Study on the *In situ* Preparation of Nano-SiO_2/THPC Nano-composite Tanning Agent

Jianping Yang, Guoquan Zhou, Kaiqi Shi, Haoqi Gao, Lan Jiang, Shuangxi Shao*

Institute of Applied Chemistry, Ningbo University of Technology, Ningbo, 315016, P.R. China

Abstract: Nano-SiO_2 and SiO_2/collagen were prepared, through which to deduce the interaction of SiO_2 and collagen fibers of leather. The precursor containing nano-SiO_2 could be introduced into leather via penetration and diffusion of supporter. Then the nano-precursor in-situ produced the nano-SiO_2 particles under special pH value. The *In-situ* preparation and *in-situ* combination tanning process of nano-SiO_2/ Tetra(hydroxymethyl) phosphonium chloride (THPC) nano-composite were studied. The application of nano-SiO_2/THPC in tanning leather showed that the shrinkage temperature of the pickled sheep skin was about 88℃. The average diameter of nano-SiO_2 particles was determined by the Nanophox, and the structure of nano-SiO_2/collagen composites was measured by Fourier Transform Infrared Spectroscopy (FT-IR).

Keywords: nano-SiO_2; THPC; nano-composite; leather

1 Introduction

With the increasing concerns on environment and human health, the research of chrome-free tanning agent has become a hot point [1]. Nano-SiO_2 has recently draw attention owing to its uniform size, shape, and composition have wide application such as in industries related to the production of pigments, pharmaceuticals, ceramics, and catalysts[2]. Significant effort is focused on the ability to obtain the nano-composite tanning agent which derived from nano-SiO_2 and other organic compounds, but the shrinkage temperature of nano-SiO_2 tanned leather was lower than corresponding chromo-tannned leather[3].

Therefore our work focuses on the preparation of new nano-SiO_2 composite tanning agent. Recently, tetra-hydroxymethyl phosphonium chloride (THPC) has been considered as an important chrome-free tanning agent, but the shrinkage temperature of leather tanned solely by sample(pH4.0, THPC content being 72%) remain around 80℃[4]. It is the fact that THPC can link mostly with amino groups and less with hydroxyl and carboxyl groups and peptide bonds of collagen in leather[5]. However no attempts are reported on synthesis of nano-SiO_2/THPC nano-composite as tanning agent. In the present work, nano-SiO_2 was firstly prepared by sol-gel technique, tetraethoxysilane (TEOS) is a common precursor. In the first step, the hydrolysis of TEOS generates precursor species containing reactive silanol groups, condensation reactions involving the silanol groups yields a sol of SiO_2 particles dispersed in the solvent. The so called sol-gel transition, occurs by further condensation reaction of the silanol groups at the surface of SiO_2 particles (sol), forming a solid network containing solvent(gel)[6]. Then the collagen was employed to react with nano-SiO_2, the parameter of tanning system was discussed, through which we can deduce the effect process with nano-SiO_2 and leather. In this paper, the *in-situ* preparation and *in-situ* combination tanning process of nano-SiO_2/ Tetra(hydroxymethyl) phosphonium chloride (THPC) nanocomposite were studied.

2 Experiment

*Corresponding author. Phone: +86-(0)573-87080148. Email: nbssx@126.com

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2.1 Materials

Collagen powder (typeI) and tetraethoxysilane(TEOS) were purchased from Shanghai Chemical Reagent Company. TEOS (the boiling point is 168℃) was redistilled under reduced press and used freshly. THPC sample (pH 4.0, purity of 72%) was purchased from Zhejiang Zengxing Chemistry Company. Pickled sheep skin supplied by Ningbo Feifan Leather Company. All other chemicals were of analytic reagent grade. All solutions were prepared using deionized water.

2.2 Preparation of nano-SiO_2

The so-called Stöber method was used for synthesis of silica nanoparticles[7]. TEOS (4mL) was added to a 100mL round-bottom flask containing absolute ethanol (60mL), deionized water (80mL) and ammonium hydroxide (1.5mL), under constant stirring. The reaction was allowed to proceed for about 16h at 25℃. The final SiO_2 particles were washed with water three times by centrifugation-ultrasonic dispersion process.

2.3 In situ synthesis of nano-SiO_2/collagen composites

Similar experiment conditions as described above were employed to prepare the nano- SiO_2/collagen composites. In a typical synthesis, 1g collagen powder was added to mixture of ethanol (60mL), H_2O (80mL) and NH_3 (1.5mL), under moderate stirring followed by addition of TEOS (4mL). The mixture was then kept for 16h under constant stirring, at 25℃. The mixture was then centrifuged at 5000 rpm for 15min to separate the composites from supernatant. The outcome was thoroughly washed with deionized water and then dried at 50℃.

2.4 In situ tanned by nano-SiO_2/THPC nano-composites

Pickled sheep skin was used in the tanning experiment. In a procedure, the conical flask, charged with TEOS (2g), deionized water (10g), ethanol (5g), modified oil (10g), and NaCl (3g, as electrolyte), were immersed in water bath at 30℃. The reaction was kept at the same temperature for 5h and pH was adjusted to 9.0 using NH_3. Then 3 piece of picked sheep skin were depickled to the above mixture, at the same time THPC (percentage based on pickled sheep skin mass was 10%) was added to the conical flask. The pH of tanning system was controlled at 5.0 by dilute hydrochloric acid. Then the flask was vibrated for another 11h.

2.5 *Characterization*

Fourier Transform Infrared Spectrometer (FTIR) analysis was performer Nicolet 6700 (Nicolet Company, American). Differential Scanning Calorimeters analysis was carried out on DSC-200F3 (Netzsch Company, German). The diameter of particles was measured by Nanophox (SYMPATEC, German).

3 Results and discussion

3.1 Influence of NH_4OH on the average diameter of SiO_2

There is a set of experimental parameters that influence the final size of SiO_2. Our efforts have been focused on obtain well-defined SiO_2 with confined distribution of diameter. We have found that the average diameter of SiO_2 was affected by the concentration of NH_4OH greatly. Fig.1 shows the average diameter of SiO_2 which obtained with different concentration of NH_4OH. It is obviously that the average diameter of SiO_2 increased followed by the increasing of concentration of NH_4OH.

3.2 In situ synthesis of nano-SiO_2/collagen composites

Since hydroxyl groups on the surface of silica particles might accept or dissociate protons to come into being charged. Moreover, collagen amino groups with opposite charges can facilitate the combination with charged silica. As it can be seen in Fig.2, the isoelectric point (IEP) for SiO_2 particles is

3.2. It is clear that surface of SiO_2 particles are negatively charged when dispersed in pH 5.0 solution, while the collagen macromelecules show opposite positive charged in such solution due to the their relatively higher IEP of 6.5. The process of SiO_2 combined with collagen facilitated by electrostatic interactions, hydrogen bonding and complexation, between SiO_2 and collagen[8]. FTIR spectroscopy studied were carried out on the pure collagen and collagen/SiO_2 composites in Fig.3.It can be seen from Fig.3a, the absorption peak 3288 cm^{-1} is affected by stretching vibrations of hydroxyl groups from collagen. Bands around 1620 and 1547 cm^{-1} are due to the amide group stretching vibrations of collagen[9]. Collagen /SiO_2 composites in Fig.3b possess bands observed at 1092 cm^{-1} of strong intensity, as well as 792 cm^{-1} appeared in fingerprint region, the observed two bands above in according with typical asymmetric stretching of inter-tetrahedral oxygen atoms of silica[8]. The change of band at 1620 cm^{-1} indicated that the interaction between hydroxyl groups on the surface of SiO_2 and amide groups of collagen.

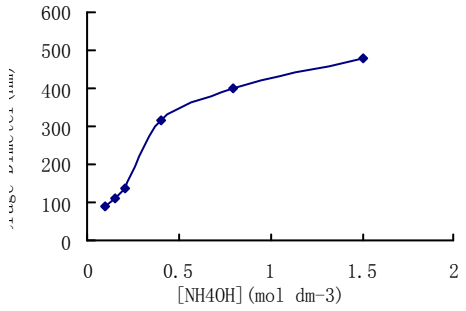

Fig.1 The influence of concentration of NH_4OH on the average diameter of SiO_2

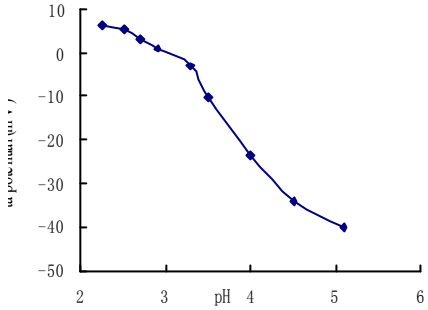

Fig.2 Variation of zeta potential with pH for SiO_2

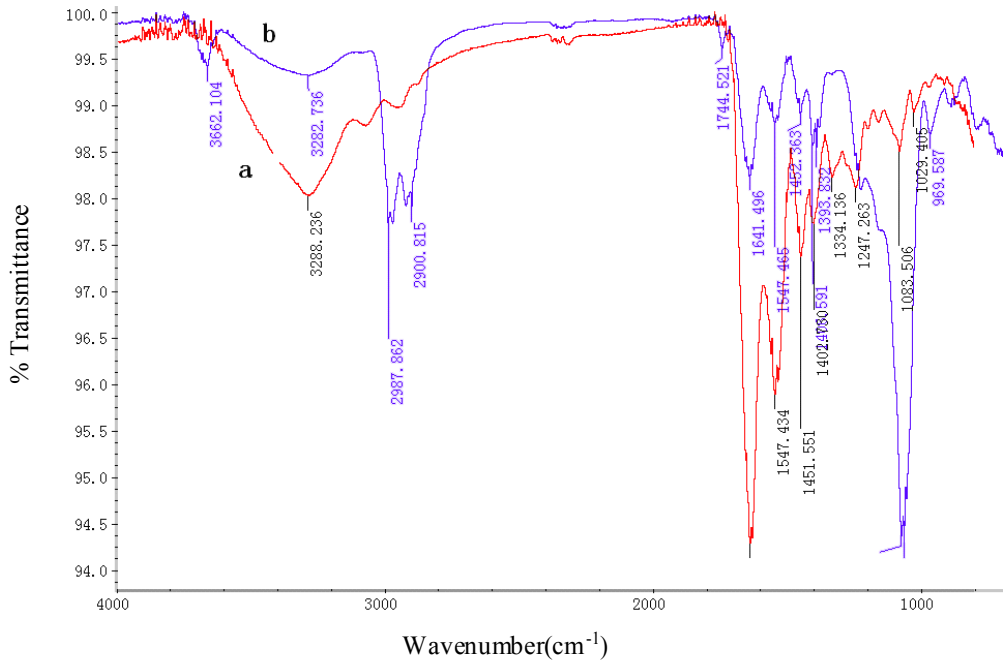

Fig.3 The spectra of pure collagen (a) and SiO_2/collagen composite (b)

3.3 In situ tanned by nano-SiO_2/THPC nano-composites

The denaturalization temperature (T_d) of tanned leather was greatly affected by the pH of the tanning solution. It is fact that the diameter of SiO_2 and interaction of nano-SiO_2/collagen are relation to the pH of

solution. Moreover the structure of THP salt is depended on the sample pH. When pH raised to 6.0, the decomposition of THPC to produce tri-hydroxymethyl phosphonium (TrPH) and tri-hydroxymethyl phosphine oxide (TrHPO). At pH 9.0, THPC will converted completely to TrPH and most TrPH is further oxidized into TrPHO[4]. So the sample pH was studied in order to get the higher T_d of tanned leather. Similar experiment conditions as described above were employed to *In situ* tanning the leather by nano-SiO_2/THPC tanning agent. The results of DSC are listed in Fig.4. It is clear that the T_d of tanned leather reached 88℃ at the pH 5.0, then the T_d of tanned leather dropped slowly by the increasing of pH. With the increasing of pH, the diameter of SiO_2 particles will increase and the electrostatic interaction between SiO_2 and collagen macromelecules will be decreased even conversed to repulsive action. Therefore the combination of amino groups of collagen and THPC as well as TrPH and TrHPO results in a large number of cross-links in collagen fibers which introduced the tanning process.

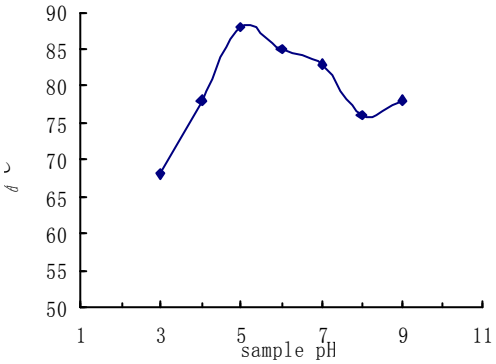

Fig.4 T_d of tanned leather with different pH

4 Conclusions

Nano-SiO_2 and SiO_2/collagen composites were studied. The diameter of SiO_2 was controlled by change the concentration of NH_3. FT-IR indicated that nano-SiO_2 was combination with collagen, which indicated that SiO_2 may be used as a new tanning agent. THPC was introduced to *in situ* preparation of nano-SiO_2/THPC nano-composite tanning agent. The T_d of leather tanned by nano-SiO_2/THPC nano-composite reached 88℃ on condition of pH 5.0.

References

[1] N.Nishad Fathima; M.Chandrabose; R.Aravindhan; J.Raghava Rao. J.AM. Lather. Chem. Assoc, 2005, 100: 273-281.

[2] K. Nozawa; H. Gailhanou; L. Raison; P. Panizza; H. Ushiki; et al. Langmuir, 2005, 21:1516-1523.

[3] H. J. Fan; L. LI; B. Shi; Q. He; B.Y. Peng. J.Am. Leather Chem. Assoc, 2005, 100: 22-28.

[4] S. X. Shao; K. Q. Shi; Y. Li; L. Jiang; C.A. Ma. Chinese Journal of Chemical Engineering, 2008, 16:446-450.

[5] Y. Li; Z. H. Shan; S. X. Shao; K. Q. Shi. J. Soc. Leather. Tech. Chem, 2006, 5:214-216.

[6] J. B. Ricardo; A. A. P. Paula; M. Ana; et al. Composites Science and Technology, 2008, 68:1088-1093.

[7] W. Stöber; A. Fink; E. Bohn. J. Colloid. Interf. Sci, 1968, 26: 62-69.

[8] X. Y. Ye; Y. M. Zhou; Y. Q. Sun; J. Chen; Z. Q. Wang. Applied Surface Science, 2008, 254: 5975-5980.

[9] K. Kojima; S. Iguchi; Y. Kajima; M. Yoshikuni. J.Appl. Polym. Sci, 1983, 28: 87.