Preparation of Leather Finishing Agent with Modified Collagen

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Abstract: The protein leather finishing agent was prepared with alkali extracted collagen hydrolyzate from the chromium-containing shavings. The monomers of acrylic acid series and nano-TiO_2 were used to modify the collagen, while the structure of the protein finishing agent was characterized by IR. The optimum technological conditions were determined by the orthogonal tests, which method could maintain low bromine number, good chemical and mechanical stability, and satisfactory repeatability of the product. The results showed that the protein finishing agent had antimicrobial performance, better dry and wet rubbing fastness and water resistance than conventional leather finishing agents.

Key words: chrome shavings; collagen; modification; leather finishing agent

1 Introduction

China is a large country of leather production which has rich leather material, cheap labor and advanced technology. China has become a centre of leather production and trade in the world from 90s of 20 century. The leather production increases a large amount of export foreign exchange, but also produces serious pollution at the same time. The pollution come from the discarded leather leftover bits and pieces is most difficult to harness in the world. The extraction of high grade collagen from the discarded leather leftover bits and pieces become the focus in the world in order to develop high profit products [1]. How to use the modified collagen extraction liquid prepares leather finishing agents is mainly discussed in this paper. The crafts of the collagen extraction are not included in this paper on which there are many reports.

The nanoscale TiO_2 is added in to the experimental products. The nano leather finishing agents has the properties of leather self-finishing and sterilizing due to its special effects of quantum size small size, surface, macroscopic quantum tunneling [2].

2 Experimental

2.1 Instruments and Agents

TiO_2, AR; leather leftover bits and pieces, Qiqihar Longcheng leather Co.Ld; E. coli and penicllium, Qiqihar University Bioscience Laboratory.

JJ-2 Enchanced electric mixer(Jiangshu Jintan Medical Instrument Factory); SCQ-300 ultrasonic

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generator (Shanghai Shengpu Ultrasonic instrument Factory)

2.2 Experiment

2.2.1 The Collagen Extraction Craft of Chrome Leather Leftover Bits and Pieces Hydrolysis

The 6%CaO relatively to weight of chrome leather leftover bits and pieces, and 6times water are inputted in a three-necked bottle. The chrome leather leftover bits and pieces and a litter peregal are input the solution and hydrolyzed for 6h at 60℃. The collagen hydrolysis liquid is gotten by suction. The solid content of the collagen liquid spared maintains over 15% by slowly vaporizing partial water in the solution at low temperature.

2.2.2 The preparation craft of hydrolysis collagen modified leather finishing agents

The mixture of the collagen hydrolysis liquid and TiO2 are dispersed in the ultrasonic generator for 30 min. The mixture then input into a three-necked bottle containing sodium dodecylbenzænesulfonate, stirred by the electric mixer to solve. 1/2potassium persulfate aqueous solution is input the solution when the temperature reach 50℃. Little monomer is dropwisely added the solution while continuously increasing the temperature, the spared monomer continuously is input at certain temperature after initiating and the initiator is replenished per 30 min. The reaction temperature is maintained at certain temperature for certain time after inputting monomer. The pH is adjusted to 6-7 when temperature decreasing to about 45℃ and the products are got by suction.

2.2.3 The product antibacterial effect experiment

Antibacterial effect experiment method: certain quantity of the product is input into the culture medium， and put on 12 plates separately. Then 3 plates are prepared for every bacteria suspension liquid rank of 10^2, 10^3, 10^4 and 10^5 times diluted solution in according to specified conditions to culture. Compared with the culture medium without the product, the antibacterial effects are observed on the different diluted solution and the different product concentration at the same rank. (E. coli, at 27℃, 24h; penicllium, at 35℃, 72h).

The live bacteria count and the calculation of sterilizing rate： The results are taken from the average value of 3 plate bacterial colony；If 2 plate are sure for the standard, he results are taken from the average value of them.

Calculation of sterilizing rate = [(the living bacterium colony count of the compared group - the living bacterium colony count of the experiment group)/ the living bacterium colony count of the compared group] ×100%.

2. 3 The product performance measurement

2.3.1 The Br value and solid content determination of the product

The determination method is given in reference 3.

2.3.2 The glue film water absorption determination of the product

The percentage of water absorption weight in the glue film after soaked in water for 24h.

2.4 The orthogonal experiment

The 5 factors and 4 levels orthogonal experiment is adopted for the modified collagen finishing agents. They are reaction temperature (70, 75, 80 and 85℃), monomer input time (30, 50, 70 and 90 min), initiator quantity （0.2%, 0.4%, 0.6% and 0.8%), collagen quantity (5%, 10%, 15% and 20%) and TiO_2 quantity (0.1‰, 0.3‰, 0.5‰ and 0.7‰), respectiv ely. The orthogonal experiment is based on L16 (4^5).

2.5 The structure characterization of the product

The structure characterization of the product is shown by IR spectrum.

3 Results and discussion

3.1 The orthogonal experiment results

3.1.1 The relationship between the solid content and 5 factors

The relationship between the solid content and 5 factors are as follows. The importance order of 5 factors is collagen quantity＞monomer input time＞reaction temperature＞initiator quantity＞TiO_2 quantity.

3.1.2 The relationship between The Br value and the 5 factors

The relationship between The Br value and the 5 factors are as follows. The importance order of 5 factors is monomer input time＞collagen quantity＞reaction temperature＞initiator quantity＞TiO_2 quantity.

3.1.3 The relationship between the water absorption and the 5 factors

The relationship between the water absorption and the 5 factors are as follows. The importance order of 5 factors is collagen quantity＞monomer input time＞TiO_2 quantity＞reaction temperature＞initiator quantity.

The optimum process is listed below through comprehensive analysis.

collagen quantity: 15%; monomer input time: 50min; reaction temperature: 85℃; TiO_2 quantity: 0.3‰; initiator quantity: 0.6%.

3.2 The factor analysis

32.1 The initiator quantity

When the initiator concentration increases, the radicals formation velocity increase and chain termination velocity also increase so that average molecular weight of the polymer decrease. But if initiator quantity is too low, the conversion rate decrease because initiators cannot react fully during limited time, as a result the tensile strength and tear strength of membrane decrease; If initiator quantity is too large, the reaction is too fast, difficulty to control and easy to form jelly leading to decreasing average molecular weigh and uneven average molecular weigh distribution that effect emulsion film-forming

properties. The optimum quantity of the initiator is 0.6% in this study.

3.2.2 The monomer input time

During a long monomer input time, the relative concentration the of the monomer becomes low as a result that the kinetics chain length, the degree of polymerization and the viscosity decreases because the kinetics chain length is proportional to the concentration the of the monomer: $\gamma = \frac{k_p}{2(fk_dk_t)^{1/2}} \bullet \frac{[M]}{[I]^{1/2}}$ 。

During a short monomer input time,， the kinetics chain length, the degree of polymerization and the viscosity increases and reaction is difficulty to control and easy to form jelly： 50min 。 The optimum monomer input time is 0.6% in this study.

3.2.3 The reaction temperature

If the reaction temperature increases, the polymerization velocity become fast, the average molecular weight of the polymer decrease and the branching-chain reactions grow in number. Whereas, the induction period is prolonged, the polymerization velocity becomes low and the monomer conversion rate becomes low. The control of the reaction temperature is in favour of the polymerization craft stability, the polymer molecular structure, average molecular weight and the average molecular weight distribution of the polymer. The optimum reaction temperature is 89℃ in this study.

3.2.4 TiO_2 quantity

When nanoscale TiO_2 quantity is low, there is a fine grafted effect and no sedimentation in the solution. When nanoscale TiO_2 quantity is high, there is a poor grafted effect and sedimentation in the solution perhaps due to nanoscale TiO_2 aggregation. The optimum TiO_2 quantity is 0.3‰in this study.

3.3 Antibacterial experiment

The antibacterial experiment of the products is performed under the optimum craft conditions.

The colony counts are beyond the scope in the two samples of the compared group as shown in table 2, the antibacterial effect decreases while the bacteria solution concentration decreases. The antibacterial effect increases while the product concentration increases as shown in Table 1 .But the difference between adjacent ratio samples is not obvious. The applicable scope of all the products is about 50%. The conclusion can be reached that the products have the effective inhibiting function on E.coli.

The living bacterium quantity of the compared group while the bacteria solution concentration increases as shown in Table 4， but there is no the living bacterium quantity of the experiment group, the bacteriostatios ratio is 100%. Although the products ratio of the experiment group is changed as shown in Table 3 there is no E.coli, the bacteriostatios ratio is 100% all along. The conclusion can be reached that the products have the some inhibiting function on penicllium.

Tab. 1 The antibacterial effects of the different concentrations on penicllium

Concentration (rank10^4)/ %	colony count	Bacteriostatios ratio/%
0	261	--
3	167	46.0
4	133	49.0
5	118	54.8

Tab. 2 The antibacterial effects of the different Dilute degrees on penicllium

Dilute degrees (cencentration5%)	the living bacterium colony count compared group	experiment group	Bacteriostatios ratio %
10^2	＞300	＞300	--
10^3	＞300	289	--
10^4	261	118	54.8
10^5	213	76	64.3

Tab.3 The antibacterial effects of the different Dilute degrees on E. coli

Dilute degrees/ (cencentration5%)	the living bacterium colony count compared group	experiment group	Bacteriostatic ratio/ %
10^2	235	0	100
10^3	192	0	100
10^4	147	0	100
10^5	63	0	100

Tab. 4 The antibacterial effects of the different concentrations on E. coli

Concentration (rank10^4)/ %	Colony count	Bacteriostatic ratio /%
0	147	--
3	0	100
4	0	100
5	0	100

3.4 The IR spectrum of the product

The two absorption peaks at wave number about 1550 $cm^{-1}$and 1450$cm^{-1}$are antisymmetry stretching and symmetry extension vibration absorption peaks of carboxylate group separately. The two absorption

peaks at wave number about 1740 cm^{-1} and 1210~1160cm^{-1} are stretching vibration absorption peak of C=O and antisymmetry stretching vibration absorption peak of -O- separately. The absorption peak at wave number about 2240 $cm^{-1}$is -C≡N stretching vibration absorption peak. The absorption peak at wave number about 1000 $cm^{-1}$is the stretching vibration absorption peak of C-O-Ti. It is not obvious.

The absorption peak at wave number about 3300 cm^{-1} is the stretching vibration absorption peak of N-H on peptides. The absorption peak at wave number about 1660 cm^{-1} is the stretching vibration absorption peak of C=O on peptides, The absorption peak at wave number about 1300~1260 cm^{-1} is the mixture stretching vibration absorption peak C-N on peptides and The bending vibration of N-H on peptides. There is an overlap between antisymmetry vibration absorption of $-COO^-$ and the bending vibration absorption of CNH on peptides at wave number about 1550 $cm^{-1}$where a split can be observed[4].

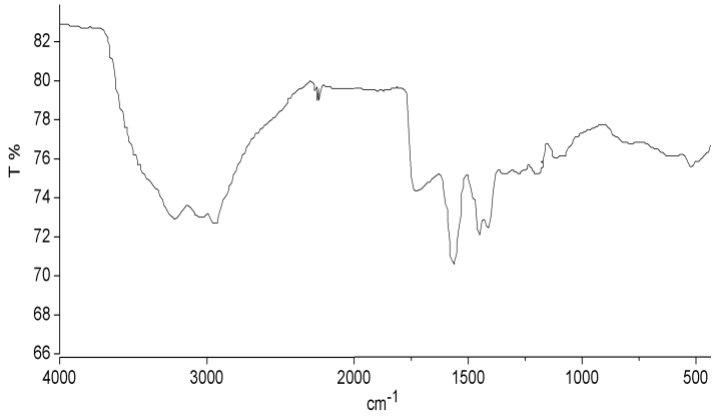

Fig. 1 The IR spectrum of the product

4 Conclusions

(1) The IR spectrum of the product indicates that the vinyl monomers, the collagen and TiO_2 Participate in the reaction.

(2) The antibacterial experiments show that the products have the effective inhibiting function on E.coli.

(3) The products have mechanical stability and chemical stabilities, Strong compatibility.

(4) The products are used as finishing agents which have strong adhesion on the leather, low water absorption, and good dry /wet rubbing performance. The surface of the leather after finishing is felt soft, leather-like and plump.

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