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Supplementary Information

Development of Hyperbranched Poly (Amine-Ester) based Aldehyde/Chrome-free Tanning Agent for Sustainable Leather Resources Recycling

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^{1}H NMR spectrum and the degree of branching (DB) of HHBPs

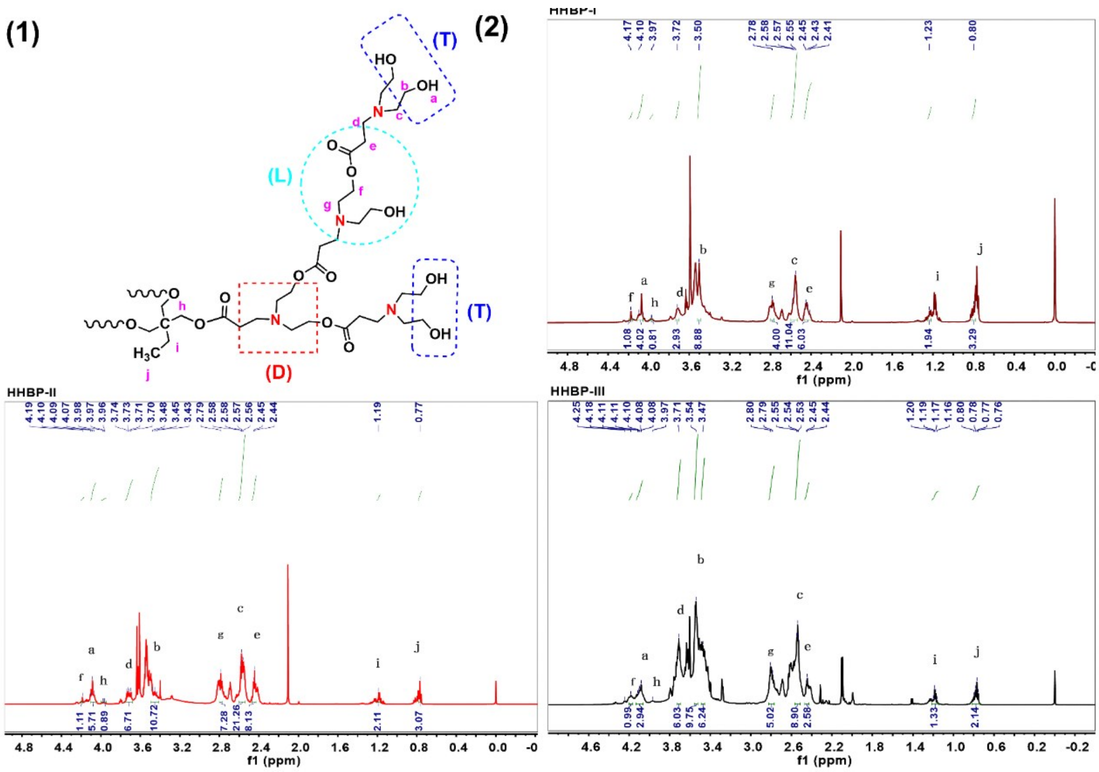

Fig. S1. (1) Dendritic unit (D), linear unit (L), and terminal units (T) of HHBPs respectively. (2) The ^{1}H NMR spectrum of HHPBs (Deuterated chloroform).

Fig. S1. (2) shows that the spectra of HHBP-I, HHBP-II and HHBP-III, which signal appeared at δ_H 4.20 ppm attachment is attributed to hydroxyl group of AB_2 monomer ($-CH_2CH_2OH$) (a). In addition, the signal at δ_H 3.49 ppm (c) belong to the $-CH_2$ of AB_2 monomer ($-CH_2OH$), and the signal at δ_H 2.57 ppm belong to another $-CH_2$ of AB_2 monomer (-NCH_2-) (b). While the methylene group linked to the ester group appears at δ_H 2.49 ppm (e), and another methylene group linked to the N atom appears at δ_H3.71 ppm (d), and the signal appeared at δ_H 0.80 ppm is attributed to the methyl (j). Furthermore, the signal appeared around δ_H 1.23 ppm is attributed to the methylene groups on the (CH_3-CH_2-C-) structure in TMP (i). The signal of the methylene structure (-CH_2-) between one AB_2 monomer and another AB_2 monomer appears around δ_H 4.20 ppm (f) and δ_H 2.70 ppm (g), respectively. As for HHBP-I, the integral area of different group is H_a (4.02), H_b (8.88), H_c (11.04),

H_d (2.93), H_e (6.03), H_f (1.08), H_g (4.00), respectively.

In a hyperbranched structure based on a branching multiplicity of 2 (AB_2 monomer), three different building units are present: dendritic unit (D), linear units (L), and end groups (“terminal units”, T), as well as precisely one single focal moiety [1](**Fig. S1. (1)**). Perfectly branched dendrimers consist only of dendritic and terminal units, the degree of branching has been normalized to 1 (i.e., 100%), whereas no linear polymers. Combined with the analysis of nuclear magnetic resonance spectrum (**Fig. S1**), it can be found that a linear unit (L) contains $2H_e$,$2H_d$,$3H_b$,$3H_c$,$1H_f$,$1H_g$; a dendritic unit (D) contains $3H_e$,$3H_d$, $2H_f$,$2H_g$; a terminal units (T) contains $1H_e$,$1H_d$, $2H_b$,$2H_c$. Therefore, according to equation by Frechet [2] the degree of branching of HHBP-I can be calculated, which is 0.5091. Similarly, HHBP-II and HHBP-III can be calculated in the same method, which is 0.5111and 0.5874 respectively.

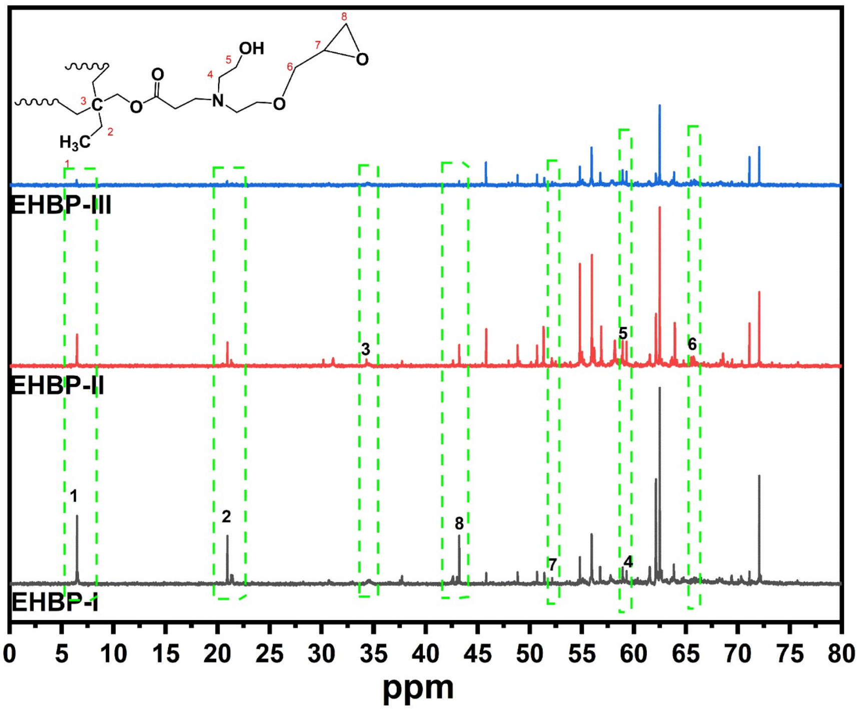

Fig. S2. ^{13}C NMR spectrum of the EHBPs.

^{13}C NMR spectrum of the EHBPs

As depicted in the ^{13}C NMR spectrum of EHBPs in **Fig. S2**, the peak at δ_C: 6.5 ppm belongs to methyl proton, and the δ_C: 21.0 ppm attributing to the methylene proton connected thereto. The core carbon proton signal peak of TMP appeared in δ_C: 34.5 ppm. In addition, the protons of methylene groups attached to hydroxyl groups (−NCH_2CH_2OH) belonged to the signals of δ_C:59.8 and 59.3 ppm, respectively, which also proved that the polymer still contains hydroxyl groups after epoxy modification. What's more, the chemical shifts separately appeared at δ_C: 65.7, 52.2 and 43.2 ppm, these were attributed to the methine connected to epoxy groups, as well as the methylene and methine groups on the epoxy group[3].

Relative molecular mass and epoxy value of EHBPs

Table S1

Theoretical relative molecular mass and theoretical & measured epoxy value of EHBPs

Samples	EHBP-I	EHBP-II	EHBP-III
Theoretical relative molecular mass	947	2237	4817
Theoretical monomolecular epoxy group/(mol/mol)	6	12	24
Theoretical epoxy value/(mol/100 g)	0.6336	0.5364	0.4982
Measured epoxy value/(mol/100 g)	0.5305	0.4397	0.2845
Measured epoxy value/(mol/mol)	5	10	14

Molecular weight of EHBPs

The molecular weight of EHBPs were determined, and the results are presented in **Table S2**.

Table S2

Molecular weight and its distribution of EHBPs.

Samples	M_w	M_n	M_p	M_z	PDI
EHBP-I	27817	25573	25555	29827	1.09
EHBP-II	193703	103086	134424	358261	1.88
EHBP-III	1290263	1050585	1742805	1531346	1.23

Note: M_w——Weight-average molecular weight
M_n——Number-average molecular weight
M_P——Peak molecular weight
M_z——Mass-average molecular weight
PDI——Polymer dispersity index

Tanning process

The process recipe for wet-white leather was shown in **Table S3**.

Table S3

Tanning processes.

Process	Chemicals	Offer/%	T/°C	t/min	Remarks
Rewetting	Water	150	25	20	Drain
	Salt	10			
Tanning	Water	50	25	4-5	Adjust the pH of the bath liquid to 6.5±, cast skin. Mechanical action for 2h, add hexamethylenetetramine, and continue to rotate for 2 - 3 hours.
	Salt	5			
	SDS	1			
	EHBPs/HHBP-III	X			
	Hexamethylenetetramine	1			
Basification	Sodium bicarbonate	1×3	30	20×3	Slowly adjust the pH of the bath liquid to 8.5± and stop mechanical action overnight.

Note:①The values of X for EHBPs (EHBP-I, EHBP-II, EHBP-III) are 10%, 12%, 14%, respectively; as for HHBP-III, which is 14%.

②The squeezed sheep pickled skin is weighed 200% as the basis for the dosage.

HHBP-III treated leather analysis

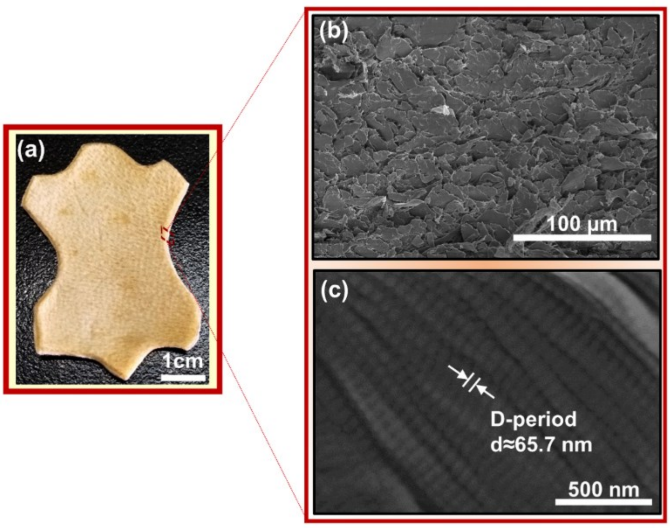

Fig. S3. The optical photo (a) of HHBP-III tanned leather, and FESEM images of the cross-sectional (samples tanned with 14% HHBP-III, 100 μm ×500; 500 nm ×70.0k).

The optical photo and the microstructure images of the 14% HHBP-III tanned leather were shown in Fig. S3. Although the Ts of HHBP-III tanned leather could reach 67.1℃, its overall macroscopic morphology was similar to those of pickled skin (control). The microstructure of collagen fibers looked very sticky and their dispersibility were poor. Therefore, it was illustrated that the epoxy groups in EHBPs tanning agent play the role of tanning and dispersing fiber, but not hydroxyl groups.

FT-IR analyses of different treated leather

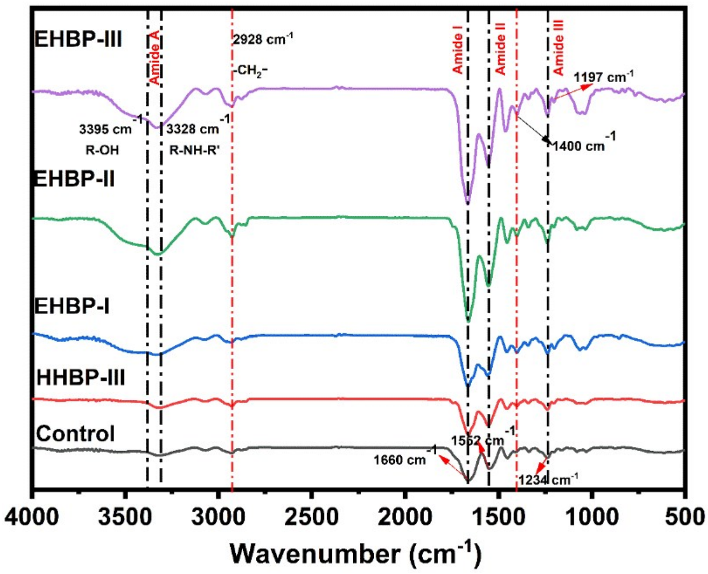

Fig. S4. FTIR spectra of leathers with EHBPs, HHBP-III treated and pickled skin.

Sampling from different treated leather by filing, and the samples were placed in a drying oven with a vacuum of -0.08 MPa and a temperature of 25℃ for 72 hours to remove moisture from the leather, and then the Fourier Transform Infrared Spectrometer (Vertex70, Brooke Germany Ltd) was used for chemical bonding identification. As demonstrated in **Fig. S4**, the characteristic absorption peak of protein amide strip was mainly presented in the pickled skin (Control), of which strong peaks at 1660 cm^{-1} was caused by the amide I (stretching vibration of carbonyl in carboxyl)[4], and 1552 cm^{-1} was the characteristic absorption peak of amide Ⅱ band (C-N-H bending vibration), then 1234 cm^{-1} was the characteristic absorption peak of amide Ⅲ band (C-N stretching vibration)[5, 6]. Furthermore, peaks at 2928 cm^{-1} was the symmetric and antisymmetric stretching vibrational absorption of methylene (-CH_2-) groups[7]. A new signal peak appeared in 1197 cm^{-1} and became stronger gradually, which may be caused by the C-O-C bond in the ester group. What's more, the stretching vibration absorption peaks of secondary amine N-H and O-H were at 3328 cm^{-1} and 3395 cm^{-1}, separately, and the intensity also enhanced gradually with the tanned leather of EHBP-I, EHBP-II and EHBP-III. To sum up, it was indicated that the epoxy group on EHBPs mainly reacts with the active amino group on collagen to stabilize the structure of collagen fiber, which enhanced the proton signals of amide bond, - NH-C-, -CH_2- , and –OH groups of collagen, but it could be seen that the main features of the modified collagen absorption peak had no obvious displacement, showing that the triple-helix structure of collagen was not destroyed by the EHBPs.

TG-DTG

Table S4

Data collected from TG and DTG curves

Samples	T_d (°C)	Residual amount of T_d（%）	Residual amount of 600°C（%）
Control	312.5	61.3	22.9
EHBP-I	319.8	62.6	27.5
EHBP-II	323.8	64.2	29.9
EHBP-III	331.0	62.7	26.6

SEM grain surface of the grain of EHBPs tanned leather and pickled skin

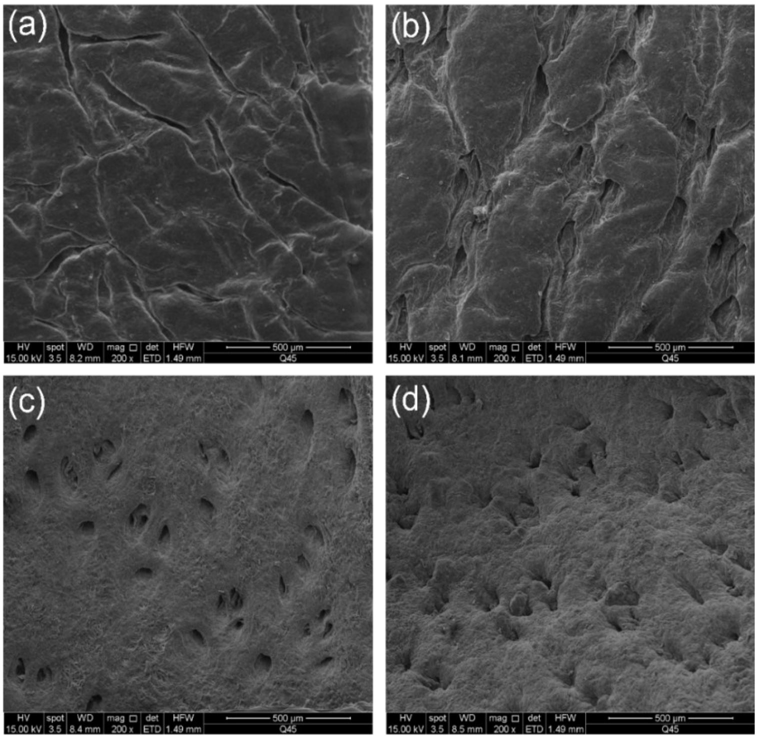

Fig. S5. SEM images of grain surface (500 μm: × 200) of untanned leather (Control, a), EHBP-I (b), EHBP-II (c) and EHBP-III tanned leather (d).

Pores structure of EHBPs tanned leather and pickled skin

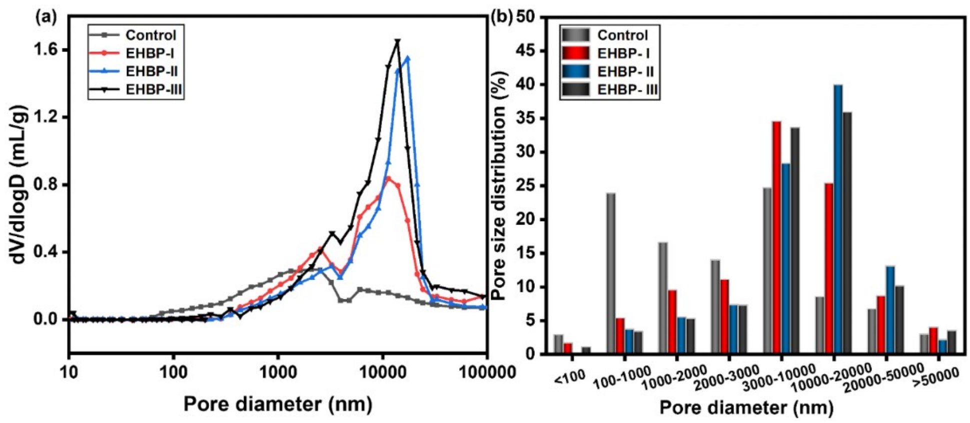

Fig. S6. Pores size distribution measured by MIP.

EHBPs bio-degradation analysis

The biodegradability study of the EHBPs compounds alone to further prove its environmental impact. Similarly, the standard method (HJ/T 399 2007) was used to analyze the chemical oxygen demand (COD) and a BOD tester (BOD TrakII HACH) was used to evaluate biochemical oxygen demand (BOD), which corresponding data were listed in the following table:

Table S5

The value of BOD_5 and COD of EHBPs tanning agent

Samples	BOD_5 (mg/L)	COD_{Cr} (mg/L)	BOD_5/COD
EHBP-I	10333.3±	27630.3±	0.37
EHBP-II	10666.7±	29580.5±	0.36
EHBP-III	12583.3±	38161.2±	0.33

Environmental impact assessment

Table S6

The relationship between the value of BOD_5/COD and the biodegradability of organic tanning agents[8]

BOD_5/COD	>0.45	0.3-0.45	0.25-0.30	<0.25
Biodegradability	Very easy	Easy	Difficult	More difficult

Reference

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