

Synthesis and Properties of Tannin/vinyl polymer Tanning agents

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Abstract: Polymer methacrylate–acrylamide (PMAA-AM) was prepared by free radical polymerization with methacrylate and acrylamide as raw materials, and then modified with tannin by Mannich reaction to prepare tannin/polymer methacrylate–acrylamide (tannin/PMAA-AM). PMAA-AM and Tannin/PMAA-AM were characterized by Fourier Transform Infrared Spectroscopy (FTIR), and X-ray diffraction (XRD) respectively. The result of FTIR demonstrates that PMAA-AM is modified by tannin successfully, the result of XRD result shows that the crystallization of tannin/PMAA-AM is decreased to 9.04% from 13.54% of PMAA-AM. Compared with 8% (based on pelt weight) chromate tanned leather 6% tannin/PMAA-AM associated with 2% chromate tannage was applied in leather making process. The application result indicates the shrinkage temperature of the leather raises by 47.0°C and the thickness increment ratio of the leather increases by 69.20%, tensile and tearing strength of the leather are far more than 8% chromate tanned leather.

Key words: tanning agents; tannin; vinyl polymer; modification; Mannich reaction

1 Introduction

Vegetable tanning agent is hailed as the "green tanning agent" because of its biodegradation. Vegetable tanned leather has excellent fullness, moldering properties, wear resistance, air permeability and solidness; hence, it is of great significance to reduce chrome pollution in leather making process. Vegetable tanning plays an important part of making heavy leather such as furniture leather, garment leather and shoe upper leather. Nowadays more attention has been paid by researchers in the world on using vegetable tanning agent to replace chrome tanning agent and have already achieved many progresses^[1-4].

Despite of its irreplaceable characteristics, using single vegetable tanning agent also cannot meet the correlative requirements. In order to overcome its disadvantages, such as massiness and solidness when making light leather and broaden its application in light leather processing as far as possible, vegetable tanning agent was modified. Researchers as Shi Bi^[5] and Fathima NN^[6] have carried through various modification methods to prepare vegetable tanning agent that satisfy different requirements.

Both of vegetable tanning agent and vinyl polymer has large number of active groups, combining advantages of them might prepare high performance tanning agent^[7]. Our team have modified valonia extract with acrylate monomers by graft copolymerization and studied its properties of application, the results show that the solution stability, permeability of modified valonia extract can be increased and astringency is decreased^[8]. Using it in retanning processing, the grain of leather is of smoothing and fineness, the softness and fullness of leather are improved obviously. In this paper, the copolymer of methacrylate and acrylamide (PMAA-AM) was prepared by amino groups in PMAA-AM reacting with

α -hydrogen in tannin, then PMAA-AM was modified by tannin. Finally 6% tannin/PMAA-AM associated with 2% chromate tannage (based on pelt weight) was applied in leather making process to study its tanning properties.

2 Experimental

2.1 Materials

Acrylamide (AM), analytically pure, was obtained from Tianjin Fucheng Chemical Reagent Factory. α -Methacrylic Acid (MAA), analytically pure, was purchased from Tianjin Jinyu Fine Chemicals Co Ltd.. Tannin, analytically pure, was made by Jiangsu Wuxi Chemical Reagent Factory. Glyoxal, analytically pure, was obtained from Tianjin Fucheng Chemical Reagent Factory. Ammonium persulfate, analytically pure, was made Tianjin No.6 Chemical Reagent Factory. Sodium bisulfite, analytically pure, was purchased from Xian Fucheng Chemical Reagent Factory.

2.2 Synthesis of tannin/PMAA-AM

A 250 mL 3-necked round-bottom flask containing deionized water, AM and MAA were equipped with a reflux condenser, a thermometer and a magnetic stirring bar. Polymerization was initiated by adding an aqueous solution with ammonium persulfate and sodium bisulfite. The reaction was allowed to proceed for 4 hours under stirring, after that an aqueous solution of tannin and glyoxal were added into the reactor by controlling the dropping speed. The modification was continued for 3h. Adjusted the pH by HCl, the tannin/PMAA-AM was obtained.

2.3 Application of tannin/PMAA-AM

Tannin/PMAA-AM was carried out on pickled sheepskins and is described as below:

Operation	Products	Quantity	T(°C)	Time	Control
Washing	Water	100%	R.T.		
	NaCl	8%		30min	
Tanning	Water	100%	R.T.		
	NaCl	8%			
	Formic acid	0.2%(1:10)		30min	Check pH=3.5
	tannin/PMAA-AM	6%		6h	
	NaHCO ₃	2%(1:20)		15min×3 + 20min	Check pH=5.0
Overnight					
Washing	Water	200%	R.T.	10min×2	
Chrome tanning	Water	80%	R.T.		
	Formic acid	0.2%(1:10)		30min	Check pH=3.5
	chromate	2%		4h	
	NaHCO ₃	2%(1:20)		15min×3 + 20min	Check pH=4.2
Overnight					
Washing	Water	200%	R.T.	10min×2	
Fatliquoring	Water	150%	55°C		
	ammonia	0.8%		30min	

	L-3	4.0%			The fatliquoring agents were emulsified by hot water 60°C
	SC	5.0%			
	Sulfited fish oil	8.0%	3h		
Fixed	Formic acid	1.5%(1:10)	30min		Check pH=3.5
	Cation Fatliquoring	2%			
Washing	8% chrome tanning procedure is described as below:				
Operation	Products	Quantity	T(°C)	Time	Control
Washing	NaCl	8%	R.T.		
	water	100%		15min	
Put the pelts into the drums	Formic acid	0.2%	R.T.	30min	Check pH 3.5
	Chrome	8%		2h	
	NaHCO ₃ (1:20)	2%		20min×4+4h	Check pH4.0-4.2
Overnight				30min	Check pH 4.0-4.2

The subsequent washing and fatliquoring procedures were in the same with the chrome and the decreased chrome tanning process.

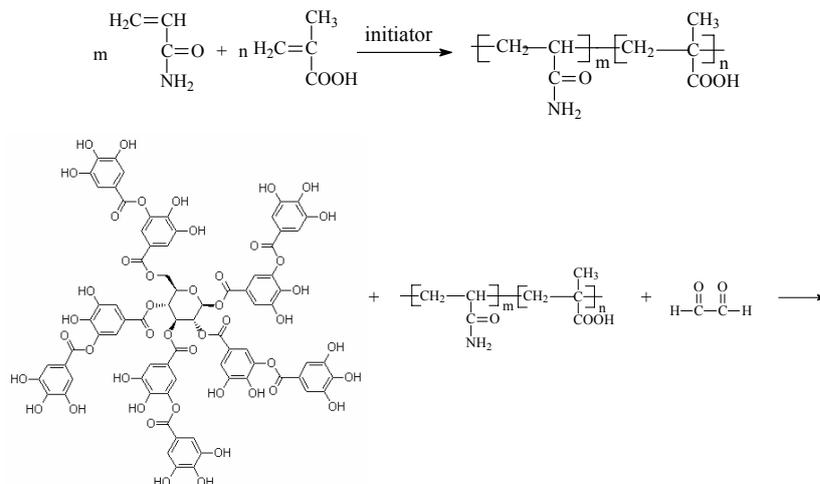
2.4 Measurement and characterization

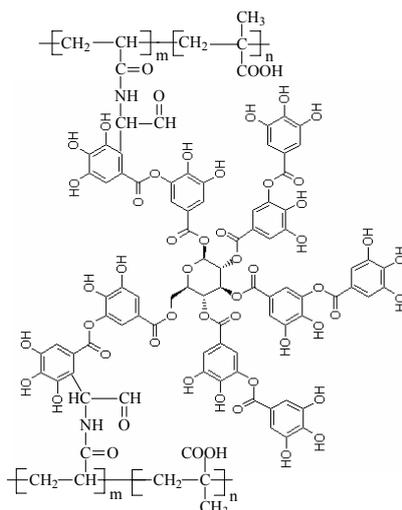
PMAA-AM and tannin/PMAA-AM were purified by ethanol, oven drying, grind to powder with mortar then investigated by X-ray diffraction (XRD) instrument (D/Max2200PC), equipped with Cu K α radiation source and the Fourier transform infrared spectrometer (EQUINX55).

The leather samples were put into air conditioner for 48h, and the tensile and tearing strength of the leather were tested with GT-U55 functional materials examination machine made by Taiwan High Iron Science and Technology Stock Company.

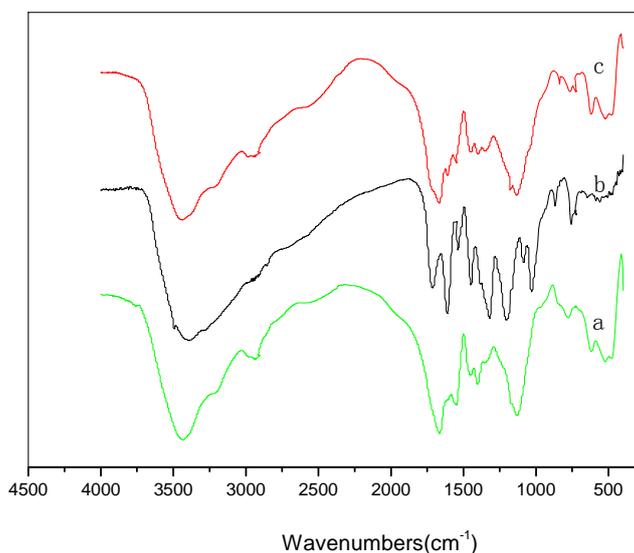
3 Results and discussion

The Mannich reaction of PMAA-AM and tannin is as follows:





3.1 FTIR Analysis



Note: a- PMAA-AM,
 b- tannin,
 c- tannin/PMAA-AM.

Figure. 1 FTIR of PMAA-AM, tannin and tannin/PMAA-AM

Figure 1 displays the FTIR of tannin, PMAA-AM and tannin/PMAA-AM. In FTIR spectrum of tannin, the band at 3437cm^{-1} is stretch vibration absorption of O-H, the band at 1710cm^{-1} is stretch vibration absorption of C=O. Moreover, bands at 1610cm^{-1} , 1540cm^{-1} , and 1450cm^{-1} are corresponding to extending vibration and at 756cm^{-1} is the result distortion vibration of C=C in benzene.

In FTIR spectrum of PMAA-AM, the absorption peak 3443cm^{-1} is affected by extending vibration of O-H and N-H, 1660cm^{-1} belongs to extending vibration of C=O, besides, the band at 1460cm^{-1} is antisymmetrical stretch vibration absorption spectra of $-\text{CH}_3$.

Compared with PMAA-AM, in FTIR spectrum of tannin/PMAA-AM, the extending vibration bands and distortion vibration band of C=C in benzene are observed at 1560cm^{-1} , 1400cm^{-1} and 766cm^{-1} . Both characteristic absorption peaks of PMAA-AM and tannin can be observed in the FTIR spectrum of tannin/PMAA-AM indicating that tannin is modified by PMAA-AM successfully.

3.2 XRD Analysis

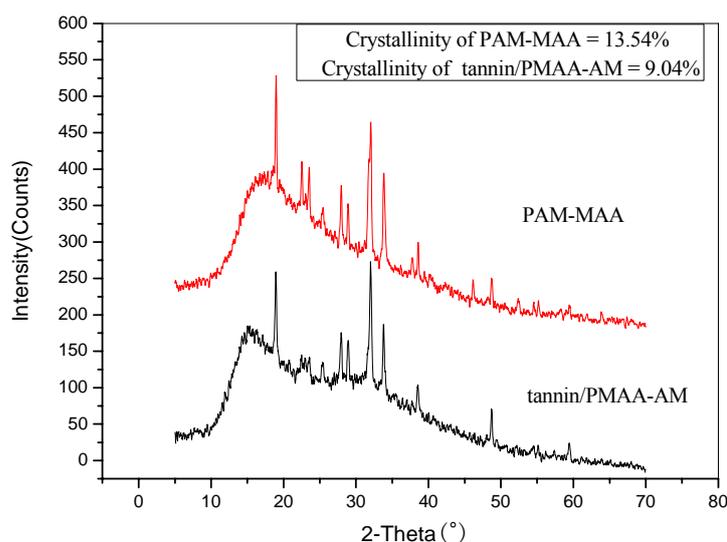


Figure. 2 XRD of PMAA-AM, tannin and tannin/PMAA

Figure 2 shows XRD patterns of PMAA-AM and tannin/PMAA-AM respectively. The crystallizations of tannin/PMAA-AM and PMAA-AM were 9.04% and 13.54% respectively. Polymers have crystalline region and non-crystalline region, the crystallizations is influenced by components, reaction condition and so on. Compared to PMAA-AM, the crystallization decreasing of tannin/ PMAA-AM indicates that the interaction force of polymer molecular chains has become weaker and the degree of regularity is decreased. The molecular flexibility of tannin/PMAA-AM is higher than that of PMAA-AM. XRD results are consistent with the application results that the leather tanned by tannin/PMAA-AM has better performance of softness, fullness and flexibility than that of the leather tanned by PMAA-AM.

3.3 Application Results

Figure 3 shows the shrinkage temperature and thickness increment ratio of leather sample. The shrinkage temperature of sample 1 is 91.6°C , lower than sample 2, which has achieved the standard of garment leather of sheep skin.

The thickness increment ratio demonstrates the extent of the thickness change before and after tanning which had corresponding relation with the fullness of the leather. Generally, the bigger the thickness increment ratio, the fuller is the leather. Tannin/PMAA-AM is high molecular polymer having long molecule chains, its infiltration and combination with collagen fibers due to the good fullness. On the other hand the $-\text{COOH}$ of tannin/PMAA-AM increases the combination with chrome, hence, the thickness increment ratio of sample 1 is

higher than sample 2 indicating that tannin/PMAA-AM has a noticeable effect on the fullness of leather.

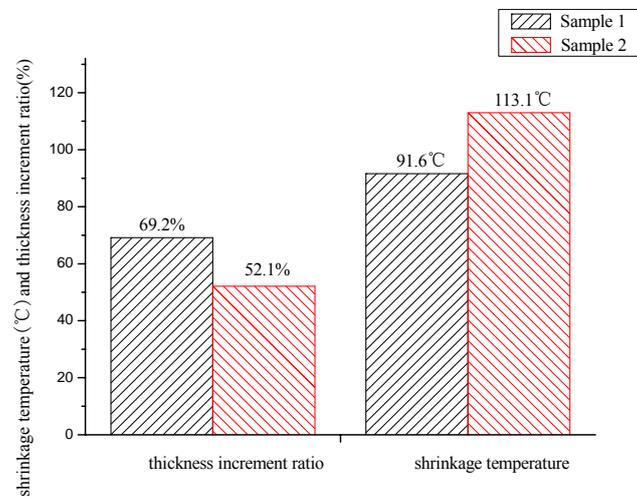
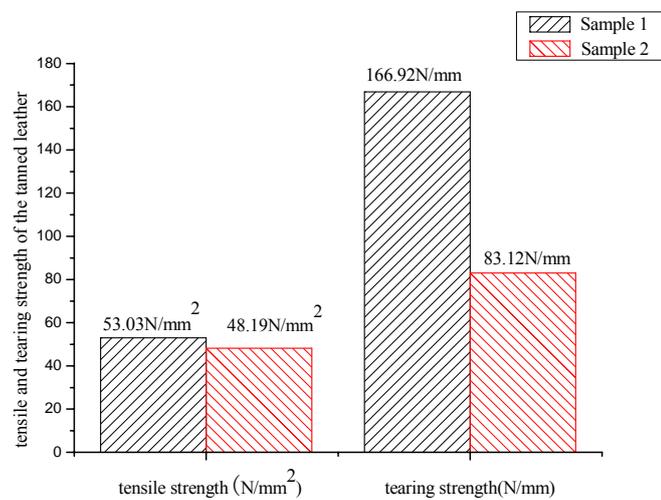


Figure. 3 the shrinkage temperature and thickness increment ratio of the tanned leather

Note: Sample 1- 6% tannin/PMAA-AM associated with 2% chromate tanned leather;

Sample 2- standard 8% chromate tanned leather.



Note: Sample 1- 6% tannin/PMAA-AM associated with 2% chromate tanned leather;

Sample 2- standard 8% chromate tanned leather.

Figure. 4 the tensile and tearing strength of the tanned leather

Figure 4 shows the tensile and tearing strength of the tanned leather. The tensile strength is affected by the weave and disperstiveness of fibers, the weave angle, and the lubrication firmness^[9]. The tensile strength of sample 1 is 53.03 N/mm² and sample 2 is 48.19 N/mm², this is due to the molecule chain of tannin/PMAA-AM is longer and softer than chrome and

disperse the collagen fibers easily.

The tearing strength varies with the firmness and flexibility, the strength of the grain and the degree of compactness and evenness of fibers^[9]. The –COOH and –OH of tannin/PMAA–AM occur coordinate reaction and electrovalent combination with chrome, this crosslinking improves the tearing strength of sample 1 that is two times more than sample 2, indicating that tannin/PMAA-AM improve the firmness and flexibility of the leather.

4 Conclusions

PMAA-AM was modified with tannin by Mannich reaction to prepare tannin/polymer methacrylate–acrylamide (tannin/PMAA-AM). FT-IR results demonstrate the modification is successful and XRD results demonstrate that the crystallization of tannin/PMAA-AM is lower than PMAA-AM.

The application results indicate the shrinkage temperature of the leather can be raised to 91.6°C and the thickness increment ratio of the leather is increased by 69.20%, strengthen and toughing properties of the leather are far more than 8% chromate tanned leather. Compared with conventional chrome tanning, the dosage of chromate is reduced by 75%.

Acknowledgements

The author wishes to thank National high-tech Research and Development Plan (863 Plan) (Item No. 2008AA032311) and the Graduate Innovation Fund of Shaanxi University of Science and Technology for their financial support.

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