

Preparation of Novel Aminated Collagen Peptide and Evaluation of Its Formaldehyde Removal to Leather

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Abstract: Collagen is a typical amphiphilic natural macromolecule with amino-, carboxylic- end and many acidic or alkaline branches. The hydrolysis of collagen will release many hydrophilic functional groups including carboxyl, hydroxyl, amino etc. These functional groups especially amino group can react with formaldehyde, so that collagen peptide can be used as natural formaldehyde scavenger. In order to increase the functional groups that reacted with formaldehyde, the aminated collagen peptide was modified with ethylenediamine as amidogen donator and carbodiimide as dehydrating agent. The characterization of Fourier Transform Infrared Spectrum (FTIR) and amino acid analyzer suggested that the content of amino group increased. The aminated collagen peptide was used to remove the formaldehyde in oxazolidine tanned leather and the results showed that the amount of formaldehyde removed by the aminated collagen peptide was significantly increased to 61.6% which was better than that of collagen peptide and commercial formaldehyde scavenger. Moreover, the thickening rate and dye absorptivity of the aminated collagen peptide were 12.5% and 96.6%, respectively and it also had thickening and assisting dyeing effects to leather. Therefore, modifying the collagen peptide and used as the formaldehyde scavenger has a good potential in achieving the innocent treatment of formaldehyde in leather.

Key words: Aminated collagen peptide; ethylenediamine; carbodiimide; formaldehyde scavenger

1 Introduction

Formaldehyde is an important raw material and is widely used in organic synthesis. The compounds which are synthesized with formaldehyde and closely related with daily life mainly are adhesives, coatings and textile auxiliaries. The manufacture technics of these products is simple and the cost is low, so they are widely used in wood processing and post-processing of textiles. As a result, a certain amount of formaldehyde will be released in the application process.^[1] In recent years, researchers pay more attention to the study on the treatment method of formaldehyde pollution. The treatment methods include oxidation-reduction method, catalytic combustion, chemical and biological treatment, physical and chemical adsorption method, and so on. But the cost of these methods is high and secondary pollution exists.^[2]

Collagen has been widely used in biomedical area, cosmetics and food products because of its lower toxicity and better biocompatibility. The study on physical and chemical modification to collagen is more, such as carboxyl modification,^[3] introduction of PEG chain into gelatin molecule,^[4] introduction of dextran, polyacrylic acid or polyacrylamide gelatin into the gelatin molecular skeleton.^[5-7] However, there is few report on aminated modification to gelatin. In the study, the collagen peptide, extracted from phosphonium tanned leather shavings, was modified with ethylenediamine as amidogen donator and carbodiimide as dehydrating agent. The aminated collagen peptide is prepared in mild conditions and its

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performance to remove formaldehyde is studied.

2 Experimental

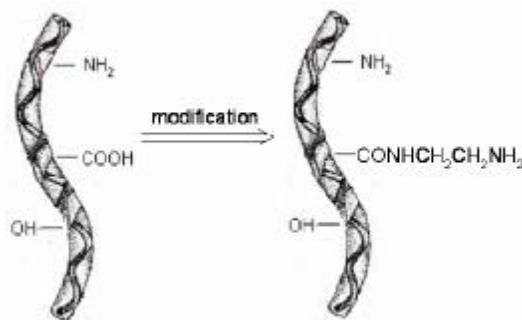
2.1 Materials and apparatus

Collagen peptide was self-prepared (extracted from phosphonium tanned leather shavings); ethylenediamine(AR)was provided by Kelong Chemical reagent Factory in Chengdou, carbodiimide(AR) was offered by Tiantangshan Chemical Co. Ltd, in Zibo; formaldehyde(AR) was supplied by Jinshan Chemical reagent Co. Ltd, in Chengdou. Others were analytical reagents.

W2-180SP rotary evaporator was supplied by Shensheng Technologies. INC; Fourier infrared spectroscopic apparatus was provided by Bruker Company in Germany; Beckman 121 amino acid analyzer was offered by Beckman Company of USA.

2.2 Modification of collagen peptide

The collagen peptide and ethylenediamine, with the weight ratio 2:1, were added into three-neck flask. Then 50% carbodiimide (basing on the weight of collagen peptide) was added. After the reaction was kept for 3.5h, the water and unreacted ethylenediamine were removed by using rotary evaporator. The light yellow product was aminated collagen peptide. The reaction schematic diagram was shown as follows.



2.3 Characterization

2.3.1 Determination of amino group

The determination of amino group content in aminated collagen peptide was shown in references [8].

2.3.2 FT-IR analysis

The collagen peptide and aminated collagen peptide were put into oven and dried at 100°C . Then they were tested by using coating method.

2.3.3 Amino acid analysis

100mg collagen peptide and 100mg aminated collagen peptide were hydrolyzed by 6mol/L hydrochloric acid of 10mL at 110°C for 24h. After filtrating and concentrating, the solution was dissolved in 50mL volume flask. 1mL solution, being dried and diluted by citric acid buffer solution whose pH was 2.2, was tested using amino acid analyzer.

The analysis conditions: time was 60min, chromatogram column was $3\mu\text{m}\times 4.6\text{mm}\times 60\text{mm}$, the flow speed of buffer solution and ninhydrin was 0.4mL/min and 0.3mL/min, respectively.

2.4 Application test

The self-prepared collagen peptide and other formaldehyde scavengers were used to remove formaldehyde in tanned leather. The determination of formaldehyde content in leather was shown in references 9. The tanning procedure was shown as follows.

Process	%	Chemicals	°C	min	pH	Comments
Depickling	80	Water	20			
	7.0	Salt		20		6~6.5°Bé
	2.0	Formic acid		2×20+40	2.4~2.6	
Tanning	2.0	ZOLDINE ZE		180		
	1.0	Feliderm DP				
	1.0	Catalix L		60		
	1.0	Sodium Formate		30		
	1.0	Sodium Bicarbonate		3×30+60	7.5~8.0	
	2.0	Tanicor KW	50	120	8.0	Ts>95°C
Removing formaldehyde	4%	Formaldehyde scavenger		60		
Washing	100	Water	35			
	0.5	Formic acid(1:10)		30	5.0	
Washing	300	Water	35	10		Drain
Retanning	100	Water	35			
	4.0	Derminol RA				
	3.0	Derminol NLM				
	2.0	Tergotan S				
	4.0	Tergotan TSP		60		
	5.0	Tanicor SCU		30		
	3.0	Tergotan EF		30		
	1.5	Dye		30		
	5.0	Granifin TA		60		
	1.0	Formic acid		10		
	1.0	Formic acid		45	3.5~3.6	Drain
Washing	300	Water	20	10		Drain
Dye	150	Water	45			
	1.5	Dye		30		
Fatliquor	4.0	Derminol SF				
	2.0	Derminol NLM				

	3.0	Dermafinish LB	60		
	1.0	Formic acid	30	3.3~3.4	Drain
Washing	300	Water	10		Horse up

3 Results and discussion

3.1 The content of amino group

The content of amino group in collagen peptide and aminated collagen peptide were shown in Tab.1.

Tab.1 The amidogen content of gelatin and modified gelatin

Samples	Content of amino group (%)
Collagen peptide	1.46
Aminated collagen peptide	3.77

As shown in TABLE I, the content of amino group in aminated collagen peptide increased from 1.46% to 3.77%. In theory, the content of carboxyl and amino group in 1mol collagen, with the relative molecular weight 100kDa, were 80mol and 110mol. Therefore, from the results of theoretical calculations, most carboxyl in collagen was transformed into the amino groups. The content of amino group had more than doubled. The reason may be when the reaction was finished; the unreacted ethylenediamine was not completely removed.

3.2 FT-IR analysis

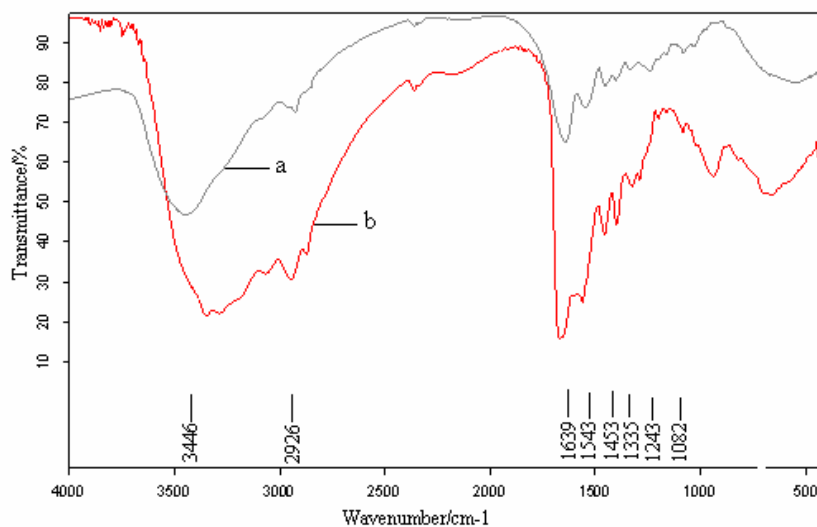


Fig.1 FT-IR spectrums of collagen peptide and aminated collagen peptide

In Fig.1, a and b were FT-IR spectrums of collagen peptide and aminated collagen peptide, respectively. The stretching vibration absorption peak of N-H in amino group and amide, appeared at 3446cm^{-1} , became strong. And the stretching vibration absorption peak of C=O in carboxyl, appeared at 1639cm^{-1} and 1543cm^{-1} , became weak. Moreover, at 2926cm^{-1} , the stretching vibration absorption peak of $-\text{CH}_2$ became obvious. These all indicated that the content of carboxyl in collagen peptide reduced and the amino group increased. Therefore, the reaction of carboxyl in collagen peptide with ethylenediamine occurred, and the amino group was successfully introduced.

3.3 Amino acid analysis

The amino acid components of collagen peptide and aminated collagen peptide were compared. The

results were shown in TABLE II.

TABLE II Analysis reports of amino acid

Number	Components	Collagen peptide	Aminated collagen peptide
		mass concentration /%	
1	Asp	7.083	3.58
2	Thr	1.562	0.907
3	Ser	2.796	1.386
4	Glu	8.76	4.947
5	Pro	10.94	5.511
6	Gly	22.18	8.899
7	Ala	6.085	3.323
8	Cys	0.121	0.086
9	Val	1.635	1.12
10	Met	1.156	0.525
11	Ile	1.526	0.534
12	Leu	2.586	1.394
13	Tyr	0.142	0.116
14	Phe	1.506	0.889
15	Lys	2.18	2.078
16	His	0.595	0.405
17	Arg	5.707	2.803

As shown in TABLE III, the collagen peptide had seventeen amino acids. The percentage of glycine in total amino acids was the most, which was accounted for 1/3. Moreover, the content of proline was more. After the collagen peptide was modified, the content of glycine reduced to 60% and other amino acids also reduced to 50%, which showed that the structure of collagen peptide was changed and amino groups were introduced.

3.4 Results of application test

The percentage of formaldehyde removal and the effect on leather properties were studied. The results were shown in Fig.2.

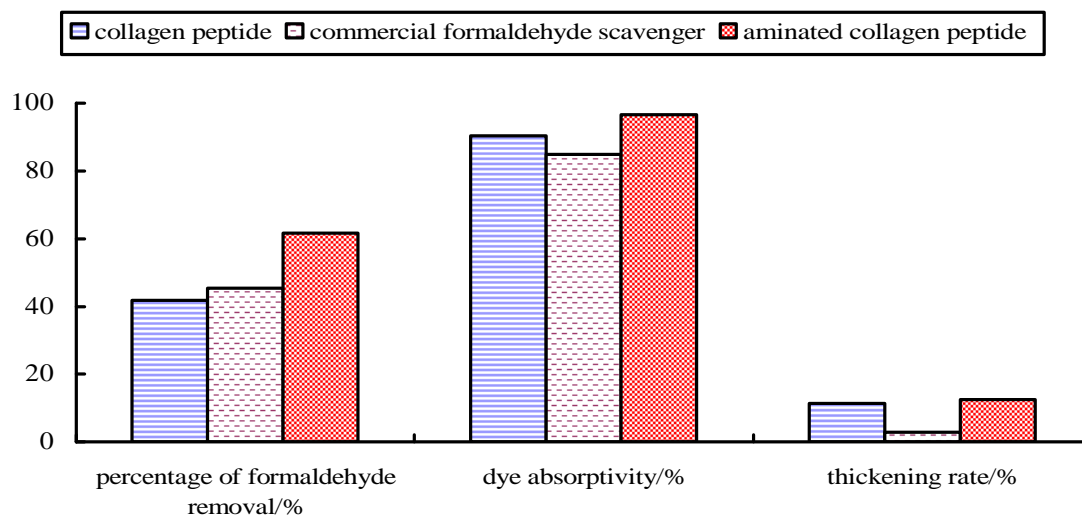


Fig.2 Comparison of formaldehyde-removal percentage and the effect on leather properties

In acid, alkaline or water medium, oxazolidine is unstable. It is easy to open the ring and produce aldehyde. So the leather tanned by oxazolidine will release free formaldehyde.^[10] As described in Fig.2, the percentage of formaldehyde removal of aminated collagen peptide reached to 61.6% which was better than that of collagen peptide. There were a large number of amino groups in collagen peptide and aminated collagen peptide and these amino groups bonded with leather formed ionic bond with dyestuff, so they fixed dyestuff and improve the dyeing effects as a kind of dyestuff carrier for leather. Because the main component in commercial formaldehyde scavenger was plant extracts, its dyeing property was not obvious. Moreover, the thickening rate of aminated collagen peptide was 12.5%. Therefore, modifying the collagen peptide and used as the formaldehyde scavenger has a good potential in achieving the innocent treatment of formaldehyde in leather.

4 Conclusions

A novel aminated collagen peptide was prepared with ethylenediamine as amidogen donator and carbodiimide as dehydrating agent. The content of amino group increased almost double. Moreover, the obtained aminated collagen peptide was characterized by FT-IR and amino acid analyzer. The results of amino acid analysis showed that aminated collagen peptide had seventeen amino acids. Compared with collagen peptide, the content of amino acids all were reduced to 50%, which suggested that the structure of collagen peptide was changed and amino groups were introduced.

The results of application test showed that the percentage of formaldehyde removal of aminated collagen peptide reached to 61.6% which was higher than that of collagen peptide and commercial formaldehyde scavenger. Furthermore, the thickening rate and dyeing of aminated collagen peptide were more obvious which were 12.5% and 96.6%, respectively.

Acknowledgments

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