Preparation of Hyperbranched Polyglycidyl by Ring-opening Polymerization for the Chrome-free Leather Production

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Abstract

Currently, minimizing the environmental impact of tanning processes is the goal of many tanners, which have forced the leather industry to develop tanning systems based on natural products. Biomass-derived polyaldehyde or vegetable-aldehyde combination tanning is the current research hotspots. While, the usage of these tanning materials may result in high organic load in the effluent leads to high biological and chemical oxygen demand. Sparked from vegetable tanning, employing excess by-products of biomass glycerol and glycidol to produce high value-added chrome-free tanning agents will be in great significant. In this paper, a series of hyperbranched polyglycidyl (HPG) with different hydroxyl group, various average-molecular weights and molecular weight distribution have been developed by cationic or anionic ring-opening polymerization of glycidol. The denaturation temperature of the wet-white leather as well as biological and chemical oxygen demand of effluent have been measured. The results show that the denaturation temperature of the wet-white leather significantly improved. The highest denaturation temperature can reach 115.6 ℃ by employing 5% HPG-C4. Compared to hydroxyl group content, average molecular weight and its distribution of HPG play a more dominant role in improving the denaturation temperature of the wet-white leather. In addition, compared to control trial, the chemical oxygen demand and biological oxygen demand of effluent tanning by HPG can reduce by nearly 1/5 and 1/3, respectively. Therefore, the use of HPG benefits to the complete elimination of chrome pollution and greatly reduce the biological and chemical oxygen demand of the effluent.

Keywords: Hyperbranched polyglycidyl, chrome-free tanning, denaturation temperature, biological and chemical oxygen demand, cleaner leather making

1. Introduction

Hide or skin, a by-product of the meat industry, is composed of collagen fibers with tight network. Leather making involves conversion of skin or hide protein (collagen) into practical products[1, 2]. In the leather manufacturing process, tanning is the key process, in which the collagen fiber bundles are separated and cross-linked by tanning agent. To date, tanning agent mainly include vegetable tannin, aldehyde tanning agents, synthetic tanning agents and metal tanning agent[3].

Currently, minimizing the environmental impact of tanning processes is the goal of many tanners[4-6]. Nowadays, environmental concerns have forced the leather industry to develop tanning systems based on natural products. Vegetable tannins, including the hydrolysable tannin and condensed tannin, could improve the hydrothermal stability of hide is not only based on numerous phenolic hydroxyl group but also on their appropriate molecule weight (usually in the range of 500-3000) and wide molecular weight distribution[7-9]. However, there is limitation in the usage of vegetable tanning materials because of its high organic load in the effluent generated, which is difficult to degrade and leads to high biological and chemical oxygen demand. Hence, aldehyde and similar-to-aldehyde tanning agents stands out among all tanning chrome-free tanning agents. Aldehyde can form a Schiff base with amino groups of collagen. Recently, biomass-derived polyaldehyde or oxidized polysaccharide (In particular, the polysaccharide with the vicinal diols structural unit can be selectively oxidized to introduce aldehyde groups for preparing dialdehyde polysaccharide) have regained a lot of attention[10-12]. While the large molecule of bio-based aldehyde tanning may limit its penetration and reaction in leather. Moreover, high organic load in the effluent generated leads to high biological and chemical oxygen demand. Develop green and easily penetrated aldehyde tanning seem good application prospects. A greener and eco-friendly D-Lysine aldehyde complex has been developed in the present investigation[13]. The results showed that aldehyde-tanned leather can promote the hydrothermal stability of skin collagen and has better water and sweat resistance properties than chrome tanning. Unfortunately, the price of D-lysine limits its application.

However, the binding strength of the tanning agent in collagen is dependent not only on the type of chemical reaction but also on the number of reaction points and the density of crosslinking in collagen. Hence, vegetable-aldehyde combination tanning have been proposed which could combines the advantages of both vegetable tanning and aldehyde tanning[14]. For example, mimosa- oxazolidine combination tanning agent has been reported, in which mimosa acting as a vegetable tanning agent and oxazolidine as an aldehydic tanning agent. Nevertheless, the empolyment of vegetable tanning leather and dialdehyde tanning agents inevitably results in aldehyde residue.

As the most widely used biomass material, sugar is easily converted into a product of raw materials under the action of microorganisms[15]. Therefore, as one of the important platform compounds for biomass development and utilization, glycerol and glycidol to produce high value-added fine or bulk chemicals has not only attracted widespread attention from the industry but also become a research hotspot in the scientific and technological community[16, 17]. In recently years, hyperbranched polyglycerols (HPG) have been used in a wide variety of applications due to their thermal stability, biocompatibility and low toxicity, originating from three-dimensional branched structure and high number of end-hydroxyl groups, which are capable of further functionalization[18-20]. In general, HPGs are synthesized by cationic or anionic ring-opening polymerization of glycidol[21, 22].

Herein, we synthesized a series of hyperbranched polyglycidyl with different hydroxyl groups and average molecular weight by cationic ring-opening copolymerization and anionic ring-opening homopolymerization and explored their potential as chrome-free tanning agents. The tanning effect including denaturation temperature, appearance of surface and morphology, COD and BOD are measured and compared with gallic acid. HPGs was used for main tanning to establish a new greener chrome-free tanning system for the leather making.

2. Material and Methods

2.1 Materials

Glycerol (99%), tetrahydrofuran (THF), methanol, dichloromethane, N-Methyl-2-pyrrolidone (NMP), and gallic acid were purchased from Aladdin (Shanghai, China). Potassium *tert*-butoxide (K-*t*-OBu, 1mol/L in THF), $BF_3 \cdot Et_2O$ was purchase from the Adamas (Shanghai, China). Glycidol (96%) was purchased from HEOWN (Tianjin, China). The chemicals such as sodium chloride, acetic acid, formic acid, used in tanning operations were those normally used in the leather industry. Pickled sheepskins were provided by Shenghui chemical CO., Ltd.

2.2 Method

Synthesis of polyglycidyl by anionic ring-opening polymerization

HPG was prepared by anionic ring-opening polymerization with glycerol and glycidol. In a glass reactor requipped with a mechanical stirrer under nitrogen atmosphere, glycerol (0.46g, 5mmol) was partially deprotonated (10%) with 1.5 mL K-t-OBu. Then *tert*-butanol and THF were distilled off from the melt under reduced pressure. The glycidol (37g, 250mmol, 50 wt % in NMP) was slowly added at 120 °C over 12 h. After completion of addition, the reaction mixture was stirred for further 2 h at the same temperature. The resulting solution dissolved in methanol and stirred overnight with ion-exchange resin. The transparent, highly viscous liquids product (marked HPG-A) were obtained by remove the solvent under reduced pressure.

Synthesis of polyglycidyl by cationic ring-opening polymerization

The mixture of THF (28.86g, 0.4mol), glycidol (7.43g, 0.1mol), and CH_2Cl_2 (50mL) was added into a 250 mL four-necked flask in an ice-water bath. Then $BF_3 \cdot Et_2O$ (1mL, 1mol/L) was dropwise added into the mixture and keep the temperature at 0~4 °C. After reaction for 4 h, distilled water (1mL) was added to terminate the reaction. The transparent, viscous liquids product (marked HPG-C4) was obtained by removing the unreacted THF and CH_2Cl_2 under reduced pressure.

HPG-C2 was prepared following the same produces as described above for HPG-C4. For the synthesis of HPG-C2, THF (28.86g, 0.4mol), glycidol (14.89g, 0.2mol), and CH_2Cl_2 (50mL) were employed.

Tanning of pickled sheepshin

Tanning of pickled sheepskin (cut into 8*8 cm, weighted as the base of dosage) is processed in 250 mL Erlenmeyer flask on a shaker. The tanning process includes pickling, tanning, and basifying. Briefly, the pickled hide was soaked in 6%wt sodium chloride, and then the pH was adjusted to 3.0 by 5%wt sulfuric acid and formic acid at 25 °C. Then the pickled hide was treated with 5%wt HPG (on weight of pickled sheepskin). For the comparison, equal amount of 5% gallic acid was added and named control trial. After tanning for 4 hours, pH of the tanning bath raised to 4 or 6 by using 10 wt% of sodium bicarbonate solution. Thereafter, distilled water (same quality to pickled sheepskin) was added and the shaker was set to 40 °C for another 4 h and stay overnight. Finally, the wet-white leather was obtained by shaking for 1 h on the next day.

2.3 Characterization

Structure characterization of polyglycidyl

FT-IR spectra of polyglycidyl (HPG-C4, HPG-C2, HPG-A) were recorded using KBr pellets in a Nicolet MX-1E FTIR spectrometer (Nicolet, Japan) between 4000 and 400 cm^{-1}. Gel permeation chromatography (GPC) was used to determine the molecular weight and polydispersity of the polyglycidyl. The polyethylene glycol (Mw=5900) was used as the standard of weight-average molecular weight and 0.2 mol/L NaNO3 as the eluent.

Denaturation temperature

The denaturation temperature of the wet-white was determined by differential scanning calorimetry (DSC, NETZSCH, Germany). The leather samples were added into aluminum pans and carried out in the range from 20 °C to 150 °C with a scanning rate of 10 °C per min under nitrogen atmosphere.

The morphology of leather

The morphology of leather were observed by using a scanning electron microscope (TM3030, HITACHI, Japan).

COD and BOD of the effluent

The COD and BOD of the effluent was measured by Pack Test (Kyoritsu Chemical-Check Lab.,Corp.)

3. Results and Discussion

3.1 Structural characterization of the polyglycidyl

The FTIR of polyglycidyl prepared by cationic or anionic ring-opening polymerization are shown in Fig.1. As can been seen in Fig.1, the absorption of HPG-A, HPG-C4 and HPG-C2 are similar. The absorption peaks at 3406 cm^{-1} and 2921 cm^{-1} are attributed to the O-H stretching vibration. The peak around 2867 cm^{-1} is attributed to the stretching vibration of C-H of alkanes. The strong and sharp peak around 1109 cm^{-1} is assigned to the stretching vibration of C-O-C of ether. These absorption peaks demonstrate that hydroxyl terminal polyglycidyl are successfully synthesized.

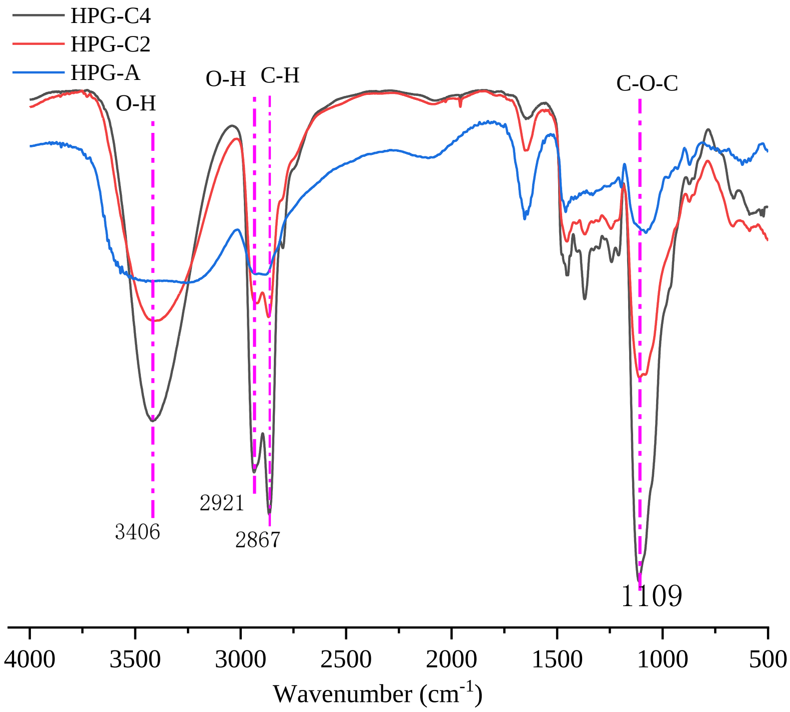

Fig.1 FTIR of the polyclycidyl

Fig. 2 presents the GPC results of HPG-C4, HPG-C2 and HPG-A. The GPC curves are also similar. The average molecular weight of polyglycidyl which was obtained according to standard substance linear polyethylene glycol (Mw=5900 g/mol) are listed in Table 1. It is clear that both HPG-C4 and HPG-A consist of two parts, the high part has a number-average molecular weight about 2700 g/mol and the low part has the number-average molecular weight about 660 g/mol. Moreover, the high molecular weight part of HPG-C4 has a wider molecular weight distribution (1.56), and the low molecular weight part has a narrower molecular weight distribution (1.04). In addition, the average molecular weight and molecular weight distribution of HPG-C2 are lower than those of HPG-C4 and HPG-A (high molecular part).

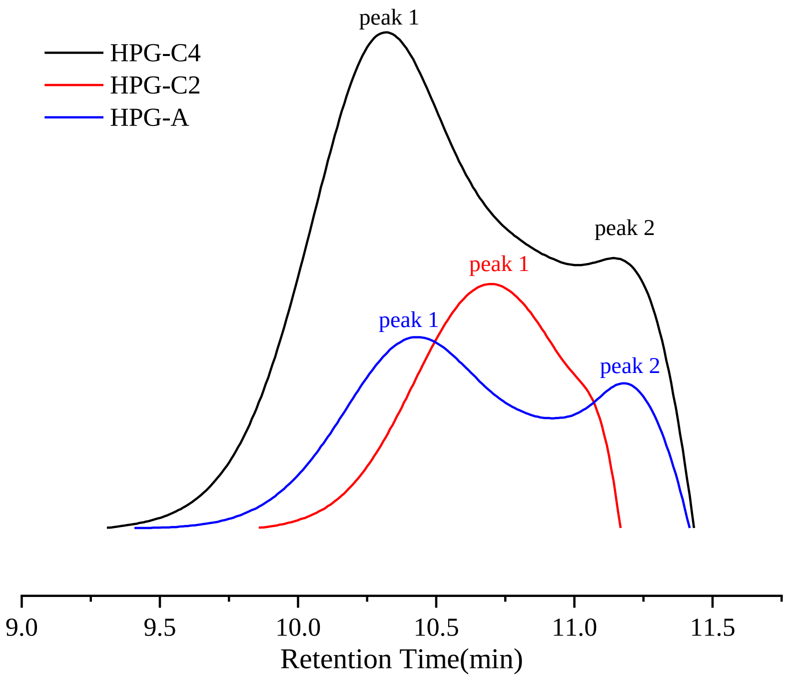

Fig. 2 The GPC results of the polyglycidyl

Table 1 The molecular weight and molecular weight distribution of polyglycidyl

	M_n(g/mol)	M_w(g/mol)	M_w/M_n	M_n(g/mol)	M_w(g/mol)	M_w/M_n
		Peak1			Peak 2	
HPG-C4	2764	4305	1.56	662	692	1.04
HPG-C2	1717	2213	1.29	-	-	-
HPG-A	2785	3740	1.34	724	775	1.07

3.2 The Denaturation temperature of leather

On the basis of the heat capacity changes of the samples during the thermally activated denaturation process, the DSC method offers an objective and reliable way of evaluating the thermal stability[23]. The peak in the DSC profiles indicates the denaturation temperature (Td). The DSC profiles of wet-white treated with polyglycidyl and gallic acid were shown in Fig. 3. Specifically, the Td value of the wet-white leather are shown in Table 2.

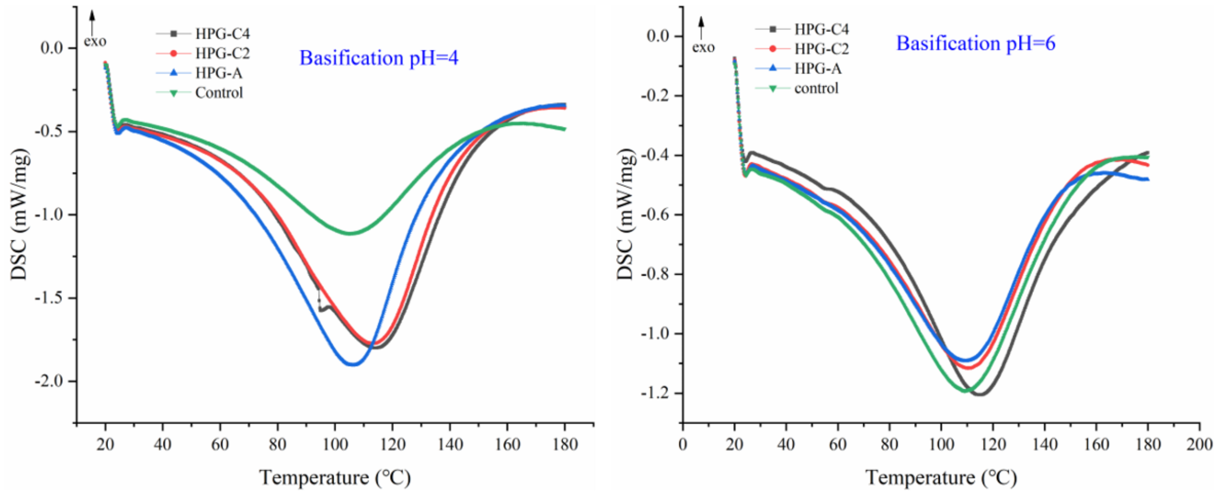

Fig. 3 DSC profiles of wet-white leather under different basification pH

It is apparent that all the wet-white leather show a single peak in the DSC profiles. The Td of wet-white leather tanned by polyclycidyl show about 4 ℃ higher than gallic acid. Among all the trial, the Td of the wet-white leather treated with HGP-C4 (which has the widest molecular distribution) show the highest value. Theoretically, the terminal hydroxyl group content of polyclycidyl prepared by cationic opening copolymer of THF and glycidol will be lower than that of polyglycidyl prepared by anionic homopolymerization of glycidol. Moreover, with the higher the tetrahydrofuran content in the feeding ratio, the lower the hydroxyl content of the copolymer. Therefore, the order of hydroxyl content is HPG-C4< HPG-C2<HPG-A. Combined with GPC results, it can be known that compared to hydroxyl group content, molecular weight of polyclycidyl plays a more dominant role in improving the Td of the wet-white leather. The wider molecular weight distribution favors crosslinking collagen fibers in various parts, thereby imparting a higher denaturation temperature to collagen fibers. And the lower molecular weight part facilitates its penetration and reaction in the hierarchical structure of leather, which is consistent with the literature [24-26].

In addition, we also studied the effect of basification pH on the thermal denaturation temperature of wet-white leather. Table 2 shows that except for HPG-C2, with the increase the pH of basification, the Td of wet-white leather is slightly higher. It can be infer that the pH of basification has little effect on the Td of the wet-white leather.

Table 2 The denaturation temperature of the wet-white leather tanning in different basification pH

	Denaturation temperature/°C Basification pH=4	Denaturation temperature/°C Basification pH=6
HPG-C4	114	115.3
HPG-C2	113.3	110.1
HPG-A	106.3	109.3
Control	102.9	105.2

3.3 The appearance of surface and morphology of wet-white leather

Fig. 4 show the digital photos of the wet-white leather. The wet-white leather tanned by polyclycidyl show a flat and white surface. In contrast, the control trial of leather has a yellowish color with a noticeable shrinkage on the surface. And with the increase of basification pH value, the yellowing and shrinkage of the leather surface become more obvious.

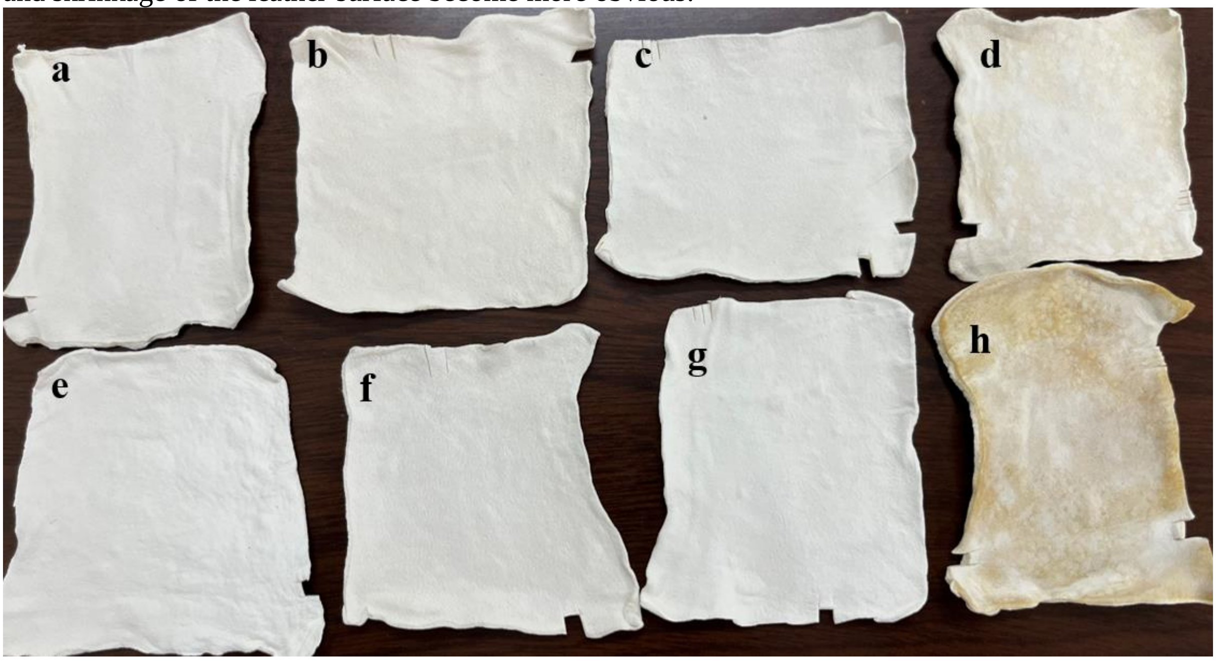

Fig.4 the digital photos of the wet-white leather.

a, b, c, d refers the wet-white leather tanned by HPG-C4, HPG-C4, HPG-A and control trial under the basification pH 4. e, f, g, h refers the wet-white leather tanned by HPG-C4, HPG-C4, HPG-A and control trial under the basification pH 6.

The morphology of the cross section of wet-white leather in the magnification scanning of 100 and 200 are shown in Fig. 5. It is obviously that the collagen bundle of the leathers tanned with the polyclycidyl are in good dispersion, especially for HPG-C4 tannned leather. Moreover, there is no obvious difference in the dispersion of the grain layer, flesh layer, and middle layer. Literatures have demonstrated that good dispersion of collagen bundle are attributed to effective crosslinking of collagen[27-29]. So this result illustrates that polyclycidyl penetrated into the skin and effectively crosslinked collagen fibers. In contrast, for control trial, most regions of the collagen bundles bind tightly. There is only a little dispersion regions closed to grain layer.

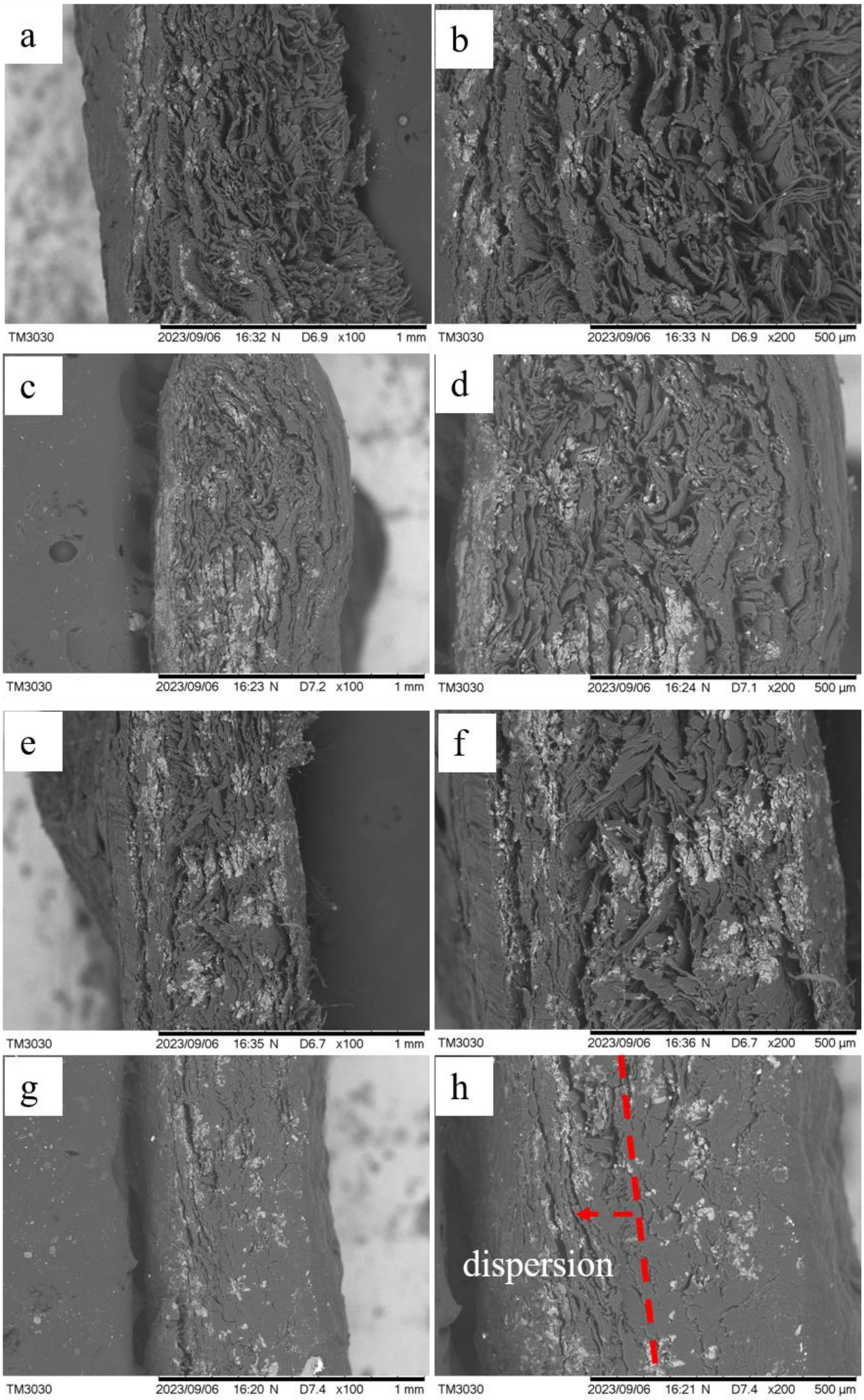

Fig.5 the morphology of leather tanned by polyglycidyl

a, b wet-white leather tanned by HPG-C4; c, d wet-white leather tanned by HPG-C2; e, f wet-white leather tanned by HPG-A; g, h wet-white leather tanned by gallic acid.

3.4 COD and BOD of the effluent

The COD and BOD of the effluent exceed the measuring range of the test paper. Therefore, the effluent is diluted for 100 times and then measured by test paper. The COD of the effluent tanned by polyglycidyl are about 2000 mg/L, which was significantly lower than the 10000 mg/L in the control group. Meanwhile, the COD of the effluent tanned by polyglycidyl are about 10000 mg/L, which is 1/3 of the control group. These results suggest that glycidyl binds more easily to collagen, which are consistent with the previous DSC and SEM results.

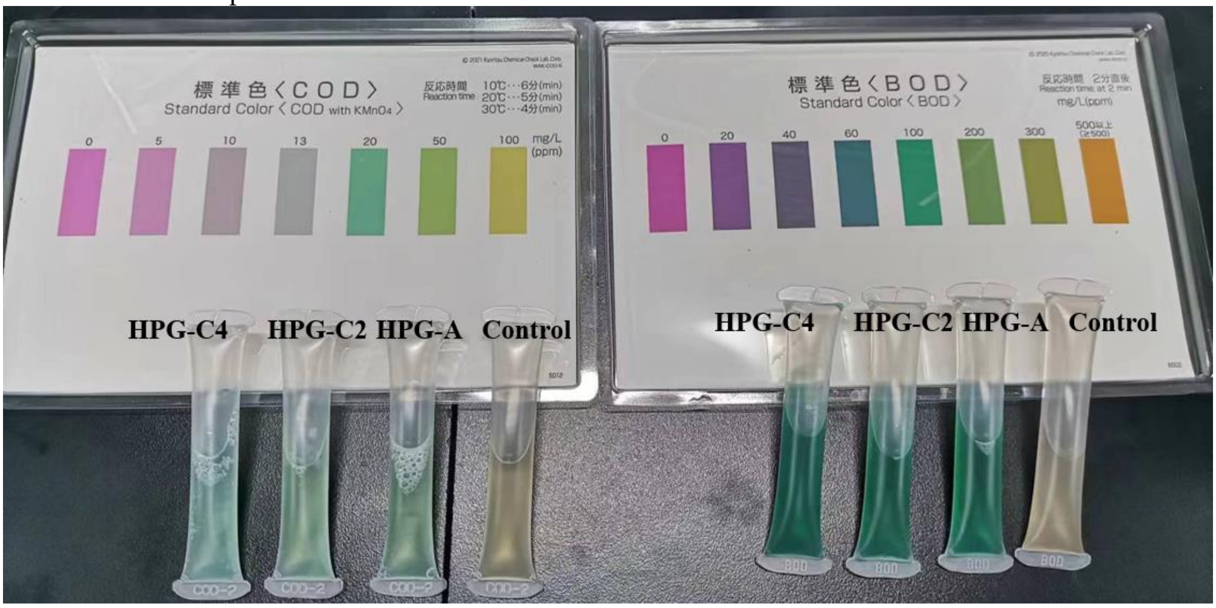

Fig.5 COD and BOD of the effluent measured by test paper

4. Conclusion

A chrome-free tanning based on polyglycidyl are explored. The polyglycidyl have number-average molecular weight 2700 and wider molecular weight distribution could improve the denaturation temperature of wet-white leather, much higher than gallic acid. Moreover, compared to hydroxyl group content, molecular weight of polyglycidyl plays a more dominant role in improving the Td of the wet-white leather. That is, the wide molecular weight distribution favors crosslinking of the tanning agent with collagen fibers in various parts, which endow the collagen bundle in good disersion. In addition, basification pH has little effect on the Td of the wet-white leather. The COD and BOD of effluent tanned by polyglycidyl are lower than that of gallic acid. Polyglycidyl holds huge promise in application of chrome-free in leather industry.

5. Acknowledgements

This work was supported by the Talent projects of Guangdong University of Petrochemical Technology (2019rc036, 2019rc038), Featured Innovative Talents Project of Guangdong Education Department (2022KTSCX085), Maoming Science and Technology Program (2022038) and Sailing project of Maoming Green Chemical Industry Research Institute (MMGCIRI-2022YFJH-Y-032).

6. References

1. Xu, S.F. and Shi, B.,A green and sustainable strategy for leather manufacturing: Endow dehydrated hide with consistent and durable hydrophobicity,*Journal of Cleaner Production*, **383**, 135526, 2023.
2. Wang, L.H., Mo, H.Z., Li, H.B., Xu, D., Gao, D.G., Liu, Z.B., Zhang, J.Y., Yao, L.S. and Hu, L.B.,Preparation and application of tremella polysaccharide based chrome free tanning agent for sheepskin processing,*International Journal of Biological Macromolecules*, **241**, 124493, 2023.

3. Covington, A.D. and Wise, W.R.,Current trends in leather science,*Journal of Leather Science and Engineering*, **2**, 28, 2020.
4. Xiao, Y.H., Zhou, J.J., Wang, C.H., Zhang, J.W., Radnaeva, V.D. and Lin, W.,Sustainable metal-free leather manufacture via synergistic effects of triazine derivative and vegetable tannins,*Collagen and Leather*, **5**, 2, 2023.
5. Yao, Q., Chen, H.L., Huang, H.H. and Liu, B.L.,Mechanism and effect of hydroxyl-terminated dendrimer as excellent chrome exhausted agent for tanning of pickled pelt,*Journal of Cleaner Production*, **202**, 543-552, 2018.
6. Zhang, C.X., Xia, F.M., Long, J.J. and Peng, B.Y.,An integrated technology to minimize the pollution of chromium in wet-end process of leather manufacture,*Journal of Cleaner Production*, **154**, 276-283, 2017.
7. Sun, Q.Y., Zeng, Y.H., Yu, Y., Wang, Y.N. and Shi, B.,An exploration of enhancing thermal stability of leather by hydrophilicity regulation: effect of hydrophilicity of phenolic syntan,*Journal of Leather Science and Engineering*, **4**, 22, 2022.
8. Luo, J.X., Feng, Y.J. and Shan, Z.H.,Complex Combination Tannage with Phosphonium Compounds, Vegetable Tannins and Aluminium Tanning Agent,*Journal of the Society of Leather Technologists and Chemists*, **95**, 215-220, 2011.
9. Kanth, S.V., Madhulatha, W., Madhan, B., Venba, R. and Chandrababu, N.K.,Stabilization of Natural Fiber Collagen Using Vegetable Tannins: An Effective Enzyme Assisted Process,*Journal of Natural Fibers*, **5**, 404-428, 2008.
10. Yuan, L.L., Yao, Q.D., Liang, Y.X., Dan, Y., Wang, Y.X., Wen, H.T., Yang, Y.Q. and Dan, W.H.,Chitosan based antibacterial composite materials for leather industry: a review,*Journal of Leather Science and Engineering*, **3**, 12, 2021.
11. Ding, W., Wang, Y.T., Sun, J., Bao, L.H. and Pang, X.Y.,Dialdehyde sodium alginate bonded dicyandiamide for formaldehyde-free leather production with enhanced properties,*Carbohydrate Polymers*, **295**, 119838, 2022.
12. Ding, W., Remon, J. and Jiang, Z.C.,Biomass-derived aldehyde tanning agents with in situ dyeing properties: a 'Two Birds with One Stone' strategy for engineering chrome-free and dye-free colored leather,*Green Chemistry*, **24**, 3750-3758, 2022.
13. Krishnamoorthy, G., Sadulla, S., Sehgal, P.K. and Mandal, A.B.,Greener approach to leather tanning process: D-Lysine aldehyde as novel tanning agent for chrome-free tanning,*Journal of Cleaner Production*, **42**, 277-286, 2013.
14. China, C.R., Hilonga, A., Nyandoro, S.S., Schroepfer, M., Kanth, S.V., Meyer, M. and Njau, K.N.,Suitability of selected vegetable tannins traditionally used in leather making in Tanzania,*Journal of Cleaner Production*, **251**, 119687, 2020.
15. Mustafa, G., Arshad, M., Bano, I. and Abbas, M.,Biotechnological applications of sugarcane bagasse and sugar beet molasses,*Biomass Conversion and Biorefinery*, **13**, 1489-1501, 2023.
16. Sheldon, R.A. and Brady, D.,Green Chemistry, Biocatalysis, and the Chemical Industry of the Future,*Chemsuschem*, **15**, e202102628, 2022.
17. Chandel, A.K., Garlapati, V.K., Singh, A.K., F., F.A. and Silva, S.S.,The path forward for lignocellulose biorefineries: Bottlenecks, solutions, and perspective on commercialization,*Bioresource Technology*, **264**, 370-381, 2018.
18. Zolek, T.Z., Izdebska, J. and Tryznowski, M.,Branched polyglycerols as performance additives for water-based flexographic printing inks,*Progress in Organic Coatings*, **78**, 334-339, 2015.
19. Maminski, M.L., Parzuchowski, P.G., Trojanowska, A. and Dziewulski, S.,Fast-curing polyurethane adhesives derived from environmentally friendly hyperbranched polyglycerols - The effect of macromonomer structure,*Biomass & Bioenergy*, **35**, 4461-4468, 2011.
20. Wang, G.T., Li, L.L., Lan, J.B., Chen, L.J. and You, J.S.,Biomimetic crystallization of calcium carbonate spherules controlled by hyperbranched polyglycerols,*Journal of Materials Chemistry*, **18**, 2789-2797, 2008.
21. Paulus, F., Weiss, M.E.R., Steinhilber, D., Nikitin, A.N., Schütte, C. and Haag, R.,Anionic Ring-Opening Polymerization Simulations for Hyperbranched Polyglycerols with Defined Molecular Weights,*Macromolecules*, **46**, 8458-8466, 2013.

22. DANIEL, W., SALAH, E.S. and HOLGER, F.,Hyperbranched Polyglycerols From the controlled synthesis of biocompatible polyether polyols to multipurpose application.pdf>,*ACCOUNTS OF CHEMICAL RESEARCH*, **43**, 129-141, 2010.
23. Yao, Q., Wang, Y.T., Chen, H.L., Huang, H.H. and Liu, B.L.,Mechanism of High Chrome Uptake of Tanning Pickled Pelt by Carboxyl-Terminated Hyper-Branched Polymer Combination Chrome Tanning,*ChemistrySelect*, **4**, 670-680, 2019.
24. Ding, W., Yi, Y.D., Wang, Y.N., Zhou, J.F. and Shi, B.,Preparation of a Highly Effective Organic Tanning Agent with Wide Molecular Weight Distribution from Bio-Renewable Sodium Alginate,*Chemistryselect*, **3**, 12330-12335, 2018.
25. Ding, W., Wang, Y.N., Zhou, J.F. and Shi, B.,Effect of structure features of polysaccharides on properties of dialdehyde polysaccharide tanning agent,*Carbohydrate Polymers*, **201**, 549-556, 2018.
26. Ding, W., Zhou, J.F., Zeng, Y.H., Wang, Y.N. and Shi, B.,Preparation of oxidized sodium alginate with different molecular weights and its application for crosslinking collagen fiber,*Carbohydrate Polymers*, **157**, 1650-1656, 2017.
27. Gao, D.G., Cheng, Y.M., Wang, P.P., Li, F., Wu, Y.K., Lyu, B., Ma, J.Z. and Qin, J.B.,An eco-friendly approach for leather manufacture based on P(POSS-MAA)-aluminum tanning agent combination tannage,*Journal of Cleaner Production*, **257**, 120546, 2020.
28. Lyu, B., Chang, R., Gao, D.G. and Ma, J.Z.,Chromium Footprint Reduction: Nanocomposites as Efficient Pretanning Agents for Cowhide Shoe Upper Leather,*Acs Sustainable Chemistry & Engineering*, **6**, 5413-5423, 2018.
29. Zhang, C.X., Lin, J., Jia, X.J. and Peng, B.Y.,A salt-free and chromium discharge minimizing tanning technology: the novel cleaner integrated chrome tanning process,*Journal of Cleaner Production*, **112**, 1055-1063, 2016.