

Copolymer of Pyromellitic Dianhydride with Diaminodiphenylether as a Tanning Agent for Leather

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Abstract: A polyamic acid has been synthesized with pyromellitic dianhydride and diaminodiphenylether, and characterized by IR spectrum, DSC and TGA. The tanning properties of the polyamic acid have been studied by applying it in pretanning and retanning for chrome tanned leather and aluminium tanned leather. The results showed that a significant increase in chromium uptake for chrome tanned leather can be obtained by pretanning with the polyamic acid, and shrink temperature and washing stability as well as physical properties of aluminium tanned leather could be predominantly improved by either pretanning or retanning with the polyamic acid.

Key words: polyamic acid; chrome tanning; aluminium tanning; pre-tanning; re-tanning

1 Introduction

Polyamic acid is a polycondensate of a tetracarboxylic dianhydride and a diamine, and is generally used as an intermediate in various fields for synthesizing polyimide^{1,2,3}. Because of its long polyamide chain and poly-carboxyl groups, it possesses a strong affinity either to collagen fiber or to metal complexes. Therefore, from the view point of its molecular structure, it might be used as a polymer tanning agent in combination tanning/retanning with metal complexes. In our previous work, the synthesis of several polyamic acids for membrane preparation has been studied⁴. In the present work, a polyamic acid suitable for mixing into chromium or aluminium tanning solution has been synthesized by polymerizing pyromellitic dianhydride and diaminodiphenylether. The structures of the copolymer have been conformed, and the effect of the copolymer on aluminium tanning has been investigated.

2 Experimental

2.1 Materials

Pyromellitic dianhydride, diaminodiphenylether, N,N-dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAc) acetone, sodium hydroxide, hydrochloric acid, sodium citrate, aluminium sulfate and normal chromium powder were purchased from Xian Chemical Company.

Delimed goatskins (pH8.0) and pickled goatskin (pH3.0) were obtained from a local tannery.

2.2 Copolymer synthesis

A three-necked flask equipped with an addition funnel and a N₂ inlet was charged with a solution of diaminodiphenylether in DMSO, then dianhydride was added all at once. The mole ratio and solid content of diamine/dianhydride mixture were 1:1 and 12 wt%, respectively. The reaction mixture was reacted for 3 h at room temperature in N₂ atmosphere affording a viscous polyamic acid solution.

Polyamic acid was deposited from the viscous polyamic acid solution by adding acetone, and re-dissolved with 10% NaOH solution affording an aqueous polyamic acid solution of 9%.

2.3 Copolymer analysis

Purified polyamic acid sample was obtained by adding hydrochloric acid to the aqueous polyamic acid

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solution and washing with acetone, and used for analysis.

The weight-average molecular weight of the copolymer was determined by its intrinsic viscosity³ using DMAc as a solvent at 25 °C according to formula $[\eta]=2.38\times10^{-4}M_w^{0.78}$.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using a STA 409PC integrated thermal analyzer at a heating rate of 10 °C under nitrogen atmosphere.

IR spectra of the copolymer were recorded by KBr disc on a Bruker ZFS66V/S IR spectrometer.

2.4 Application of the copolymer on chromium tanned leather

2.4.1 Pretanning with the copolymer

In a typical laboratory scale experiment, 100 g of delimed goatskin was continuously drummed in 40 ml water at 25 °C, and 4-16g of aqueous polyamic acid solution was added and run for 3 hours. Then the pelt was pickled in 60 ml of sulfuric acid solution to pH 3.5, and 3% of normal chrome powder was added and drummed for 90 minutes, and then 0.3% of MgO was added and run for another 2 hours. After the pH value of tanning bath attained 3.8~4.2, 100 ml of hot water (60~70 °C) was added to raise the temperature to 38-40 °C, and run for another 8 hours. In the end, the shrink temperature of the wetblues and the chromium content in effluent (200 ml) were determined.

The wet blue was neutralized, fatliquored, dried, staked and toggled according to conventional process. The physical properties of the crust were measured.

2.4.2 Retanning with the copolymer

In a typical laboratory scale experiment, 100 g of goatskin wet blues tanned with 3% chromium powder was continuously drummed in 100 ml water at 30 °C, and 6 — 15g of aqueous polyamic acid solution was added and run for 3 hours. Then the wetblue was neutralized, fatliquored, dried, staked and toggled according to conventional process. The physical properties of the crust were measured.

2.5 Application of the copolymer on aluminium tanned leather

2.5.1 Pretanning with the copolymer

0.3 mol/L aluminium sulfate tanning solution was prepared by dissolving 200g aluminium sulfate, 26g sodium citrate in 1000mL water. The pH value of the solution was brought to 4.5-5.0 by adding small amount of magnesium oxide.

100 g of delimed goatskin was continuously drummed in 40 ml water at 25 °C, and 6 — 18g of aqueous polyamic acid solution was added and run for 3 hours. Then the pelt was pickled in 60 ml of sulfuric acid solution to pH 4.0 according to conventional process, 200mL aluminium sulfate tanning solution was added and drummed for 3h. The temperature was then raised to 40 °C, and the bath was brought to pH 4.5 in the course of 6 h by adding a total of 1.2 g of magnesium oxide a little at a time. The leather was then allowed to stand in the bath for a further 12h.

The aluminium-tanned leather was neutralized for 60 min in 200 mL of dilute sodium carbonate to pH5.5, and fatliquored at 50 °C for 90 min in 200mL of fresh bath with 8 g mixture of fatliquoring agents. The pH value of the bath was adjusted to 3.5 by dilute formic acid. The leather was then horsed up, dried, staked and toggled.

2.5.2 Retanning with the copolymer

Pickled goatskin was tanned with 0.3 mol/L aluminium sulfate tanning solution according to conventional process.

100 g of aluminium tanned wet leather was continuously drummed in 100 ml water at 30 °C, and 6 — 15g of aqueous polyamic acid solution was added and run for 3 hours. Then the leather was neutralized, fatliquored, dried, staked and toggled according to normal process. The physical properties of the crust were measured.

2.6 Analysis of leather and tanning liquor

Shrink temperature was determined by typical industry equipment. The tensile and tearing strength as well as elongation of the crust leather were measured on a Gotech GFU55 universal testing machine according to the Methods QB/T 2710-2005 and QB/T 2711-2005 of China Leather Industry Specification. Measurements were made in five replications.

Chromium content in spent solution was determined by atomic absorption spectroscopy. Chromium standard solutions with various concentrations were prepared by dissolving potassium dichromate in water, and the standard curve of the concentration versus the atomic absorbency was obtained at 357.9 nm. 50ml diluted spent solution was taken, and 5ml nitric acid and 2ml perchloric acid were added and boiled. Then 4ml of 2mol/L ammonium chloride was added, and diluted to 100ml. The absorbency at 357.9 nm was determined on Shimadzu AA-6501 atomic absorption spectrophotometer. The chromium content in spent solution was calculated from the absorbency and the standard curve.

Washing stability of aluminium tanned crust was assessed by washing the crust with dilute formic acid (pH3.5-4.0) for 6 h and measuring the Ts of the crust.

3 Results and discussions

3.1 Copolymer characterization

The purified polyamic acid was dissolved in DMAc, and the intrinsic viscosity of the solution ³ was determined at 25°C. The weight-average molecular weight calculated from the formula $[\eta]=2.38 \times 10^{-4} M_w^{0.78}$ is 18940 Dalton.

The IR spectrum of the polyamic acid is shown in Fig. 1. The acylamino bond (—NHCO—) showed C=O stretching band at 1650 cm^{-1} and N—H bending band at 1549 cm^{-1} . The carboxylic group showed C=O stretching band at 1710 cm^{-1} and O—H stretching band at 3440 cm^{-1} . The benzene ring showed C=C stretching band at 1500 cm^{-1} . All N—H stretching band appeared at 3330 cm^{-1} and 3060 cm^{-1} . These indicate that the synthesized copolymer is of typical aromatic polyamic acid.



Fig. 1 IR spectrum of the polyamic acid

The DSC curve and TGA curve of the polyamic acid are shown in Fig. 2. An endothermic peak from 140°C to 200°C was observed on the DSC curve (Fig. 2a) due to the glass transition and the thermal

imidization of the polyamic acid. At the same time, corresponding weight loss from 160°C to 260°C (Fig. 2b) was also observed on the TGA curve due to the water release of thermal imidization. These indicate that the synthesized polyamic acid has the typical characteristics of thermal imidization, and is thermostable at the temperature below 140°C

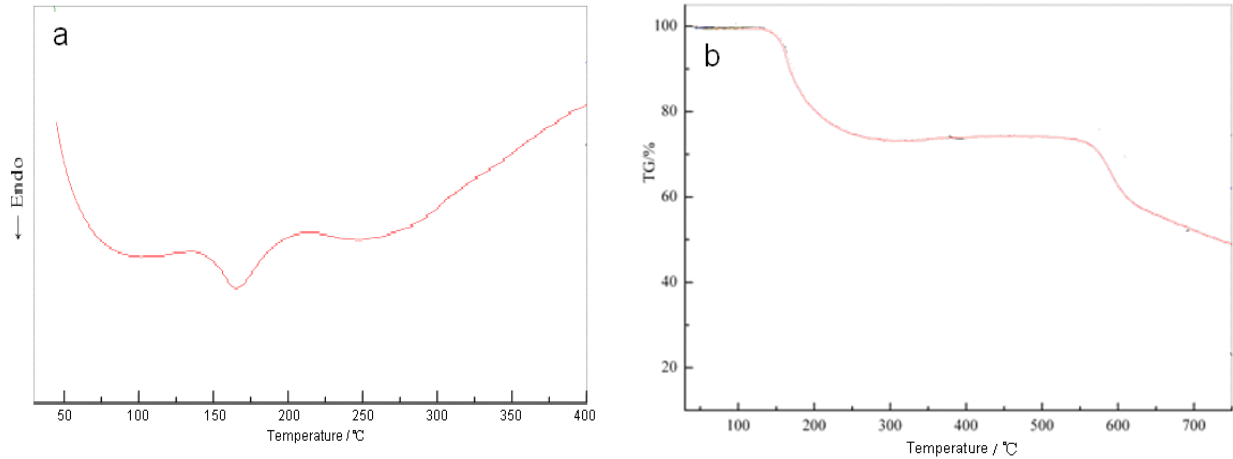


Fig. 2 DSC curve (a) and TGA curve (b) of the polyamic acid

3.2 Tanning properties of the copolymer to chromium tanned leather

Four pieces of delimed goatskin were pretanned with various amounts of the polyamic acid solution at pH7-8 and pickled to pH3.5, and then tanned with 3% of normal chromium powder according to conventional process. The results are reported in Table 1. It was clear that the pretanned pelts had an almost same shrink temperature with the control, but subsequent chrome tanning resulted in a significant increase in shrink temperature and chrome uptake. Even with 12% of the polyamic acid solution and 3% of normal chrome powder a wetblue with a shrink temperature of 95°C was obtained. These results indicate that chrome offer could be reduced by pretanning with the polyamic acid solution.

Table 1 Results of tanning with 3% of chrome powder after pretanning with the polyamic acid solution

Copolymer / %	Ts after pretanning / °C	Ts after Tanning / °C	Chromium in effluent / g Cr ₂ O ₃ ·L ⁻¹
0	54	89.0	2.121
4	57	93.5	0.185
8	56	94.0	0.990
12	55	95.0	0.059
16	55	94.5	0.060

Table 2 Physical properties of the chrome tanned crust pretanned with 12% of the polyamic acid solution

	control	pretanned
Tensile strength / N·mm ⁻²	24.40	22.64
Extension at 10N·mm ⁻² / %	23.70	30.41
Tearing strength / N·mm ⁻¹	47.90	48.33
Thickness / mm	0.60	0.76

Table 3 Physical properties of the chrome tanned crust retanned with 9% of the polyamic acid solution

	control	pretanned
Tensile strength / N·mm ⁻²	24.40	21.51

Extension at 10N·mm ⁻² / %	23.70	42.89
Tearing strength /N·mm ⁻¹	47.90	57.70
Shrink temperature / °C	89.0	99.0
Thickness / mm	0.60	0.80

Physical properties of the crust that pretanned with 12% of the polyamic acid solution and tanned with 3% of normal chrome powder, as well as the crust that tanned with 3% of normal chrome powder and retanned with 9% of the polyamic acid solution, are shown in Table 2 and Table 3. The crusts pretanned and retanned with the polyamic acid were much thicker and fuller than the controls. Although tensile strength of the crusts was slightly reduced, their extension and tearing strength were increased by the pretanning and the retanning with polyamic acid. Therefore, the reduced chrome offer can be achieved by the pretanning or retanning with the polyamic acid.

3.3 Tanning properties of the copolymer to aluminium tanned leather

Four pieces of delimed goatskin (each 100g) were pretanned with various amounts of the polyamic acid solution at pH7-8 and pickled to pH4.0, and then tanned with 0.3 mol/L aluminium sulfate tanning solution according to conventional process. The results are reported in Table 4. It is observed that the shrink temperature of the aluminium tanned crusts was increased to various extents by the pretanning. The washing results in much less decrease in shrink temperature for the crusts pretanned with the polyamic acid than for the control. It is indicated that the polyamic acid can predominantly improve the shrink temperature and the washing stability of the aluminium tanned leather.

Table 4 Results of tanning with 18% of aluminium after pretanning with the polyamic acid solution

Copolymer / %	Ts after pretanning / °C	Ts after Tanning / °C	Ts after washing / °C
0	54	78	67
6	57	83	76
10	56	85	79
14	55	86	80
18	55	85	78

Table 5 Physical properties of the aluminium tanned crust pretanned with 14% of the polyamic acid solution

	control	pretanned
Tensile strength / N·mm ⁻²	20.45	18.23
Extension at 10N·mm ⁻² / %	30.05	36.12
Tearing strength /N·mm ⁻¹	28.24	32.01
Thickness / mm	0.58	0.82

Table 6 Physical properties of the aluminium tanned crust retanned with 12% of the polyamic acid solution

	control	pretanned
Tensile strength / N·mm ⁻²	20.04	21.051
Extension at 10N·mm ⁻² / %	30.05	36.99
Tearing strength /N·mm ⁻¹	28.24	31.52
Shrink temperature / °C	78.0	87.0
Thickness / mm	0.58	0.65

Physical properties of the aluminium tanned crust that pretanned with 14% of the polyamic acid solution, as well as the aluminium tanned crust that retanned with 12% of the polyamic acid solution, are shown in Table 5 and Table 6. The crust pretanned or retanned with the polyamic acid was much thicker

and fuller than the control. Its extension and tearing strength were significantly increased by the pretanning and the retanning with the polyamic acid. The results show that an aluminium tanned leather with higher extension and tearing strength can be obtained by the pretanning and the retanning with the polyamic acid.

4 Conclusions

A polyamic acid has been synthesized by polycondensing pyromellitic dianhydride with diaminodiphenylether, and used in pretanning or retanning for chrome tanned leather and aluminium tanned leather. The weight-average molecular weight of the polyamic acid is 18940 Dalton. The IR spectrum of purified polyamic acid reveals characteristic absorption of amide, benzene ring and carboxyl groups. The synthesized polyamic acid has the typical characteristics of thermal imidization, and is thermostable at the temperature below 140 °C. Pretanning with the polyamic acid can significantly increase the shrink temperature and chromium uptake of chrome tanned crust, and therefore, the chrome offer in conventional chrome tanning can be reduced in large amounts. Even with 3% of normal chrome powder a wetblue with a shrink temperature of 95 °C can be obtained by the pretanning. Pretanning with the polyamic acid can also significantly increase the shrink temperature and washing stability of aluminium tanned crust. Retanning with the polyamic acid can predominantly improve the extension and tearing strength of either the chrome tanned leather or the aluminium tanned leather.

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