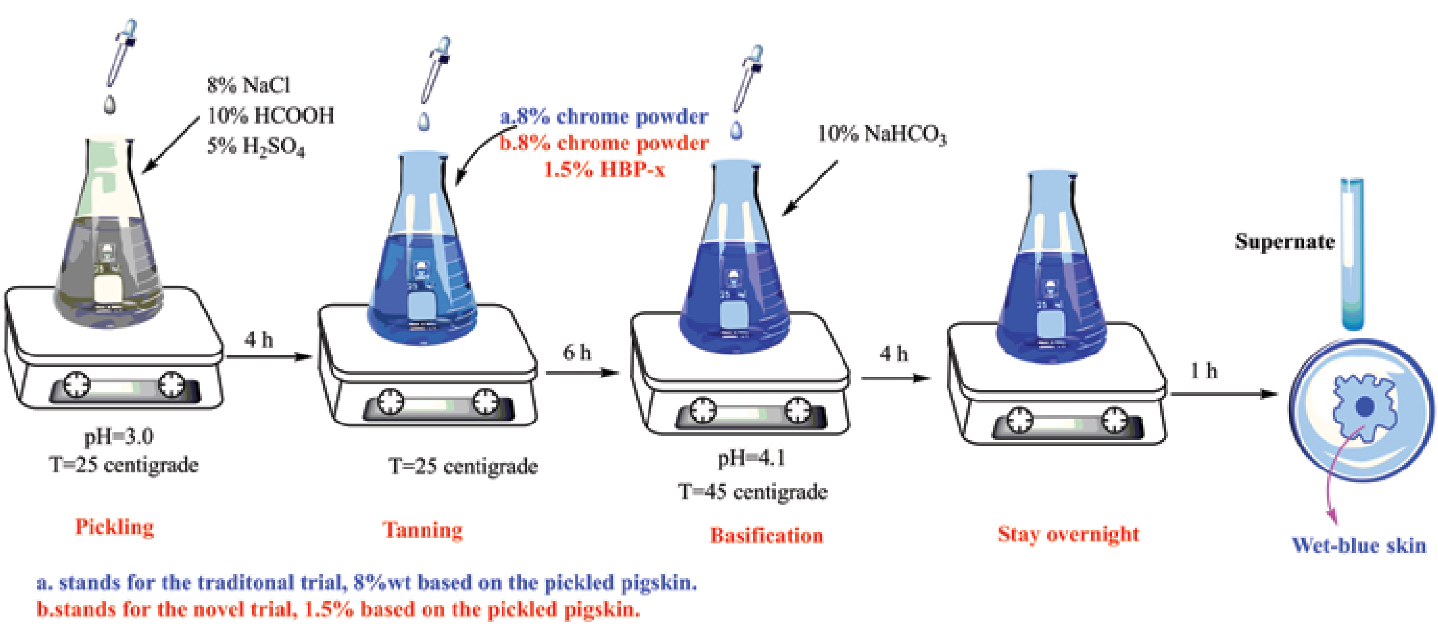


Figure 2. Schematic of traditional and novel chrome tanning process.

FTIR of the HBP-1

FTIR spectra provide a rapid means for the characterization of functional groups of organic molecules. Figure 3 shows the FTIR spectra of HBP-1.

The apparent strong absorption peak at 1735cm^{-1} was consisted of a superposition of three close peaks at 1748.3cm^{-1}, 1735.4 cm^{-1} and 1711.2cm^{-1}. The absorption peaks at 1748.3 and 1711.2cm^{-1} was the stretching vibration absorption of -C=O in -CO-OH of remaining CA[25] . And the absorption peak at 1735.4 cm^{-1} was the signal of C=O in ester groups. Absorption peaks at 1395.4cm^{-1}, 1332.0cm^{-1} attributed to the O-H in-plane bending vibration and 1193.7cm^{-1}, 1057.9cm^{-1} were the C-O stretching vibration absorption of tertiary hydroxyl in CA and primary hydroxyl in TMP respectively. Compared with initial mole ratio of two monomers, both these two groups of absorption peaks showed

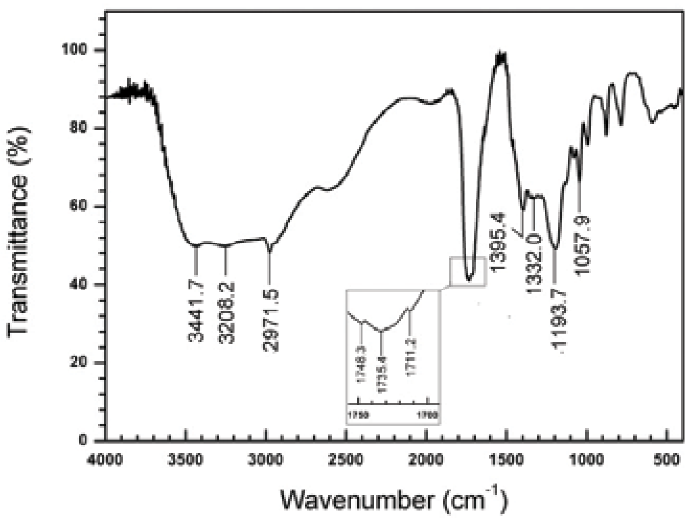


Figure 3. FTIR spectrum of HBP-1.

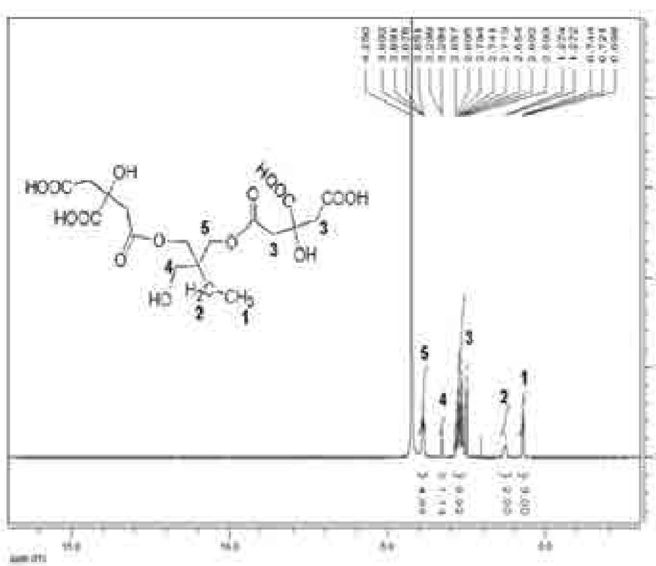


Figure 4. ^{1}H NMR spectrum of HBP-1 at 25°C.

that the vast majority of tertiary hydroxyl group in CA was retained in HBP-1 instead of involving in esterification.

^{1}H NMR of the HBP-1

It should be noted that the molecular structure diagram in Figure 4 does not represent the real structure of HBP-1. It was only used to demonstrate the chemical environment of HBP-1 protons in all cases. The chemical shifts of HBP-1 are ^{1}H NMR (d, ppm. Solvent, DMSO-d6), 0.74 ($C\underline{H}_3CH_2C(CH_2OH)_2$-), 1.32 ($CH_3C\underline{H}_2C(CH_2OH)_2$-), 2.60-3.86 ($COOHC\underline{H}_2C(COOH)(OH)CH_2$-)[26, 27], 3.3 ($CH_3CH_2C(C\underline{H2}OH)_2$-), 3.9 ($CH_3CH_2C(CH_2OH)_2C\underline{H2}$-)

Estimation of the DB

Related experiment[14] had proved that the reactivity of tertiary hydroxyl and carboxyl groups attached to quaternary carbon atom in citric acid is poor and it requires higher temperature and longer reaction time to participate in esterification. Therefore, under the experimental conditions of this article, no more than two carboxyl groups in citric acid are actually involved in the esterification reaction, and this polymerization is actually equivalent "A2+B3" type classic polymerization.[28] In this case, the branched structure in HBP-x is entirely formed by TMP structure.

Figure 5 shows all possible modes of the TMP structure in HBP-1. When the number of esterified hydroxyl groups in TMP structure changes from 3 to 1, it becomes dendritic unit (A), linear unit (B), and terminal units(C) respectively. Taking into consideration the high reaction temperature, large excess of carboxyl groups and high activity of hydroxymethyl, the cases represented by C and D in Figure 5 can be ignored under these experimental conditions. Thus, all signal of H_4 (δH_4=3.3ppm) in

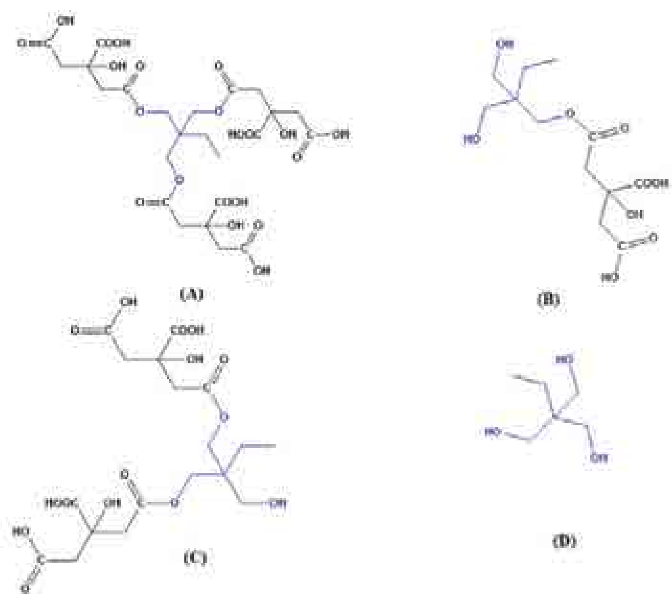


Figure 5. Structures of TMP in HBP-x for the calculation of DB.

^{1}H NMR spectrum comes from linear unit and the integrated area of H_5 protons in linear unit is 1.14×2=2.28.

$$DB = \frac{D+T}{D+T+L} \tag{2}$$

Equation (2) is a formula for calculating the degree of branching defined by Frechet[28]. In this Equation, D, T and L represent the proportion of dendritic, terminal and linear unit, respectively. According to the foregoing assumptions, the degree of branching of HBP-1 can be calculated as follows:

$$D+T+L=6.0$$
$$D+T=4.89-2.28=2.61$$
$$DB=\frac{D+T}{D+T+L}=\frac{2.61}{6}=0.43$$

The DB of all HBP-x(x=1, 2…7) is calculated in the same method.

Molecular Weights and Polydispersity

GPC is one of the most widely used techniques for the determination of the molecular weight and polydispersity of oligomers. Figure 6 illustrated the result of HBP-1 from the GPC analysis.

The molecular weight, polydispersity and DB of all the HBP-x are listed in Table II.

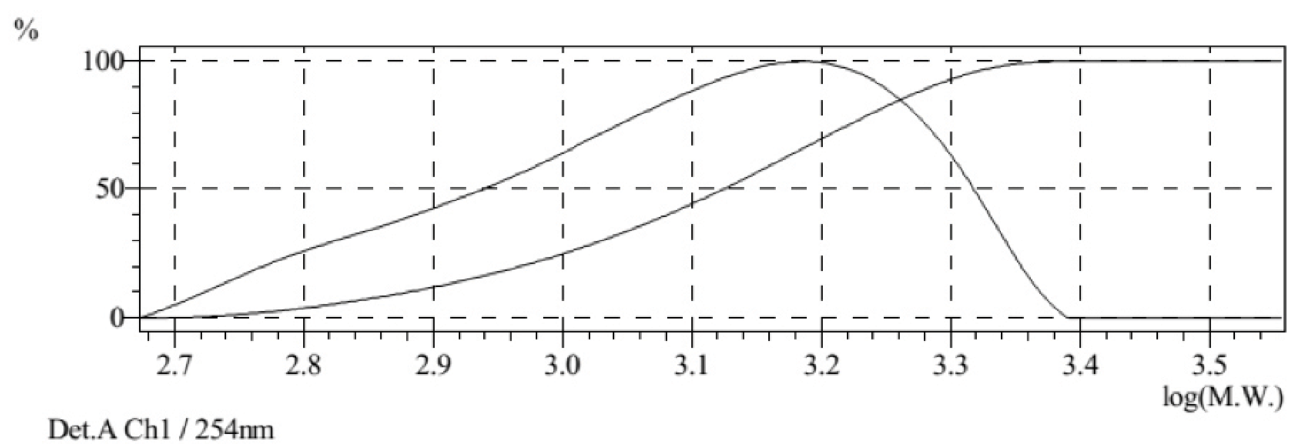
Chrome Uptake

Chrome uptake is one of the most important parameters for reduced chrome tanning. High chrome exhaustion or increased chrome uptake can increase the shrinkage temperature.

In this paper, the chrome uptake is relatively lower because the shaker was used instead of a drum in both the experimental and control trials. So, the difference of chrome uptake of each trial

Table II
Structural parameters of HBP-x(x=1,2…9).

Code name	$M_{n(Da)}$	$M_{w(Da)}$	PDI	DB
HBP-1	1190	1341	1.13	0.43
HBP-2	2162	2826	1.31	0.70
HBP-3	954	1027	1.08	0.71
HBP-4	1713	1909	1.11	0.72
HBP-5	697	1210	1.74	0.53
HBP-6	1097	1290	1.18	0.61
HBP-7	649	748	1.15	0.76



GPC Summary

Chromatogram Det.A Ch1

Title	Mn	Mw	Mz	Mz1	Mv	Mw/Mn
1-2.5-2 ok.lcd	1190	1341	1479	1595	0	1.13
Average	1190	1341	1479	1595	0	1.13
%RSD	0.000	0.000	0.000	0.000	0.000	0.00
Maximum	1190	1341	1479	1595	0	1.13
Minimum	1190	1341	1479	1595	0	1.13
SD	0	0	0	0	0	0.00

Figure 6. Molecular weights and polydispersity of HBP-1 as measured with GPC.

can also make sense. For the experimental trials, 1.5%wt HBPs, CA and PAA was added, respectively. The tensile strength, chrome uptake and Ts of chrome tanning leather in all trials are listed in Table III.

Effect of DB on the Chrome Uptake

DB is one of the most important characters which affect the chrome uptake. Figure 7 depicted the relationship between the DB and chrome uptake under the condition that the used HBP-x had similar Mw of 1300 Da.

It is clear that, incorporation of 1.5%wt HBP led to a remarkable improvement of chrome uptake with 28.8% (at least) comparing with that in the control trial. Furthermore, the larger the DB of the HBP is, the higher the chrome uptake leather can be obtained. Meanwhile, the chrome uptake of the leather tanned

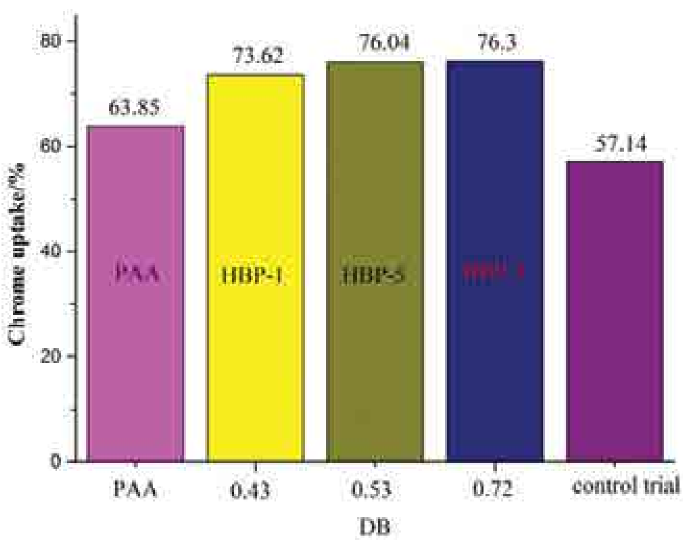


Figure 7. the effect of DB on the chrome uptake of leather.

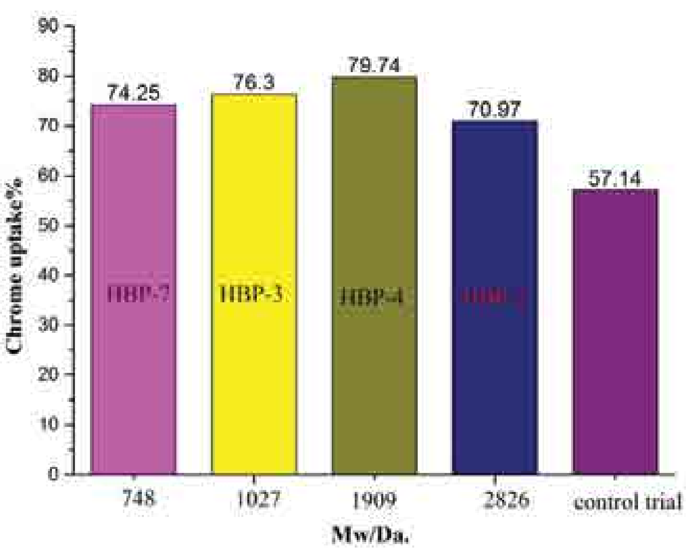


Figure 8. The effect of Mw of HBPs on the chrome uptake of leather.

with HBPs was much higher than PAA. These apparent improvements in chrome uptake were attributed to the higher DB of HBP, which imparts ellipsoidal structure and large numbers of terminated carboxyl groups, which could increase the permeation and combination of chrome with leather.

Effect of Mw on the Chrome Uptake

Figure 8 illustrates the relationship between Mw of HBP and its effect on the chrome uptake. As reported in literature,[30] HBP with Mw of 500-3000 could promote the chrome uptake of leather during the tanning process. For the HBPs with similar DB (0.7-0.8), the chrome uptake is much higher than the control trial. It attributed to the terminated carboxyl of the HBPs, which strengthened the coordination ability between chromium(III). When the Mw of the HBP is 1909, the chrome uptake reached maximum value 79.74%. Once the Mw of HBP is higher than 2000, it is difficult for the HBP and chromium(III) transfer from tanning bath to hides, resulting in lower chrome uptake.

In the past chrome tanning technology, CA was widely used as a masking agent. As shown in Table III, the chrome uptake is 69.62%, which outperforms that in the control trial. However,

Table III
Tensile strength, Chrome uptake and Ts of the chrome tanning leather.

Sample	Mw/ Da.	DB	Tensile strength/MPa	Ts/°C	Chrome uptake/%
HBP-1	1341	0.43	24.52	105.7	73.62
HBP-2	2826	0.7	31.10	109.8	70.97
HBP-3	1207	0.72	23.66	107.4	76.30
HBP-4	1909	0.72	32.37	109.3	79.74
HBP-5	1210	0.53	29.92	105.5	76.04
HBP-6	1290	0.61	27.13	107.9	73.53
HBP-7	748	0.76	25.61	108.7	74.25
PAA	2516		23.48	99.81	63.85
CA	210		21.95	105.5	69.62
Control trial			21.39	101.97	57.14

Based on the experimental results in Table III, the effect of structure of HBP-x on the properties of chrome tanning leather need to be further studied.

the chrome uptake assisted with CA is lower than that of HBPs, which may attribute to HBPs having more carboxyl content that can form a multisite cross-linked structure showing stable fixation with chrome.

Reduced Tanning with HBP

Shrinkage temperature (Ts), as previously mentioned, is an indicative parameter to evaluate the efficiency of the tanning process. In other words, shrinkage temperature reflects the reaction between chrome tanning agent and hide proteins which results in the fibers being stabilized by crosslinking. Accordingly, the increase of Ts of the tanned hides refers to the improvement of exhaustion and fixation of chrome during process.

HBP-4 has a high DB of 0.72 and Mw similar to 2000Da, which results in higher chrome uptake and Ts. Therefore, the HBP-4 was found to be the proper one to study the reduced tanning.

It is clear that, incorporation of 7.5%wt HBP-4, the tensile strength, chrome uptake, and shrinkage temperature were improved by a large margin. In traditional chrome tanning process, Ts can be achieved above 100°C with a chrome content of 5wt%. Once the HBP-4 was incorporated, the Ts of leather could reach 100.2°C just needing the chrome content of 3.5wt%. In addition, the chrome uptake is higher and the tensile strength is better than the specimen which tanned with 5.0wt% chrome powder.

Figure 9 (a) and (b) illustrate the reason that HBP could find its application in reduced chrome tanning. In traditional chrome tanning process, just four chrome molecules bridge gap of

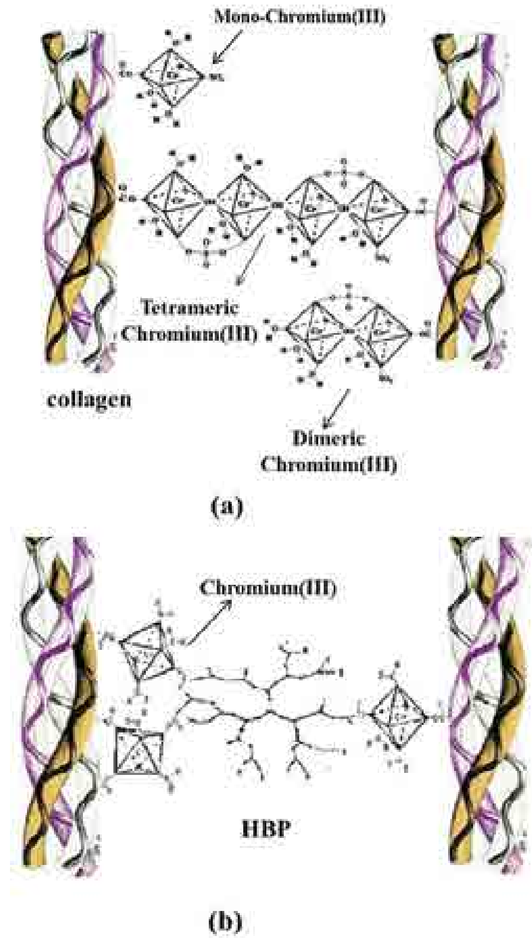


Figure 9. Crosslinking model between chromium, collagen and HBPs. (a) Stands for traditional chrome tanning; (b) stands for the novel chrome tanning with HBP as the auxiliary agent.

Table IV

The mechanical properties and chrome uptake of leather through reduced tanning with HBP-4.

Specimen	Chrome powder/ wt% of hide	Tensile strength /MPa		Chrome uptake/%		Shrinkage temperature/°C	
		C	E (HBP-4*)	C	E(HBP-4*)	C	E(HBP-4*)
1	3.0	13.41±0.23	20.53±0.21	71.8	76.5	93.8±0.3	98.8±0.2
2	3.5	14.72±0.16	18.92±0.18	65.1	67.4	94.1±0.2	100.2±0.1
3	4.0	9.63±0.14	13.36±0.21	64	69.8	93.8±0.2	105.6±0.2
4	4.5	9.12±0.14	15.56±0.20	65.3	67.3	98.9±0.3	103.9±0.2
5	5.0	17.48±0.13	28.54±0.18	62	66.7	100.7±0.2	104.1±0.2

Note: C is the abbreviation of control trial; E is the abbreviation of experimental trial. 7.5wt% (based on dosage of chrome power) HBP-4 was added in each experimental trial.

collagen fibers to crosslink the collagen effectively. Moreover, chrome (about 80%) could be mono-combined with collagen, which can be released during the washing, retanning, and degreasing process.[30] Therefore, more chrome would be disposed in the effluent.

Figure 9 (b) illustrates the role that HBPs played on crosslinked of collagen and chrome. It is clear that incorporation of HBP changes the crosslinked pattern between the chrome and collagen. It forms a stable crosslinking network based on the multisite cross-linked structure, thus improving the chrome fixation. Furthermore, the chrome dosage could also be reduced during the novel chrome-tanning process.

Conclusion

A series of carboxyl-terminated oligomers were synthesized and their structure, including DB and Mw, was characterized by FTIR, ^{1}H NMR and GPC. The effect of DB and Mw on the chrome uptake and shrinkage temperature of leather (Ts) was investigated. Experimental results show that the chrome uptake was affected by both degree of branching and molecular weight. The HBP, which has the Mw close to 2000 and high DB, was found to have better performance in chrome uptake and Ts. Meanwhile carboxyl-terminated oligomer found its application in reduced chrome tanning by promoting the permeation and fixation of chromium(III), which suggests a foundation for the usage of HBP in chrome tanning.

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