

Cationic Graft Copolymer of Gelatin with Acrylates as a Binder in Sealing Coat for Leather

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Abstract: A cationic copolymer was prepared by grafting 2-hydroxypropyl acrylate and 2-methacryloyloxyethyl trimethyl ammonium chloride (DMC) to gelatin, and characterized by IR spectrum. The physical and thermal properties of the film formed from the cationic copolymer were determined. The effect of the copolymer as a coating sealer on the penetration and adhesion of the whole finish into leather was investigated. The results showed that the cationic copolymer could form a thin levelling film with a lower glass transition temperature (T_g) and higher elongation, and effectively prevent the color finish from penetrating too deeply into leather to retain the suppleness and elasticity of the grain.

Key words: cationic polymer; cationic gelatin; leather finishing; gelatin; graft copolymer

1 Introduction

Cationic sealing coat is a coat applied directly to a leather substrate to seal the porous leather surface, so that the subsequent color finishes do not penetrate too deeply into the leather but forms a thin levelling coat that does not overload the grain. Cationic casein, cationic polyurethane and cationic polyacrylate were usually used as a binder in the sealing coat. They provide the necessary levels of adhesion to the leather surface, and give a soft, natural, well-filled look to leather while providing excellent coverage to mask defects such as pin-hole, scars, mange and others. In so doing, they offer an excellent means of upgrading a wide variety of full grain leathers. Like above cationic binders, cationized gelatin possesses strong affinity to leather and could form a feel natural film. Accordingly, it is thought to be a good candidate for seal coating binder. Cationized gelatin could be prepared by introducing primary diamine to carboxyl group of gelatin or grafting amine functional monomers onto gelatin, and used as a gene carrier, paper sizing agent and coating auxiliary.^{1,2,3,4} However, in all the works mentioned, there is no information regarding the preparation of cationized gelatin for leather sealing binder. Hence, in our present work attempts have been made to develop a cationized gelatin suitable as leather sealing binder by esterifying the carboxyl group of gelatin with methanol and then graft copolymerizing 2-hydroxypropyl acrylate and 2-methacryloyloxyethyl trimethyl ammonium chloride (DMC) to the esterified gelatin. The cationic graft copolymer obtained from gelatin and acrylates has been characterized by IR spectrum. The physical and thermal properties of the film formed from the cationic copolymer were determined. The effect of the copolymer as a coating sealer on the penetration and adhesion of the coat was investigated.

2 Experimental procedure

2.1 Materials

Gelatin, 2-hydroxypropyl acrylate (HPA), 2-methacryloyloxyethyl trimethyl ammonium chloride (DMC), ammonium persulfate, sodium bisulfite, N, N-dimethylformamide, anhydrous acetone and

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absolute methanol were purchased from Xian Chemical Company.

2.2 Synthesis of cationic graft copolymer

2.2.1 Esterification of gelatin

Gelatin (10g) was stirred into 100mL of 0.01mol/L H_2SO_4 in methanol at room temperature. The mixture was shaken at intervals during the first 2 h. to prevent caking of the gelatin. After standing for 18 h with occasional shaking, the esterified gelatin was filtered and then dried.

2.2.2 Graft copolymerization of esterified gelatin with acrylate

Esterified gelatin (24g) was dissolved in 180 mL of water. 2-Hydroxypropyl acrylate(8g) and 2-methacryloyloxyethyl trimethyl ammonium chloride (12g) was added. Ammonium persulfate (1.2g) and sodium bisulfite (0.8g) were dissolved in 20 mL water, and used as initiators.

The graft copolymerization was carried out by gradually adding the initiator solution to the mixture of esterified gelatin and monomers in 90min under the constant stirring. During the reaction the temperature was kept at 70 °C, and the stirring speed was 100~150 rpm. After the addition of the initiator solution, the graft copolymers were agitated for another 60 min, and then cooled to room temperature. A solution of cationic graft copolymerized gelatin with 18% solids was obtained.

2.3 Preparation of cationic graft copolymer film

The cationic graft copolymer was dissolved in water and diluted to a solution with a dry solid content of 10%. The solution was cast in a Teflon mould, and the water was allowed to evaporate at 50 °C for 48 h. The resulting films were cured at 20 °C for 24 h to further promote coalescence of the film. Dried film with a thickness of 0.15–0.25mm were peeled from the mould, and stored at a relative humidity of 65% and 20 °C for at least 24 h prior to the determination.

2.4 Application of the cationic graft copolymer in leather finishing

Sealing coat formula: cationic graft copolymer 100, wax emulsion 50, water 100. Spray 1 times. Iron at 70 °C/3MPa.

Base coat formula: pigment paste 100, modified soft casein 80, wax emulsion 100, polyacrylate dispersion 100, soft polyurethane dispersion 200, modified polyacrylate dispersion 50, water 500. Spray 2 times. Iron at 70 °C/3MPa.

Top coat formula: nitrocellulose emulsion 100, aqueous polysiloxane handle feeling agent 3, water 100. Spray 1 times. Iron at 60 °C/3MPa.

2.5 Determination of the cationic graft copolymer and its film

IR spectra of the cationic graft copolymer as well as gelatin were recorded by KBr disc on a Bruker ZFS66V/S IR spectrometer. The samples of graft copolymerized gelatin were deposited from the solution by adding acetone, and purified by extracting with DMF and acetone before determination.

The thermal behavior of the cationic graft copolymer film was recorded on a Netzsch 2000PC differential scanning calorimeter (DSC). The exact amount of samples were weighed and placed into aluminum pans, and heated at the rate of 5 °C/min. The moisture content of the sample was determined by oven drying at 105 °C. The glass transition temperature of the specimens was determined from the midpoint of the heat capacity change observed on the second run, to eliminate the effect of sample history.

The tensile strength and elongation of the film were measured on a Gotech GFU55 universal testing machine. Films specimen 10×2.5 cm strips were pre-conditioned at 20 °C and 65% RH for 48 h before testing. Measurements were made in five replications.

The air permeability of the film was measured on a HC air permeability tester with reference to the Method GB/T 4689.22-96 of China Leather Industry Specification.

The water vapor permeability was measured using a water vapor permeability tester with reference to

the Method QB/T1811-93 of China Leather Industry Specification (wet cup).

The swelling behavior of the film was examined by immersing film directly in deionized water or toluene at room temperature for 24 hours. After the immersion, the swollen product was dried under vacuum to a constant weight. The equilibrium percentage of swelling (% swelling) of the product was calculated as follows:

$$\% \text{ Swelling} = (W_e - W_d) / W_d \times 100$$

where W_e is the weight of the product after immersion in water or toluene for 24 hours, and W_d is the weight of the dried product.

2.6 Determination of coating performances

The Penetration of finishes into crust leather was examined by observing the cross-section of finished leather using a JSM-5800 scanning electron microscopy. The samples were sputter coated with gold prior to examination.

The peel strength measurements of leather coat were performed in a Gotech GFU55 universal test machine using a crosshead speed of 100mm/min according to the Method GB/T4689.20-96 of China Leather Industry Specification.

The flex resistance measurements of leather coat were performed in a GJ9C2 flexometer according to the Method QB/T 2714-2005 of China Leather Industry Specification.

The color fastness of leather coat to rubbing was measured according to the Method B/T 2537-2001 of China Leather Industry Specification.

3 Results and discussion

3.1 IR Characteristics of cationic graft copolymer

Cationic graft copolymer were deposited from the solution by adding acetone, and purified by extracting with DMF and acetone. The IR spectrum of the cationic graft copolymer as well as gelatin is shown in Figure 1. For the cationic graft copolymer, characteristic amide A, I, II and III bands are easily observed at 3435 cm^{-1} , 1637 cm^{-1} , 1538 cm^{-1} and 1250 cm^{-1} respectively. The bands at 2924 cm^{-1} and 1451 cm^{-1} are caused by C—H stretching and bending vibrations of hydrocarbon chain. As compared to the IR spectrum of gelatin, the appearance of the C—H stretching vibration of $\text{N}^+ - \text{CH}_3$ group in the neighborhood of 3256 cm^{-1} and the C=O stretching vibration of ester groups at 1751 cm^{-1} is an evidence for grafting of 2-hydroxypropyl acrylate and 2-methacryloyloxyethyl trimethyl ammonium chloride to gelatin.

3.2 Thermal properties of cationic graft copolymer film

The DSC thermograms of the cationic graft copolymer films, as well as the gelatin films are shown in Fig. 2. The films were known to have moisture content of approximately 19%. The cationic graft copolymer film displays a glass transition at 51.7°C and a melting isotherm at 89.8°C , while gelatin film displays a glass transition at 61.5°C and a melting isotherm at 92.5°C . This difference of the thermal property is reasonable due to the effect of grafted polymer chains. The grafting modified the thermal property of gelatin with decreased T_g and T_m values, indicating the formation of a new product.

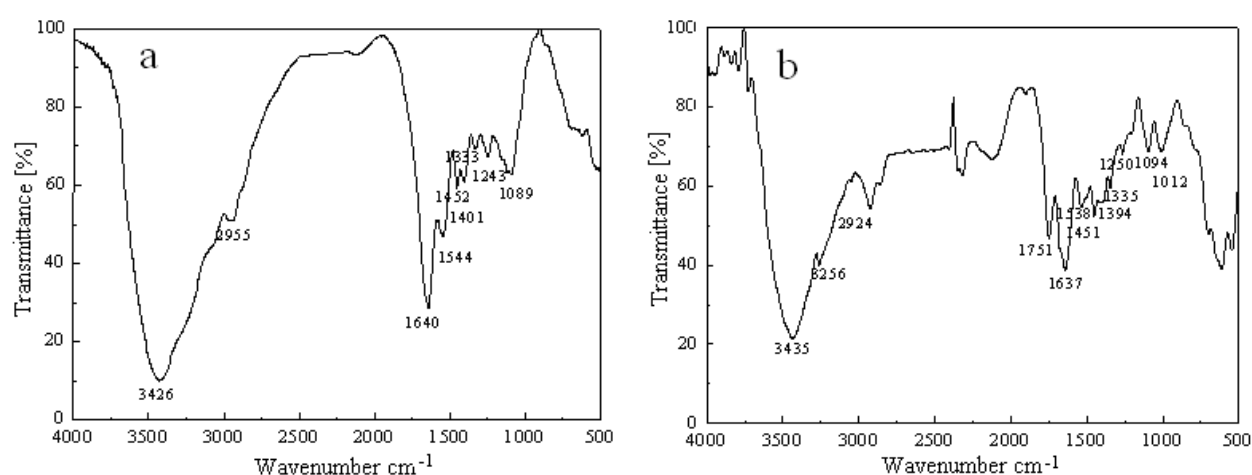


Fig. 1 IR spectra of gelatin (a) and cationic graft copolymer (b)

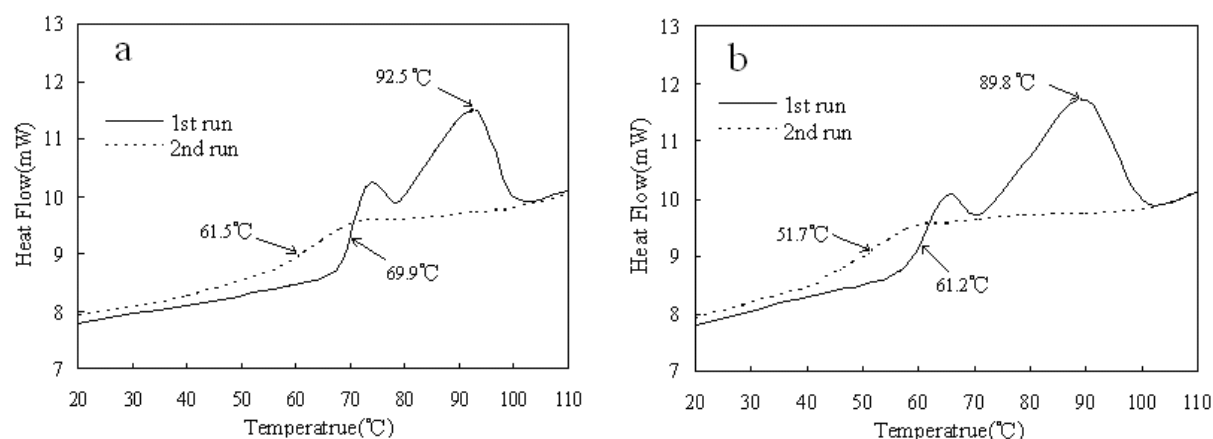


Fig. 2 DSC thermograms of gelatin film (a) and cationic graft copolymer film (b)

3.3 Physical performances of cationic graft copolymer film

Table 1 shows that the film prepared from cationic graft copolymer possess either much higher tensile strength or much higher elongation than gelatin film. This remarkable difference is due to longer polymer graft chains and esterification of carboxyl group of cationic graft copolymer. In general, increased tensile strength is followed by the decrease of elongation at break, but it seems not to be shown here. As the polymer chains grafted to gelatin are cationic or nonionic, and the carboxyl group of gelatin was esterified, therefore, beside the existence of intermolecular attraction with gelatin chain leading to increased strength, it might extend macromolecular relaxations leading to increased elongation.

Table 1 Physical performances of cationic graft copolymer film and gelatin film

	Gelatin film	Cationic graft copolymer film
Tensile strength / N·mm ⁻²	22.49	33.73
Elongation at break / %	5.13	32.42
Elongation at 10N·mm ⁻² / %	1.38	3.36
Air permeability / mL·cm ⁻² ·h	634.29	590.16
Water vapor permeability / mg·10cm ⁻² ·24h	2.13	1.59
Swelling in water / %	64.18	38.46
Swelling in toluene / %	3.18	2.07

Table 1 also shows that the graft copolymer film has lower air permeability and water vapor permeability than gelatin film. This indicates that the graft copolymerized gelatin film possesses a more compact and hydrophobic matrix than gelatin film.

The swelling of cationic graft copolymer film in water is lower than that of gelatin film, but is still up to 38.46%, so it can be categorized as absorbent. From the synthesis of the graft copolymer, it is clear that the whole carboxylic group of the gelatin has been esterified but the free primary and quaternary amino groups are present. From this fact it can be hypothesized that these free amino groups play an important role in water uptake because of their hydrophilic nature.

3.4 Effect of cationic graft copolymer on coating performances

The goatskin crust was cut into two sides along backbone. One side was sealed with cationic graft copolymer. Another was not sealed and used as a control. The same base coat and top coat were applied on the two sides. The cross sections of the finished sides are shown in Fig 3. It can be observed that the crust sealed with cationic graft copolymer has a predominantly reduced absorption to color finishes as compared to control. This implies that cationic graft copolymer could effectively prevent the colour finishes from penetrating too deeply into leather to retain the suppleness and elasticity of the grain.

The adhesion of coat to crust was obtained from peel tests. Table 2 shows a slight increase in peel strength of coat after sealing with the cationic graft polymer.

Table 2 also shows that flex resistance and color fastness to rubbing are not affected by the sealing.

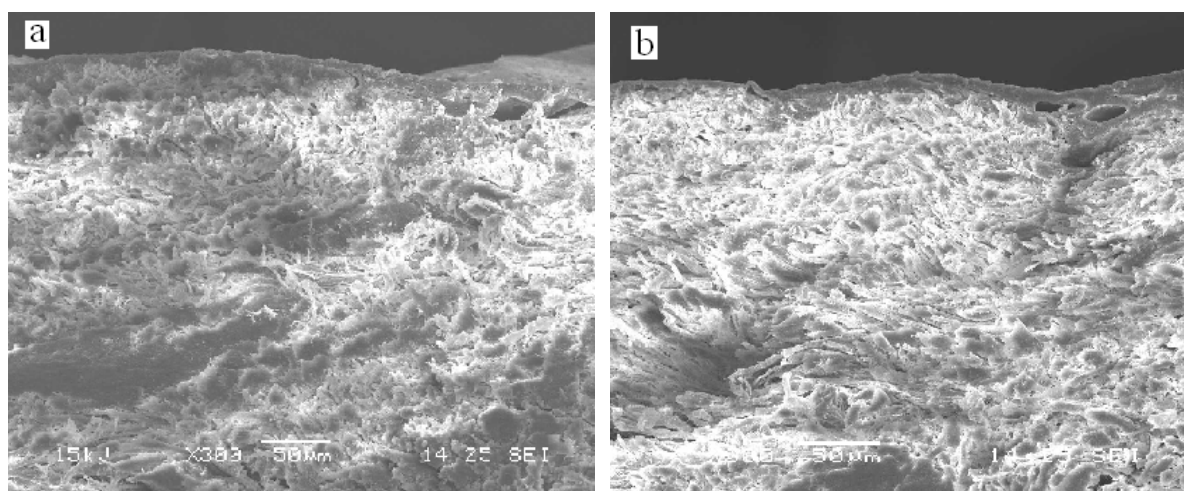


Fig. 3 SEM of cross section of finished leather

(a) Cross section of finished side without sealing; (b) Cross section of finished side with sealing

Table 2 Effect of cationic graft copolymer on coating performances

	Coating without sealing	Coating sealed with cationic graft copolymer
Peel strength /N·10 ⁻¹ mm ⁻¹	78.3	87.4
Flex resistance /times	20000	20000
Color fastness to dry rubbing /grade	5	5
Color fastness to wet rubbing /grade	4-5	4-5

4 Conclusions

A cationic graft copolymer has been successfully synthesized by esterifying the carboxyl group of

gelatin with methanol and then graft copolymerizing 2-hydroxypropyl acrylate and 2-methacryloyloxyethyl trimethyl ammonium chloride to the esterified gelatin. The IR spectrum of purified cationic graft copolymer reveals characteristic absorption of peptide, $N^+(CH_3)_3$ group and ester groups. The cationic graft copolymer could form a thin film with a lower glass transition temperature and higher elongation, and effectively prevent the colour finish from penetrating too deeply into leather to retain the suppleness and elasticity of the grain. A natural looking leather with acceptable physical properties can be obtained by sealing with the cationic graft copolymer.

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