Application of Y-shaped Polyurethane and Polyacrylic Acid as a Complex Retanning Agent in Aldehyde-tanned Goat Leather

by
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Abstract

A kind of Y-shaped amphiphilic block polyurethane copolymers (PUGs) with different molecular weights were successfully synthesized to be used as retanning agent combined with polyacrylic acid (PAA) for modified glutaraldehyde tanned goatskin. The structures of resulting products were characterized by FTIR, and the molecular weights of products were measured with GPC. The application performances were investigated by measuring the organoleptic and physical mechanical properties of resulting leathers according to the alone or combined use of PUG and PAA, the molecular weight of PUG, and the offer percentage of retanning agent. The best performance was found in the leather retanned by PUG750 and PAA complex retanning agent at the total offer percentage of 4 wt%. Finally, the free formaldehyde contents in the leathers retanned with 4 wt% PUG750 and PAA at different pH conditions were analyzed with acetyl acetone colorimetric method. The mechanical properties as well as the fibers morphologies of the experimental and control groups were also investigated. The results demonstrated that when the pH value at the later stage of retanning process was controlled at 4.0 or 3.0, the free formaldehyde content was significantly reduced by 20.3% or 38% respectively; and the physical mechanical properties of leathers were also very excellent to meet the performance requirements of goatskin garment leathers. According to these results, the method for using PUG and PAA as a complex retanning agent might be a good choice in chrome-free tanning process.

Introduction

Chrome tanning methods are still very popular in the leather industry,[1] but researchers have found that Cr(III) will be converted to Cr(VI) when oxidants are present, which is certainly harmful to human health and environment.[2,3] In order to reduce the negative health and environmental impacts of chrome tanning, wet-white tanning is increasingly used based on chrome-free tanning process, in which aldehyde tanning agents are a kind of commonly used chrome-free tanning agents.[4] Formaldehyde, as a kind of aldehyde tanning agent, can react with amino groups in the collagen to form reactive hydroxymethyl groups. Therefore, crosslinking can occur at second amino groups to improve the shrinkage temperature of leathers. The crosslinking is relatively inefficient for the formation of paraformaldehyde in the solution, and the health and safety problems of formaldehyde also make it completely banned.[5] Nowadays, modified glutaraldehyde has become a kind of the most commonly used aldehyde tanning agent. The modified glutaraldehyde has a mild tanning effect, which can make the leathers not only a good light resistance, but also a good soft and plump sense. However, the performances of leathers tanned by modified glutaraldehyde are not comparable to that of chrome tanned leathers and need a further improvement by using retanning process. The presence and release of free formaldehyde is still a challenge when modified glutaraldehyde tanning is used. At present, the use of formaldehyde capture agents to reduce the free formaldehyde content in leathers is the most widely used method. The formaldehyde capture agents mainly include amino derivatives, strong oxidizing substances, compounds containing α-hydrogen, and so on. Among the capture agents mentioned above, polymers with amino/amide groups[6] are a kind of promising capture agents as they can be immobilized in the gaps of leather fibers to avoid the disadvantage of small molecule capture agents that are easy to be washed out in the leather tanning process.

As the one of important steps in leather manufacturing process, retanning process follows the tanning process, which can further improve the performance of leathers. Retanning agents used in chrome tanning process can coordinate with chromium ions to achieve the purpose of retanning. Because of the absence of metal ions in the process of chrome-free tanning, such as aldehyde tanning, retanning agents can achieve the retanning purpose only by the hydrogen bonding interaction with the collagen fibers. Polyurethane[7,8] and polyacrylic acid[9,10] are two

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kinds of best candidates for leather retanning, for polyurethane can afford leathers with excellent ductility and flexibility and polyacrylic acid can significantly change the fullness and other physical and mechanical properties of leathers. Since polyacrylic acid and polyoxyethylene ether chains in polyurethane can produce multiple hydrogen bond interactions at appropriate pH conditions,[11,12] the combined use of these two kinds of retanning agents should be able to achieve better retanning efficiency. The aldehyde group can react with the amide group under certain conditions, and the introduction of polyurethane with amide groups in retanning stage may act as a formaldehyde capture agent to reduce the free formaldehyde contents in modified glutaraldehyde tanned leathers.

In this paper, a kind of Y-shaped amphiphilic block polyurethane copolymers (PUGs) with different molecular weights were prepared and used for the retanning of modified glutaraldehyde tanned goatskin alone or combined with polyacrylic acid (PAA). The thickness, softness, shrinkage temperature, and mechanical properties of the leathers obtained under different retanning conditions were investigated. Then, an attempt was made to study the effects of PUG and PAA complex retanning agent on the contents of free formaldehyde in the leathers under different pH conditions. At the same time, the mechanical properties as well as the collagen fibers morphologies of leathers were also investigated to evaluate the performances of leathers. The improvement of leather performance and the reduction of free formaldehyde content indicated the promising application of PUG and PAA as a complex retanning agent in aldehyde tanning process.

Materials and Methods

Materials

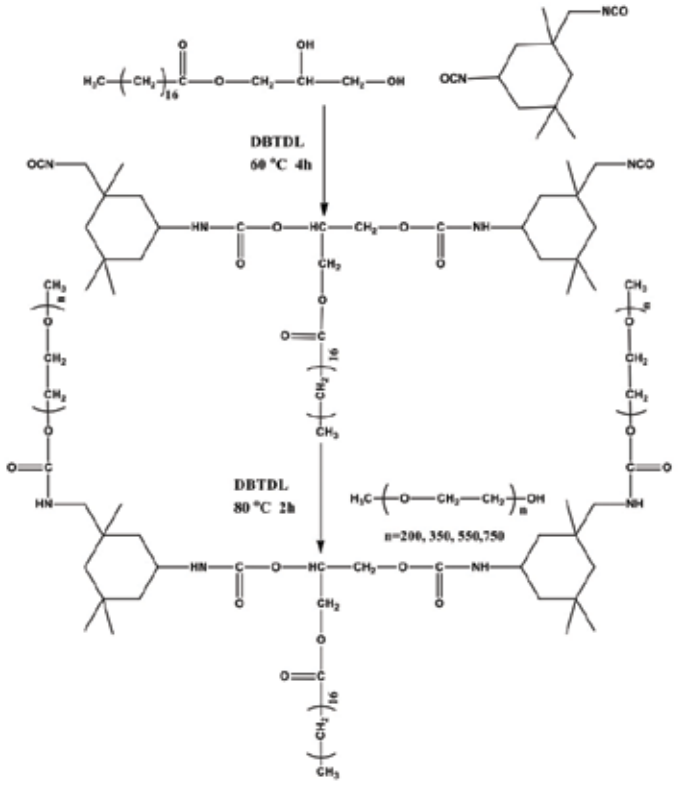
Pickled goat skin was from Sichuan, China. Sodium chloride, sodium thiosulfate, sodium bicarbonate, formic acid, formaldehyde, acetylacetone, dibutyltin dilaurate (DBTDL), and sodium dodecyl benzene sulfonate (SDBS) were purchased from Kelong Chemical Reagent Factory (Chengdu, China). SWA, NL-20, JM, JMK, FS-90, DF, and dispersing tannin were supplied by Sichuan Dowell Science and Technology Inc (Chengdu, China). Modified glutaraldehyde (hydroxymethyl glutaraldehyde, which total carbonyl compound content is 32.0%~34.0%) was supplied by Wuhan Organic Industrial Co., Ltd (Wuhan, China). Glyceryl monostearate (GMS) and isophorone diisocyanate (IPDI) were obtained from Aladdin Industrial Corporation (Shanghai, China) and Shanghai Chemical Reagent Corporation (Shanghai, China) respectively. Methoxypolyethylene glycols (MPEG-200, 350, 550, 750) were provided by Aladdin Industrial Corporation (Shanghai, China). All chemicals were used without further purification.

Synthesis of Y-Shaped Amphiphilic Block Polyurethane Copolymers (PUGs)

PUGs were synthesized according to the method of our laboratory.[13] In the typical experiment, a 100 mL three-neck flask fitted with a thermometer and a mechanical stirrer was charged with the calculated GMS (7.171 g, 0.02 mol), IPDI (8.891 g, 0.04 mol). After the addition of DBTDL (0.025 g, 0.04 mmol) as a catalyst, the equipment was transferred to a water bath condition and stirred at 60°C for 4 h. Then, MPEG (M_n=200, 350, 550 or 750, respectively) was added with a molar ratio of GMS/MPEG=1:1 (0.02 mol) and kept the reaction mixture stirred at 80°C for another 2 h. After the reaction mixtures were cooled to the ambient temperature, the Y-shaped amphiphilic block polyurethane copolymers with different hydrophilic chain lengths were obtained. And the resulted products were denoted as PUG200, PUG350, PUG550, PUG750. The synthesis procedure mentioned above is depicted in the Scheme 1.

Synthesis of Polyacrylic Acid (PAA)

Initially, 20 g acrylic acid was added into a little beaker with 20 g water, and after stirring for five minutes, the sodium hydroxide aqueous solution was added dropwise into the solution to adjust the pH value to 4.0~4.5. At the same time, 50 g water and 0.2 g ammonium persulfate were placed in a 200 mL three-neck flask equipped with a mechanical stirrer, and the equipment was placed in a water bath condition at 80°C. While stirring, 5 g the



Scheme 1. Synthesis procedure of PUGs.

Table I
The Process Recipe for Manufacture of Goatskin Garment Leathers.

Process/chemicals	Offer (%)	Time (min)	Temperature (°C)	Remarks
Washing				
Water	100		30	
Sodium chloride	8			
SWA	0.2	60		
Tanning				
Modified glutaraldehyde diluted fivefold	12	60	30	
Sodium formate	3	20		pH 4.5
Modified glutaraldehyde	7	90		
Sodium thiosulfate	1	30		pH 4.5
Sodium bicarbonate	1-3	60		pH 7.5-8.0 Rest overnight Drain
Retanning				
Water	100		38	
Polyurethane	x			
Polyacrylic Acid	x	60		
Dispersing tannin	0.5	20		
NL-20	2	30		
Formic acid	0.4	20		
Formic acid	0.1-0.4	40		pH 4.0 Drain & Wash
Fatliquoring				
Water	100		40	
JM	3			
JMK	4			
FS-90	3			
OF	2	60		
Formic acid	0.25	30		
Formic acid	0.25	30		pH 3.8-4.0 Drain & Wash
Horse up, hang-drying overnight.				

prepared acrylic acid aqueous solution was slowly dropped into the flask every 15 minutes. The reaction was allowed to keep another 30 minutes after all of the prepared acrylic acid aqueous solution was added. Thus, the product was obtained.

Fourier Transform Infrared Spectra (FTIR)

Fourier transform infrared (FTIR) spectra were measured with a NICOLET iS10 spectrometer (USA) between 400 and 4000 cm^{-1}. After separation and purification, the samples were painted on KBr thin pellets for FTIR study.

Gel Permeation Chromatography (GPC)

The molecular weight and polydispersity index (PDI) of PUGs were tested on a HLC-8320 GPC using polystyrene as a standard and THF as an eluent.

Application of Polyurethanes and Polyacrylic Acid

In this experiment, the pickled goat skins were chosen as raw materials for the manufacture of goatskin garment leathers. The raw material was cut along the spine to make sure the same fiber woven status; then two pieces with the same size (20cm×15cm) were obtained after the split again. The one of skin pieces was used as the control sample and the other was used as the experimental sample. The weights of skin pieces were noted, and the chemicals used in the experiments were offered according to the weights of skin pieces. The process recipe for the manufacture of control and experimental goatskin garment leathers from pickled goat skins is shown in Table I. The only difference between the control and experimental samples was that the control samples were not subjected to retanning treatments. The study experiments about the effects of alone or combined use of the retanning agents, the molecular weight of PUG, the offer percentage of retanning agent, and the pH condition at the later stage of retanning process were carried out as follows:

Experiment 1: PUG750, PAA, and the equal mass mixture of PUG750 and PAA were used as retanning agent respectively. The offer percentage of retanning agents was controlled at 4 wt% in this experiment. The pH value at the later stage of retanning process was controlled at 4.0.

Experiment 2: PUG, with the different molecular weights, combined with the same weight ratio of PAA was used as a complex retanning agent respectively. The total offer percentage of the complex retanning agents was controlled at 4 wt%. The pH value at the later stage of retanning process was controlled at 4.0.

Experiment 3: PUG750 and PAA were used as a complex retanning agent, and the offer percentage of complex retanning agent was controlled at 2 wt%, 4 wt%, 6 wt%, 8 wt% respectively. The pH value at the later stage of retanning process was controlled at 4.0.

Experiment 4: PUG750 and PAA were used as a complex retanning agent, and the offer percentage of the complex retanning agent was controlled at 4 wt%. The pH value at the later stage of retanning process was controlled at 5.0, 4.0, 3.0, 2.5 respectively.

Analysis of Leather Properties

Thickness Measurement

The thickness of samples was measured by a GJ9B1 digital thickness tester. Measurements were carried out at three locations and reported as an average value.

Hydrothermal Stability Evaluation

The hydrothermal stability of the control and experimental leather samples was characterized with shrinkage temperature (T_s) using a MSW-YD4 shrinkage temperature recording instrument according to the standard method.[14]

Softness Measurement

The softness of leathers was carried out using a GT-303 digital leather softness tester. After the temperature and relative humidity was conditioned at about 20°C and 65%, respectively, the measurement was carried at the left, middle, and right three locations and reported as an average value, and the higher average value indicated higher softness.

Physical Mechanical Properties Characteristics

The physical mechanical properties of leather samples were tested according to the standard method from QB/T2710-2005 and QB/T2711-2005. The leather samples were placed in a 20°C and 65% relative humidity condition for 48 h; then their physical mechanical properties such as tear strength, tensile strength, elongation at break were measured using a tensile machine AI-7000S.

Scanning Electron Microscopy Analysis

A JSM-7500F scanning electron microscope was used for the analysis. The samples were cut into specimens, then pasted onto the stage by conductive tape and coated with gold. The micrographs of the cross section were obtained by operating the SEM at low vacuum with an accelerating voltage of 5kV in the same magnification level.

Determination of Free Formaldehyde Contents in Leathers

The free formaldehyde contents of leathers were detected by acetyl acetone colorimetric method according to the standard method in this experiment.[15] In a typical experiment, the standard working curve was drawn according to a series of formaldehyde solutions which had been known the concentration. Then the aqueous solution of SDBS (40°C) was used to extract the leathers. After adding acetyl acetone solution as the chromogenic agent, the absorbance of obtained sample solutions was measured under the wavelength of 412nm by a

UV-1900 spectrophotometer. Finally, the accurate free formaldehyde contents in the leathers can be calculated after comparing the obtained results with the standard working curve.

Results and Discussion

Synthesis of Polyurethane Copolymers and Polyacrylic Acid

The FTIR spectra of the prepared polyurethane and polyacrylic acid products (PUG200, PUG350, PUG550, PUG750, PAA) are shown in Fig. 1. The characteristic features related to PUGs were observed at 3330 and 1540cm^{-1}, corresponding to the N-H stretching and bending vibration of the carbamate group. Also, a peak for –C=O bending vibration at 1720cm^{-1} can be seen. And the obvious peak at the wave number of 1110cm^{-1} was corresponding to the absorption of C-O-C stretching. For the characteristic features of PAA, the peaks at 1721 and 1571 cm^{-1} were corresponding to the bending vibration of carboxyl and carboxylate, respectively. The broad -OH stretching peak can be seen at 3440cm^{-1}, and C-O stretching coupled with O-H bending vibration peaks can be seen at 1418, 1245, and 1158 cm^{-1}.

In addition to FT-IR analysis, GPC experiment was also carried out to evidence the molecular weight and polydispersity index (PDI) of PUGs. The results are presented in Table II. Based on the above results, we concluded that we had successfully prepared the target products.

Effect of Different Retanning Agents on the Organoleptic and Physical Properties of Leathers

The organoleptic and physical mechanical properties of leathers are shown in Table III and Fig.2. It can be clearly seen that the alone used of PAA and the combined use of PUG750 and PAA had better effect on the improvement in the thickness of leathers than that used PUG750 alone, and the thickness increment ratio were 21.4% and 10.7% respectively. For PAA has the ability to interact with collagen fibers through hydrogen bonds at low pH condition, so PAA can be fixed to fill the fibers gap of leather and increase the thickness of leather. At the same time, PAA and PUG750 can also form intermolecular hydrogen bonds; then the stable hydrogen-bonding aggregates[16] can be formed between these two kinds of molecules at specific pH condition. So, PUG750 and PAA complex retanning agent can also play a thickening effect. The difference of softness and shrinkage temperature values between the control and experimental groups were not significant. Researcher have found that the motion behavior of collagen fibers is the main factor influencing the handle of leathers,[17] and the interaction of the retanning agents with collagen fibers will change the motion behavior of collagen fibers, which may lead to a slight decrease in the softness of leathers. Furthermore, because the interaction force between collagen fibers and retanning agents are only the hydrogen bond interaction force, and the hydrogen bonds are easily damaged at high temperature condition, so that the shrinkage temperature of leathers was not remarkably improved.

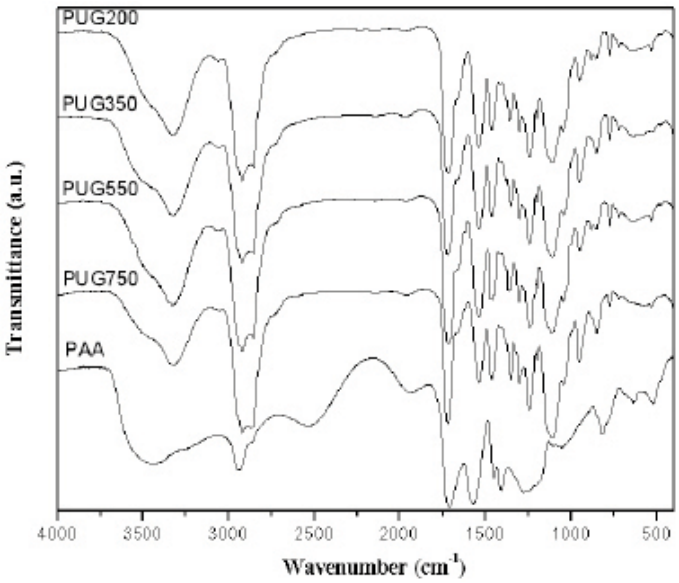


Figure 1. FTIR spectra of PUG200, PUG350, PUG550, PUG750, PAA.

The values of tensile strength and tear strength had a significant improvement compared with the control group when PUG750 and PAA used as a complex retanning agent, and the tensile strength and tear strength were increased by 20.4% and 19.5%, respectively. Aforementioned results demonstrated that the combined use of PUG750 and PAA had a better retanning performance. Since PUG750 is a sort of amphiphilic copolymer, which also a typical non-ionic surfactant with good permeability to promote the penetration and dispersion of PAA. Therefore, when PUG750 and PAA were used as a complex retanning agent, the interaction force between the collagen fibers and retanning agents would increase with the improved penetration and dispersion, and ultimately lead to the improvement of the mechanical properties of leather. Hence, the application performance of the mixture of PUG and PAA was superior to those of PUG and PAA alone, which allowed them to be used as a complex retanning agent in the following studies.

Table II
The Molecular Weight and Polydispersity Index of the PUG.

Sample	PUG200	PUG350	PUG550	PUG750
M_n	1445	1644	2056	2565
PDI	1.60	1.16	1.23	1.13

Effect of the Molecular Weight of PUG on the Organoleptic and Physical Properties of Leathers

The properties of leathers retanned by PUGs, with different molecular weights, and PAA complex retanning agent can be seen in Table IV and Fig.3. The leather retanned by PUG750 and PAA complex retanning agent exhibited the greatest thickness increment ratio of 10.7%. And the values of tensile strength, elongation, and tear strength were increased by 20.4%, 23.0%, and 53.0%, respectively, for the hydrogen bonding sites between PUG and PAA increase with the increase of polyoxyethylene ether chain lengths in PUG.[18] The intensity of hydrogen bond interaction between PAA and PUG750, therefore, was stronger than that of PAA and PUG200/PUG350/PUG550. The stronger the interaction between PUG and PAA, the more favorable for the penetration and dispersion of PAA in the collagen fibers, which also lead to the increase of the interaction force between the collagen fibers and retanning agents as mentioned previously. So, the increment ratios of thickness and mechanical properties of the leathers between control and experimental groups retanned by PUG750 and PAA complex retanning agent were larger than those of other groups. Hence, PUG750 and PAA complex retanning agent was chosen for further experimental trials.

Effect of the Amount of Complex Retanning Agent on the Organoleptic and Physical Properties of Leathers

The test results of the properties of leathers are presented in the Table V and Fig.4. Obviously, with the increase of offer percentage of retanning agent, the thickness increment ratios of

Table III

The Organoleptic Properties and Shrinkage Temperature of Leathers Retanned with PUG750, PPA, PUG750 and PAA.

Samples	Group	Thickness (mm)	Softness	Shrinkage Temperature (°C)
4% PUG750	Control	2.02	9.81	80.5
	Experimental	1.86	9.50	80.7
4% PAA	Control	1.87	9.13	82.2
	Experimental	2.27	9.41	81.7
4% (PUG750+PAA)	Control	1.86	9.60	84.5
	Experimental	2.06	9.33	85.4

Table IV

The Organoleptic Properties and Shrinkage Temperature of Leathers Retanned with PUGs and PAA.

Samples	Group	Thickness (mm)	Softness	Shrinkage Temperature (°C)
2% PUG200+2% PAA	Control	1.79	5.90	84.6
	Experimental	1.93	5.70	82.1
2% PUG350+2% PAA	Control	1.84	6.72	83.1
	Experimental	1.95	5.87	82.7
2% PUG550+2% PAA	Control	1.88	6.22	82.3
	Experimental	1.95	5.68	82.6
2% PUG750+2% PAA	Control	1.86	6.32	83.6
	Experimental	2.06	5.98	85.3

leathers were increased first and then decreased. When the offer percentage was controlled at 4 wt%, the thickness increment ratio showed the highest value at 24.7%. The values of tensile strength, elongation and tear strength were higher than that of control group, and the increased ratios were16.9%, 9.0%, and 53.0%, respectively. When the offer percentage was controlled from 2 wt% to 4 wt%, the amount of complex retanning agent that were fixed in the leathers through hydrogen bonds increased with the increase of offer percentage; With the further increase of offer percentage, PAA and PUG750 might form larger aggregates attached to the surface of leathers, which led to the reduction of the amount of complex retanning agent in leathers. So, when the offer percentages were controlled at 6 wt% and 8 wt%, the thickness increment ratios of leathers became smaller, and some of the mechanical properties were also reduced. Therefore, the total offer percentage of PUG750 and PAA was optimized as 4 wt% for retanning process after comprehensive consideration.

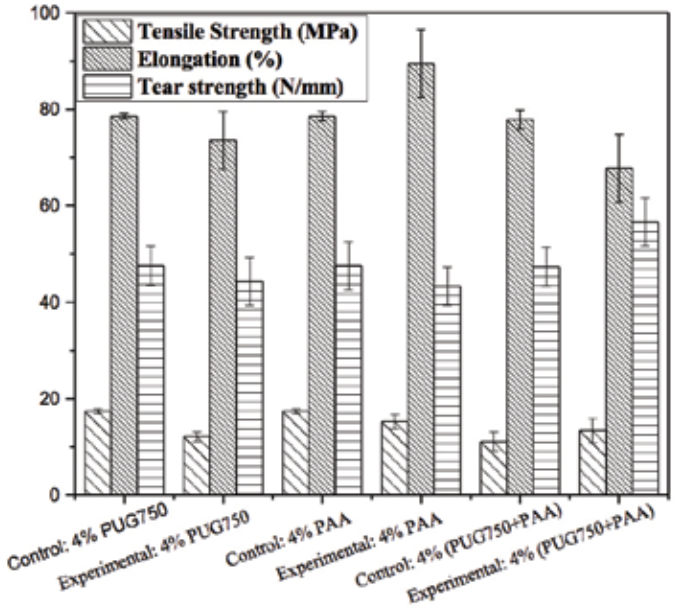


Figure 2. Physical mechanical properties of leathers retanned with PUG750, PAA, PUG750 and PAA.

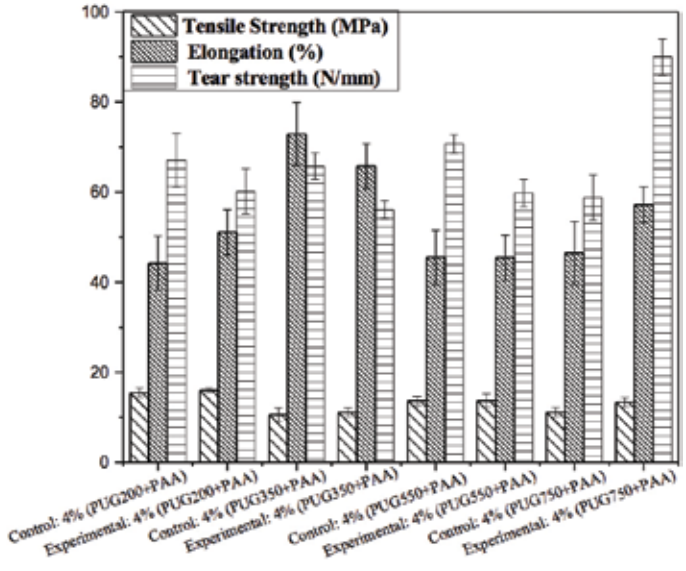


Figure 3. Physical mechanical properties of leathers retanned with PUGs and PAA.

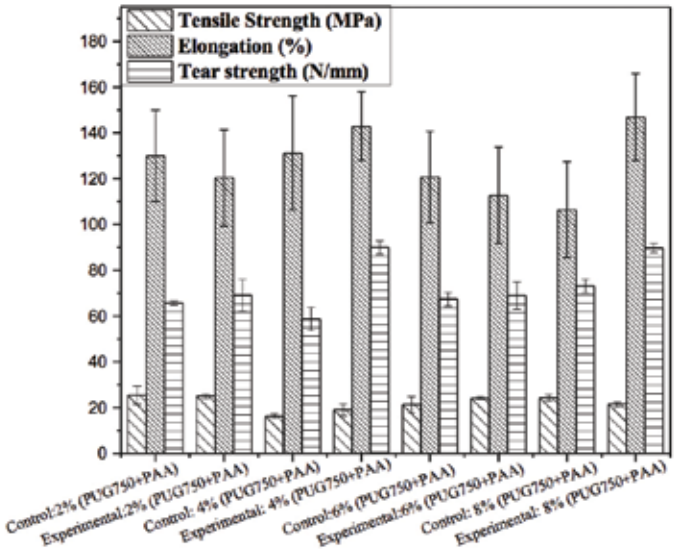


Figure 4. Physical mechanical properties of leathers retanned with different offer percentages of PUG750 and PAA.

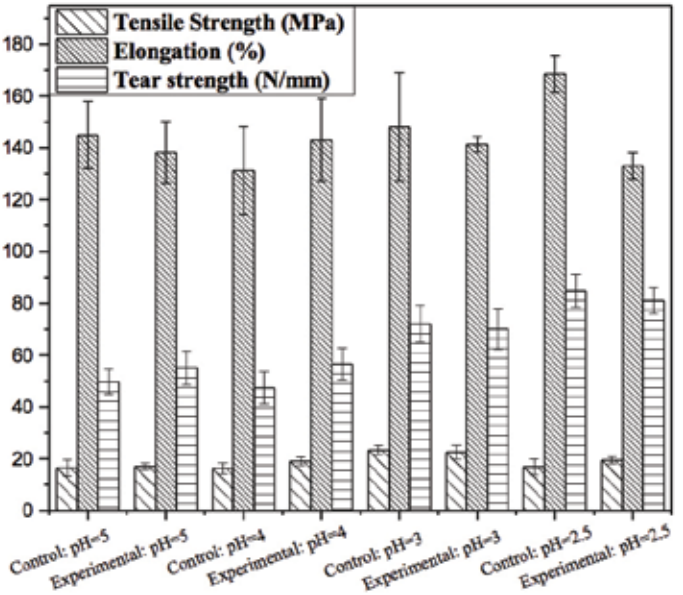


Figure 5. Physical properties of leathers treated under different pH conditions.

Table V
The Organoleptic Properties and Shrinkage Temperature of Leathers Retanned with Different Offer Percentages of PUG750 and PAA.

Samples	Group	Thickness (mm)	Softness	Shrinkage Temperature (°C)
1% PUG750+1% PAA	Control	1.86	7.42	80.3
	Experimental	1.96	7.32	80.6
2% PUG750+2% PAA	Control	1.86	6.32	82.3
	Experimental	2.32	5.98	82.4
3% PUG750+3% PAA	Control	1.84	7.44	81.8
	Experimental	1.97	7.21	80.0
4% PUG750+4% PAA	Control	1.82	7.05	81.9
	Experimental	2.11	6.62	81.5

Application of the Complex Retanning Agent Under Different pH Conditions

The Physical Mechanical Properties of Leathers Retanned Under Different pH Conditions

Taking into consideration the fact that the pH conditions have great effect on the formation of hydrogen bonding between PUG750 and PAA, the influences of pH conditions on the properties of leathers were analyzed by physical mechanical properties, which are shown in Fig.5. It could be seen that the physical mechanical properties of leathers were increased when the pH conditions were controlled at 5.0 and 4.0, and it showed the greatest increment at 4.0. At the lower pH values, 3.0 and 2.5, the mechanical properties of leathers showed a small amount of reduction. Although the interaction between PUG750 and PAA was enhanced at the pH values of 3.0 and 2.5, which accompanied the increase of hydrogen bonding sites between PUG750 and PAA, the binding sites between retanning agents and collagen fibers decreased with a small extent. Therefore, the interaction force between the collagen fibers and retanning agents decreased lightly at the pH values of 3.0 and 2.5, which will lead to the slight decrease of the mechanical properties.

SEM Analysis

The cross-section micrographs of leathers from the control and experimental are shown in Fig.6. Obviously, the control sample showed cemented fiber bundles, while the fiber bundles of experimental groups were more compact. It proved that the PUG750 and PAA complex retanning agent was effective in dispersing collagen fibers. And it can be seen that the fibers of resulting leathers became more compact when the pH values were controlled at 4.0, 3.0, and 2.5. This was because the protonation of

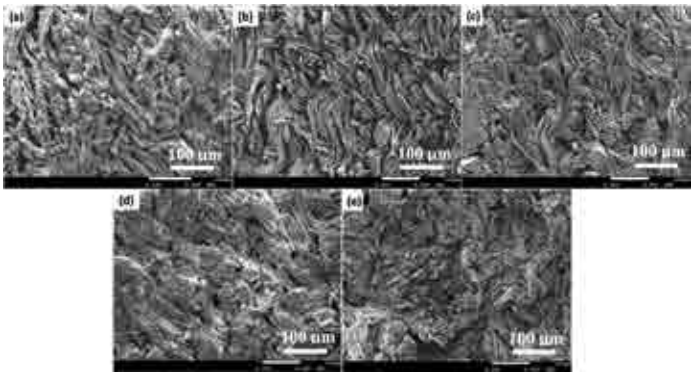


Figure 6. SEM images of cross section of the leathers from (a) control group and experimental groups with different pH conditions at (b) pH=5.0; (c) pH=4.0; (d) pH=3.0; (e) pH=2.5.

the carboxylate in PAA promoted the formation of hydrogen bond between PAA and PUG750 when the pH was less than or equal to 4.0. As described in the previous study, the formation of hydrogen bonds between PAA and PUG750 made the complex retanning agent achieve better penetration and dispersion effect.

Free Formaldehyde Content Analysis

The variations of free formaldehyde contents with different pH conditions are presented in Fig.7. With PUG750 and PAA used as a complex retanning agent, the contents of free formaldehyde in the leathers were reduced all less than 300mg/kg, which were blow the permitted limits. Furthermore, as the pH value dropped from 5 to 3, the reduced percentage of free formaldehyde contents in the leathers relative to the control groups gradually increased from 7.9% to 38.7%. As mentioned above, the hydrogen

bonding interaction between PUG750 and PAA increased significantly with the decrease of pH value.[11] As a result, the amount of PUG750 and PAA in collagen fibers gradually increased and the dispersion of PUG750 and PAA in leathers became more uniform with pH value decreases. Since formaldehyde could react with the amide group in PUG750 under certain conditions,[19] with the increase of the filling amount of PUG750, the free formaldehyde content in the leather reduced. However, when the pH value decreased to 2.5, the reduced percentage of formaldehyde content showed a downward trend. We speculated that the stronger hydrogen bonding interaction between PUG750 and PAA could be formed due to the serious reduction of the pH value, which led to the formation of more closely aggregates between PUG750 and PAA, and the partial PUG750 molecules could encapsulated by PAA and cannot react with the free formaldehyde. Therefore, the pH value at the later stage of retanning process from 3.0 to 4.0 could be used to obtain the leathers with good physical mechanical properties and relatively low free formaldehyde content.

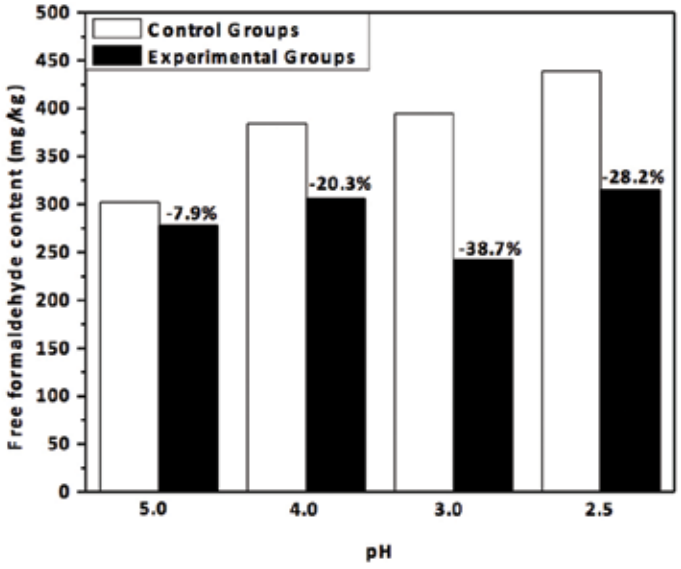


Figure 7. Free formaldehyde contents of the leathers with different pH conditions.

Conclusions

In this work, a kind of Y-shaped amphiphilic polyurethane copolymers with different molecular weights was synthesized to be used as retanning agent. We examined the alone or combined use of PUG750 and PAA, the molecular weight of PUG, and the offer percentage of retanning agent to the performance of leathers. The best performance was found in the leathers retanned by PUG750 and PAA complex retanning agent at the total offer percentage of 4 wt%. When retanned the leathers under different pH conditions with 4 wt% PUG750 and PAA, the results showed that with the decrease of pH value, the fibers of leathers became more dispersed and dense, accompanied by a small amount of reduction in mechanical properties when the process was controlled at low pH conditions. At the same time, the retanning pH conditions had a great impact on the contents of the free formaldehyde in the leathers. When the pH value was controlled at 4.0 and 3.0, the reduced percentage of free formaldehyde content in the leathers were 20.3% and 38.7% respectively. The results confirmed the great potential of PUG and PAA used as a complex retanning agent to improve the mechanical properties as well as reduce the free formaldehyde contents of aldehyde-tanned leathers.

Acknowledgements

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