Synthesis, Characterisation and Application of Novel Valonia Tannin Based Waterborne Polyurethane with Natural Colour

YANG LIU[1], HAIHANG LUO[2], BENYAPATHITIWONG RUJ[1], TAO YOU[2] and YOUJIE HE*

[1] The Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu 610065, China

[2] National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, China

Abstract

A novel natural coloured waterborne polyurethane (PU) based on valonia tannin was successfully synthesised and characterised. A structural study of the polymer by Fourier Transform Infra Red (FTIR) spectroscopy confirmed the incorporation of valonia tannin into the backbone of the PU. The dispersion of valonia tannin and homogeneity of surface of the PU samples were confirmed by scanning electron microscopic (SEM) analysis. Chromaticity and colour difference further verified the colour depth and uniformity of the cured films. Thermogravimetric analysis (TGA) results indicated that the synthesised PU samples exhibited an improved thermal decomposition temperature. Particle size analysis, mechanical testing and water absorption of the synthesised PU samples further showed the effect of the cross-linked structure in the molecular chain segment. Moreover, the colour fastness and folding [flexing] resistance of the leather coating finished with synthesised PU was better than that of valonia tannin blending.

1 INTRODUCTION

Polyurethane (PU) is a polymer with excellent properties, which is widely used in leather, construction and textiles for coatings, elastomers, adhesives, and so on.[1-5] By adjusting the formulation and reaction conditions during synthesis, it is possible to obtain PU with desired properties for specific applications. In the leather field, waterborne PU is usually mixed with pigment or dyestuff for colouring in order to increase the added value and performance of the product. However, the properties (such as colour fastness, dispersibility of the dyestuff) of the coating obtained through physical blending are relatively poor,[6] which reduces the economic benefits of the product. Moreover, the pollution caused by azo dyes and organic solvents can produce a bad influence on the environment and operator, so further improvements in the coating process and coating materials are desirable.

The essential components of the waterborne PUs are diisocyanates and polyols, recent researches on polymers based, saccharid,[7] lignin[8] and plant oils[9-11] signify the role of natural polymers in improving the properties of PU. Tannins are polyhydric phenols obtained from the extraction of plants, the structure of a tannin is very complex, studies show that tannin extracted from different sources can be used for preparation of various polymer resins.[12,13] Valonia tannin, a hydrolysed tannin, is usually extracted from acorn shells and whiskers, which can be used the main tannage of leather instead of chrome or as an excellent retanning agent. Meanwhile, valonia tannin contains a large number of chromophores and colour-assisting groups, further expanding the range of applications of polyphenols.

In recent years, with the increasing pressure of environmental protection, renewable resources have been taken seriously. In this work, waterborne PU was synthesised mainly by toluene diisocyanate (TDI), polypropylene glycol (PPG), dimethylolpropionic acid (DMPA) and valonia tannin. Hopefully, this method can partly replace the traditional way of mixing pigments with PU in leather finishing. Meanwhile, the colour fastness, folding resistance and fastness to solvent of finished leather were improved. The objective behind this work is to develop a novel material for leather finishing by studying the effect of valonia tannin.

2 MATERIALS AND METHODS

2.1 Materials

Toluene diisocyanate (TDI) and N, N-dimethylformamide (DMF) were purchased from Shanghai First Reagent Co., Shanghai, China. Polypropylene glycol (PPG Mn = 1000), Dimethylolpropionic acid (DMPA) and triethylamine (TEA) were purchased from Macklin Biochemical Co., Shanghai, China. The valonia tannin was purchased from Wuhan Far Cheng Co. Creation Technology Co., Wuhan, China. WAX Cl-C (white wax emulsion, pH: 9.0-10.0) was supplied by Bayer Chemical Co., Germany. All the other chemicals and solvents used

were of analytical grade and used without further purification.

Valonia tannin was further purified as followed: using a solid-liquid ratio of 1:100 (g/mL), the mixed liquor consisted of 62% methanol and 38% water,[14] the mixture was dispersed by ultrasound at 60°C and 100W for 50 minutes. The mixed liquor was centrifuged at 3000rpm for 30 minutes, then the supernatant liquid was spray-dried for later use.

2.2 Synthesis of polyurethane

The synthetic route is shown in Fig. 1, PPG and DMPA were dehydrated for 3 hours at 120°C. In brief, TDI and PPG (the molar ratio of NCO/OH is 2/1) were taken into the vessel under the protection of nitrogen and the temperature was raised to 75°C for 1 hour 30 minutes. DMPA (dissolved by DMF) was introduced to the reaction solution and the reaction temperature needed to be lowered to 70°C for 2 hours until the NCO content of the prepolymer was detected to reach the theoretical value. According to the content of residual isocyanate group, different amounts of valonia tannin (0%, 20%, 40%, 60%, 80% and 100% of the remaining isocyanate group molar content) were added to the solution for 2 hours until the NCO content attained the theoretical value. The temperature of the reaction system was reduced to below 35°C, and the appropriate volume of acetone was added to the system when the reaction mixture became more viscous. After adding TEA for 30 minutes, deionised water was added for emulsification. Finally, acetone was removed under reduced pressure to obtain a waterborne PU emulsion with a natural colour. Waterborne PU samples containing different contents of valonia tannin were recorded as PU0, PU1, PU2, PU3, PU4 and PU5, respectively. PU5' was obtained by physically blending PU0 with certain content of valonia tannin (relative to PU5).

2.3 Preparation of polyurethane films and finished leather samples

Waterborne PU emulsions with different amounts of valonia tannin were poured onto polytetrafluoroethylene templates and placed at room temperature for 48 hours, further we put the cured films into an oven at 50°C for 24 hours. Films of equal thickness were obtained and placed in desiccator for later use.

Standard pig crust leather from China with a thickness of 1.5mm was taken for the evaluation. The leather finish materials of test group are the mixture of PU5, WAX Cl-C and H2O (the mass ratio is 6:1:2). The leather finish materials of the control group are the mixture of PU5' (physically blended with valonia), WAX Cl-C and H_2O (the mass ratio is 6:1:2). The leather was sprayed once with the finishing material and allowed to dry at 60°C for 2 hours. The same procedure as outlined above was repeated twice.

2.4 Measurements

2.4.1 FTIR spectral studies

The FTIR analysis of valonia tannin and valonia tannin based PU samples showed different absorption bands for the different functional groups which were present in the compound. The FTIR scans were carried out in Perkin-Elmer 1000 FTIR spectrometer at 25°C.

2.4.2 Scanning electron microscopy

SEM images were taken on an S2400, HITACHI instrument with a secondary electron detector. The PU
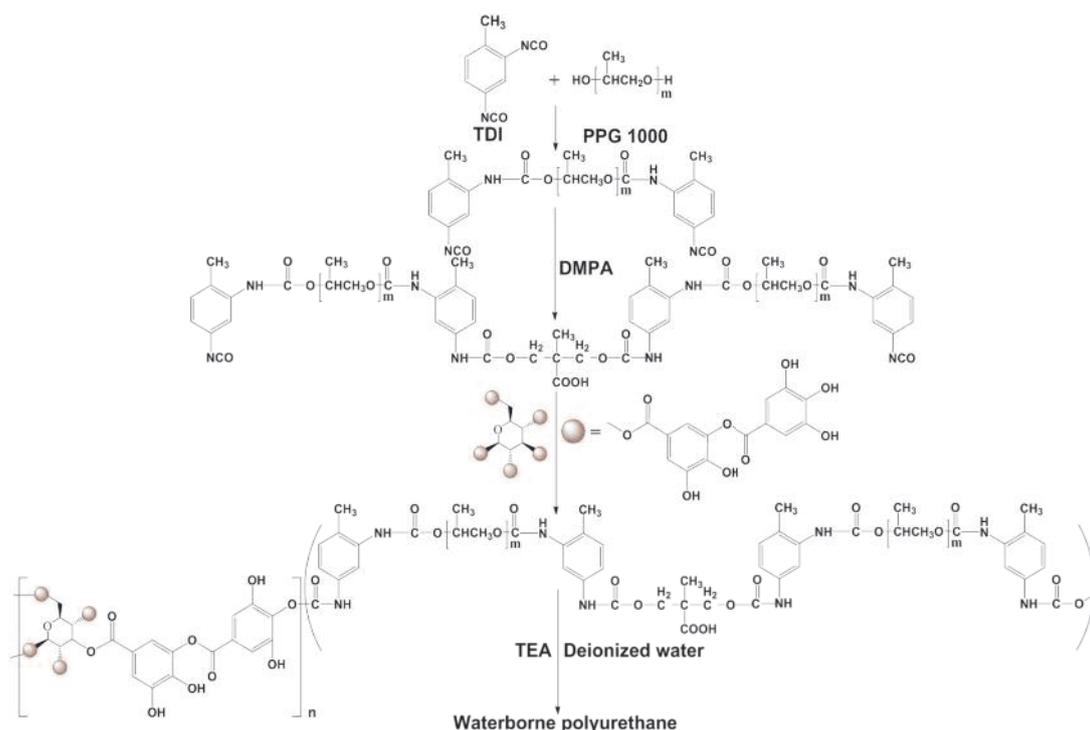

Figure 1. Synthetic route for the waterborne PU containing valonia tannin.

samples were made electrically conductive by coating with a thin layer of gold film using Hitachi E-1010 ion sputter before analysis.

2.4.3 Chromaticity and colour difference studies

The surface colour depth and colour uniformity of the PU films were measured using a Chromatic Colour Difference Analyzer (X-RITE 8200, USA). All the sample tests were carried out under the condition of D65 light source, 10° viewing angle.

2.4.4 Particle size studies

The particle size of the synthesized waterborne PU emulsion and the blending solution was measured using a ZEN-3600 dynamic laser light scattering instrument from Britain. Emulsion was diluted to a certain ratio and the measuring temperature was 25°C and the laser scattering angle was set to 90°.

2.4.5 Thermal studies

The thermal property was influenced by the cross-linking, hard and soft segments and molecular weight.[15,16] TGA analysis was performed on instrument Q5000IR. Approximately 5mg of PU samples were heated at a rate of 10°C/min from 50°C to 600°C under N_2 atmosphere.

2.4.6 Mechanical studies

Tensile strength and elongation at break were carried out using an EMIC universal testing machine (DL10000) with a displacement rate of 100mm/min at room temperature. Five specimens were tested and the average was calculated.

2.4.7 Water and solvent resistance tests

The synthesised PU film and the blended film were both cut into a squares of 3cm x 3cm, the mass was recorded as M_0. After weighing, the films were immersed in water or acetone. After 24 hours, films were taken out and the surface was quickly blotted with filter paper, the mass was recorded as M_1 after weighing. Water absorption rate/acetone absorption rate (Q) was calculated according to formula (1). Five specimens were tested and the average was calculated.

$$Q = (M_1 - M_0) / M_0 \text{ x } 100\% \qquad (1)$$

2.4.8 Determination of applied properties

Colour fastness tests: The finished leather was sampled according to BS EN ISO 11640,[17] and the wet and dry rubbing fastness tests were performed. The finished leather was sampled according to BS EN ISO 11643,[18] and solvent fastness testing was performed using ethanol as solvent. Water vapour permeability (WVP) of finished leather was measured according to ASTM method E96 Desiccant method, *i.e.* the sample was placed in a test chamber at 20°C with a constant relative humidity of 65%. WVP of five specimens for each group were measured and the average was calculated. Folding [flexing] resistance test: the finished leather was cut into a rectangular shape of 80mm x 50mm, further tested through the light leather folding resistance tester and we recorded the number of cracks or peelings of different leather coatings.

3 RESULTS AND DISCUSSION

3.1 FTIR spectral studies

The FTIR spectrum of valonia tannin (Fig. 2) showed a characteristic broad absorption band at 3320cm^{-1} which corresponded to O-H group. Bands at 1602cm^{-1} and 1447cm^{-1} corresponded to aromatic ring stretching, 1720cm^{-1} due to carbonyl stretching vibration. C-O stretching bands appeared at 1173cm^{-1}, 1108cm^{-1} and 1042cm^{-1}. FTIR spectrum of PU5 showed an intense absorption peak than PU0 at 3320cm^{-1}, which attributed to -NH and -OH stretching. Band at 3393cm^{-1}, the absorption peak of PU5 was significantly reduced compared with that of valonia tannin, indicating that valonia tannin has been successfully introduced to the PU main chain. No absorption peak at 2270cm^{-1} was found which revealed that there was no residual free NCO in synthesised waterborne PU. The peaks at 2937cm^{-1} and 2874cm^{-1} correspond to the CH_2 anti-symmetric stretching and symmetric stretching vibrations, respectively, and the peak at 2973cm^{-1} showed the CH_3 anti-symmetric stretching. For PU0 and PU5, a sharp and intense band appeared at 1725cm^{-1} corresponded to carbonyl stretching vibration of PU, which was the characteristic absorption peak of urethane group. The peaks at 1602cm^{-1} and 1520cm^{-1} represented asymmetric stretching of single and double bonds of aromatic compound. The bands at 1227cm^{-1} and 1075cm^{-1} corresponded to CN and C-O stretching vibrations.

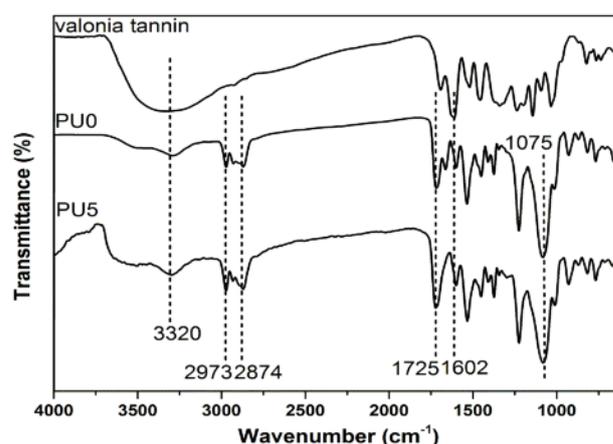### 3.2 Scanning electron microscope (SEM) analysis

Figure 2. FTIR spectra of valonia tannin and waterborne polyurethane.

Fig. 3 shows the scanning electron microscope picture of the surface of PU samples. It can be seen from the SEM images of the blended film (PU5') that there was a change in surface micro-structure and the resulting heterogeneous surface upon the blended film

of PU0 with valonia tannin. The compatibility of two kinds of materials could be evaluated from the degrees of homogeneity and compactness of the blend film.[19] Compared with PU0 and PU5, the phenomenon of agglomeration of PU5' was due to the interaction between molecules, which also caused the surface of film to be rough. The physical blending method made part of valonia tannin to be randomly dispersed in the PU emulsion. However, the coloured PU sample synthesised by introducing valonia tannin into the molecular chain as a monomer had a uniform film formation and a good dispersion state. It was suggested that the compatibility of the tannin and PU can be significantly improved by this synthesised method.

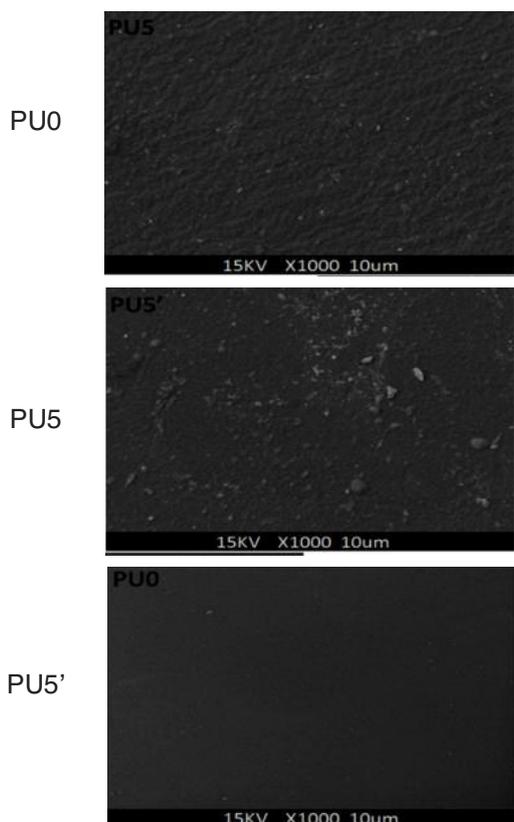### 3.3 Chromaticity and colour difference analysis

Figure 3. SEM images of PU0, PU5 and blended film (PU5').

It can be obviously seen from Fig. 4, that with the increase of valonia tannin amount, the colour of synthesised PU film gradually deepened. Although the colour of PU5' deeper than other samples, it also showed the coarse surface. Valonia tannin can be observed visually to accumulate on the surface, indicating that the dispersibility of valonia tannin was poor through the blending method. The results also agreed with the conclusions from SEM. The data of chromaticity and colour difference is shown in Table I. L* dropped from 77.96 to 20.43 among the synthesised PU samples, indicating that the brightness of the PU films was gradually reduced and the transparency was lowered. b* increased from -0.02 to 5.98, revealing that the colour of the PU films tended to be yellow. As the number of chromophoric groups increased, the colour of the coating became more vivid. It can be seen from ΔE that the value of PU5' was higher than the synthesised PU, suggesting that the synthesised PU had a good film forming effect.

3.4 Particle size analysis

TABLE I Chromaticity and colour difference of the PU samples			
Sample code	L* (D65)	a* (D65)	b* (D65)	ΔE (D65)
PU0	77.96	-0.03	-0.02	0.08
PU1	34.97	0.02	1.29	0.67
PU2	28.88	0.25	2.98	0.53
PU3	25.05	0.76	3.80	0.42
PU4	24.42	1.12	4.15	0.41
PU5	20.43	1.41	5.98	0.26
PU5'	18.26	1.56	7.01	0.73
The data in the table was averaged three times in parallel				

For the synthesised PU, the data revealed that the average particle size increased with increasing dosage of valonia tannin, from 43.46nm to 86.43nm in Table II. It can be seen intuitively by combining the particle size distribution diagram of Fig. 5, that PU0 exhibited a smaller particle size and a more uniform dispersion, the particle size of PU5 was significantly increased and its distribution was much broader. In part due to the
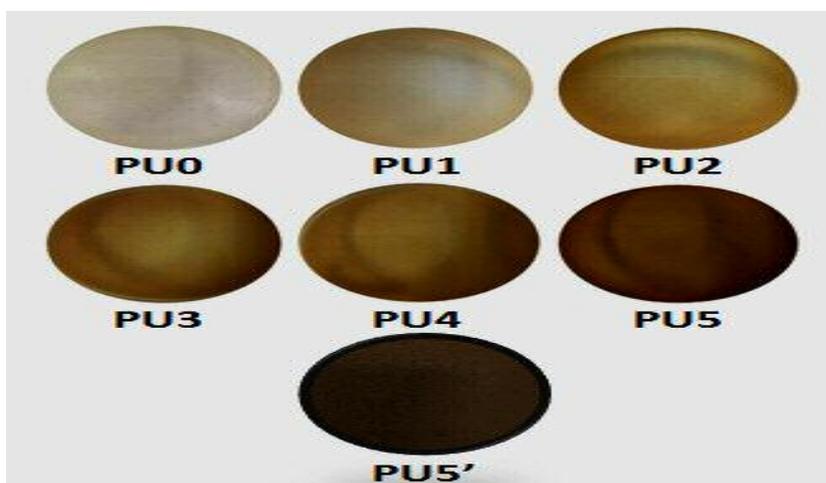

Figure 4. The colour of the PU samples.

polyhydroxy functional group of valonia tannin which formed the cross-linked structure with the molecular chain segments, which was more difficult to emulsify and led to the formation of larger particle size. The blended solution (PU5') showed the bigger average particle size and wider distribution than other PU emulsions, that's because the valonia tannin was just randomly distributed throughout the system and some of the valonia tannin came together by the effect of the intermolecular forces. In general, the synthesised PU emulsion showed a relative satisfactory particle size and can reach the current standards for leather finishing.

TABLE II
The average particle size of the PU samples

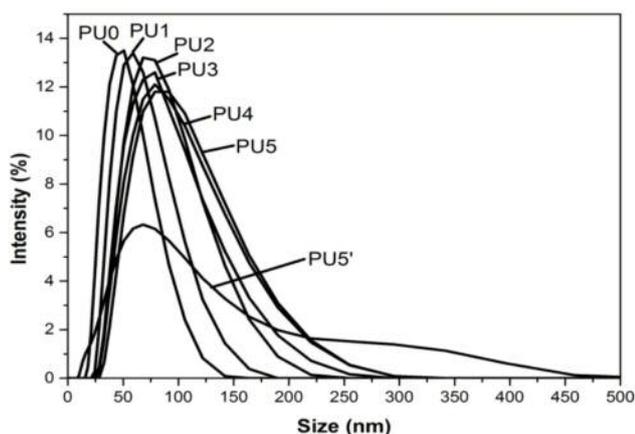| Sample code	Average particle size (nm)
PU0	43.46
PU1	48.31
PU2	60.28
PU3	72.13
PU4	82.60
PU5	86.43
PU5'	143.26

Figure 5. Particle size analysis of the PU samples.

3.5 Thermal stability

Compared with synthesised PU films, the thermal stability of PU0 was the lowest and began to break down firs, shown in Fig. 6. The curve of PU5 showed that the first step degradation occurred at around 230°C (the percentage mass loss was about 10%), which was attributed to the degradation of the isocyanate groups. The polyol segments decomposed in two steps (step II: from 260°C to 350°C; step III: from 350°C to 430°C) regarding the ester groups and the carbonyl groups of tannin. Besides, the de-cross-linking of PU moiety and post-curing process were also responsible for the results.[16] The curve of PU5' showed a higher residual rate after thermal decomposition, this was due to the presence of valonia tannin which created an heterogeneous system in the physically blended film. The curve of PU5 showed the third step degradation ended at 430°C (increased by about 40°C compared to PU0) indicating that the valonia tannin caused the cross-linked structure, which improved the thermal stability of the film.
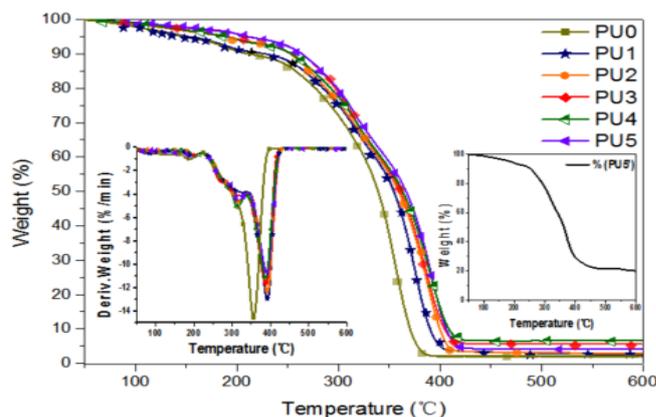

Figure 6. The TG curves and derivative TG of the PU samples.

3.6 Mechanical testing

From PU0 to PU5, we can see that the tensile strength increased from 5.68Mpa to 17.36Mpa and the elongation at break decreased from 456.28% to 359.48% in Fig. 7. The reason for the results might be that the hydroxy of valonia tannin reacted with -NCO to form a complex cross-linked network structure and limited the movement of molecular segments. Meanwhile, valonia tannin was embedded as the hard segment in the main chain of PU and, with the amount of the hard segment increased, the intermolecular force of PU was enhanced. Moreover, the rise in rigidity of the molecular chain caused a corresponding increase in tensile strength and hardness of the film. The tensile strength and the elongation at break of PU5' were not so good relatively, indicating that there was no cross-linked structure in blended film.
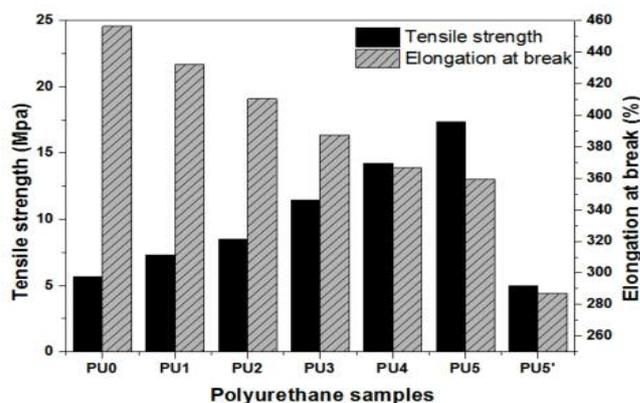

Figure 7. Tensile strength and elongation at break of the PU samples.

3.7 Water and solvent resistance

We can obviously see from Table III that, with the dosage of valonia tannin increased, the water absorption rate and the acetone absorption rate of the synthesised PU samples gradually decreased. However, the blended films showed higher water absorption and acetone absorption. This was due to the pyranose heterocyclic structure in the synthesised PU molecule which greatly enhanced the cross-linked strength so that it reduced the intermolecular voids and hindered the infiltration of water molecules or solvent molecules.

TABLE III

Water and solvent resistance of PU samples

Test projects	The synthesised samples						The blended samples				
	PU0	PU1	PU2	PU3	PU4	PU5	PU1'	PU2'	PU3'	PU4'	PU5'
Water absorption (%)	43.69	27.53	27.06	22.41	20.16	19.54	46.88	47.56	67.92	83.29	116.20
Acetone absorption (%)	59.26	46.97	45.29	40.31	40.08	36.22	66.97	72.49	79.86	100.30	139.40

PU1', PU2', PU3', PU4' and PU5' were obtained by physically blending PU0 with different content of valonia tannin (relative to PU1, PU2, PU3, PU4 and PU5).

TABLE IV

Properties of finished leather samples

Test projects		The test group	The control group
The wet rubbing fastness		5 class	3 class
The dry rubbing fastness		5 class	4 class
The fastness to solvent		4 class	2 class
	15000 times	No crack	No crack
	20000 times	No crack	Minor crack
The folding resistance			
	25000 times	No crack	Coating shedding
	30000 times	Minor crack	Coating shedding
Water vapour permeability (kg/m_·24h)		2.245	2.486

3.8 Property analysis of leather coating

Table IV shows that the colour fastness, fastness to solvent and folding [flexing] resistance of leather finished by PU5 has been improved, because the network structure of PU5 limited the movement of molecular chains. As the water resistance of the leather coating was increased, the fastness to wet rubbing became better. In the control group, the dispersion of valonia tannin in the PU system was poor and, as more and more valonia tannin accumulated on the surface of leather coating it resulted in easier fall off [loss] when subjected to external forces. Water vapour permeability influences the wear comfort of PU leather decisively and will decline after the leather is finished. The permeability data of leather finished by PU5 was slightly lower than the control group and this result also corresponded to the good water resistance of the cured film of the synthesised PU. In addition, the presence of valonia tannin particles increased the interspaces of the leather coating using PU5' during the film forming period, thus the WVP of test group was better than that of the control group.

4 CONCLUSIONS

A series of waterborne PUs with a natural colour were successfully synthesised. The FTIR and TGA analysis confirmed the existence of valonia tannin in the polymer chains and improved thermal decomposition temperature of the cured film. The SEM analysis revealed that the synthesised PU films exhibited a uniform surface morphology superior to that of the blended film. With the increase of valonia tannin dosage, the chromaticity of the coating and the particle size of the synthesised PU emulsion increased gradually, meanwhile, the tensile strength and solvent resistance of cured film showed a significant improvement compared with pure PU. In addition, the leather finished by PU5 exhibited excellent colour fastness, fastness to solvent and folding [flexing] resistance, but the WVP slightly declined. The synthesised waterborne PU has shown that it has the potential to be used in the leather finishing industry and can partly solve some problems with the properties of film formation, which is a preliminary step towards the novel coating material.

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