Preparation and Characterisation of Sulfonated Calix[4]arene and Its Application in Chrome-free Tanning

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Abstract

Chrome tanning is the main tanning leather method. However, the absorption of chromium is incomplete and residues are present in waste liquors thus polluting the environment. Moreover, Cr^{3+} will oxidise into carcinogenic Cr^{6+} under certain conditions. Here we a present a novel chrome-free tannage. The calix[4]arene was synthesized using tert-butyl phenol and formaldehyde as raw materials. The calix[4]arene was then sulfonated with concentrated sulfuric acid. The structure was characterised by FTIR and 1HNMR. The sulfonated calix[4]arene was applied in goatskin tanning. The results showed that the sulfonated calix[4]arene had a tanning effect. The physical and mechanical properties of the tanned leather were better than those of conventional chrome-tanned leather.

摘要：铬鞣法是主要的皮革鞣制方法。鞣制过程中铬吸收有限，废液中残留大量铬，污染环境，且Cr^{3+}在一定条件下可被氧化成Cr^{6+}。因此提出一种新型的无铬鞣剂制备方法。以对叔丁基苯酚和甲醛为原料，制备杯[4]芳烃。通过浓硫酸磺化得到磺化杯[4]芳烃，采用红外光谱、核磁共振光谱表征其结构。将磺化杯[4]芳烃应用于山羊皮鞣制中。结果表明：磺化杯[4]芳烃具有一定的鞣制性能，且物理机械性能优于传统铬鞣革。

INTRODUCTION

Calixarenes are named as the third generation supramolecular hosts after crown ethers and cyclodextrins. They have hydrophobic cavities and can form a wide variety of host-guest type of inclusion complexes. Meanwhile, various kinds of interactions often happen, including hydrogen bonding, coordination, electrostatic interaction and so on. Therefore, calixarenes are widely used in chemical, biochemical and biomedical research. For instance,in chemical separation,[1] synthetic dendrimer,[2] as a chemical receptor for molecules.[3] However, the water solubility of calix[4]arene is poor, which limits its application range. In order to extend the potential usage of calix[4]arene and improve its water-solubility, the introduction of hydrophilic groups, such as amino,[4] carboxy,[l5] sulfonate,[6] *etc.,* is a common method.

Chrome tanning is the main tanning leather method. However, the absorption rate level of chromium in traditional chrome tanning is only 60%~70%, the residual concentration of Cr(III) in waste liquid is up to 3~8g/L(Cr_2O_3)[7] thus causing possible chromium pollution.[8] Moreover, Cr^{3+} can convert into carcinogenic Cr^{6+} under certain conditions. In order to reduce chromium pollution, leather workers have already developed many technologies and methods.[9] According to extensive reports, the methods could be divided into two types: one is reducing the chromium content by treating wastewater;[10] the other is decreasing chromium usage by recycling chromium tanning liquid or increasing the absorptivity of chromium.[11] These conventional methods are expensive, and present difficulties. Therefore, development of clean materials as a chrome-free tannage is a current hotspot. We synthesized sulfonated calix[4]arene and applied it in a goatskin tanning process. Sulfonated calix[4]arene can improve the shrinkage temperature. The properties of the tanned leather (tensile and tear strength) were better than those of chrome tanned leather. This work provided an efficient method to reduce chromium pollution and promote cleaner production in the leather industry.

EXPERIMENTAL PROCEDURES

Materials

P-tert-butylphenol and formaldehyde were purchased from Beijing Bailingwei Chemical Reagent Co. Ltd. The chemical reagents were commercially available as analytical grade and used as received.

Synthesis of sulfonated calix[4]arene

P-tert-butylphenol(7.5g), sodium hydroxide(0.08g) and formaldehyde (3.7mL) were mixed in a 250mL three-necked round-bottom flask fitted with magnetic stirrer. Then the mixture was heated to 110°C and was

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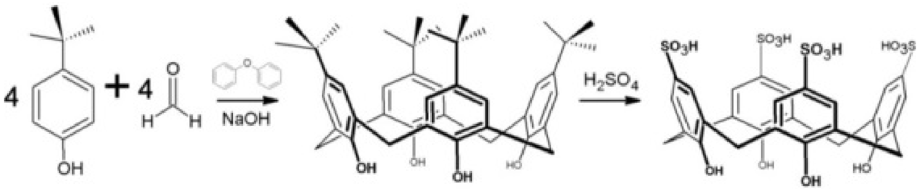

Scheme 1. Synthetic route to the sulfonated calix[4]arene.

kept for 2 hours followed by cooling. 30mL diphenyl ether was then added. The mixed solution was heated to 180°C and reacted for 2 hours. Then the mixed solution was cooled to room temperature and suction filtered. The precipitate was washed with ethyl acetate, acetic acid, and distilled water respectively and dried at room temperature. Calix[4]arene (2g) and concentrated sulfuric acid (12mL) were added. The liquid was heated to 90°C, and was kept thermostated for 4 hours, Then it was cooled to room temperature yielding sulfonated calix[4]arene solution, Scheme 1. To the solution, we added a saturated aqueous NaCl solution in an ice-water bath, this was stored in a refrigerator overnight generating a large number of bar-like grey crystals. Recrystallized by water-ethanol solution. The crystals would be characterised by FTIR and ^{1}HNMR.

Characterisation

FTIR spectra were recorded in the range 4,000-400cm^{-1} with a Vector-22 spectrometer (Bruker, Germany) using KBr pellets. ^{1}HNMR spectra were recorded on a Bruker AvanceIII (400MHz) spectrophotometer in DMSO-d6 and D_2O with TMS as an internal standard.

Application and detection method

Tanning was at a liquid ratio of 150% with 6% of salt, and 13% of sulfonated calix[4]arene. The permeate pH was 2.0, temperature 25°C, and drum time was 4 hours; the final pH after 'basification' was 5.0 for a total time of 16 hours. Each trial used approximately one quarter of a goatskin.

The Ts values of the tanned leather were determined using a shrinkage tester (MSW-YD4 Sunshine Electronic Research Institute of Shaanxi University of Science and Technology). Physical and mechanical properties were measured with a AI-3000 following the standard ISO 3376-1976. Atomic force microscopy(AFM) was used to investigate the roughness of the sample surface. The microstructure of the tanned leather was observed by scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

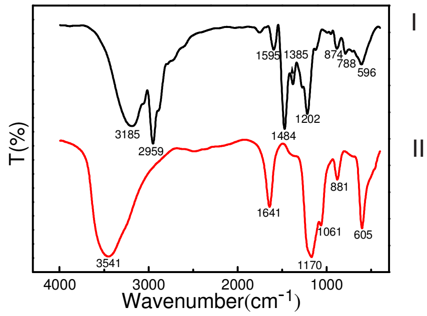

Figure 1. FTIR spectra of calix[4]arene (I) and sulfonated calix[4]arene (II) (KBr).

^{1}H-NMR spectra of calix[4]arene shows signals at 6.97 ppm (s, 8H, ArH), 3.47 ppm (s, 8H, -CH_2-), and 1.06 ppm (m, 36H,-$C(CH_3)_3$).

The appearance of two signals assigned to -OH and methylene protons of Ar-CH_2-Ar unit shows that calix[4]arene is in a ring-like structure.

Figure 1 (I) is the FTIR of calix[4]arene. The peaks at 3185cm^{-1} are assigned to -OH stretching vibrations of phenol and the peaks at 2959cm^{-1} are assigned to -CH_3 or -CH_2 stretching vibrations. At 1595cm^{-1} and 1484cm^{-1}, the peaks are assigned to the characteristic aromatic ring absorption band and the peaks at 874cm^{-1} are assigned to the isolated hydrogen from benzene ring. Figure 1 (II) is the FTIR spectrum of sulfonated calix[4]arene. The peaks at 3541cm^{-1} are assigned to -OH stretching vibrations. At 1170cm^{-1}, the peaks are assigned to S=O band and the peaks at 1061 and 605cm^{-1} are assigned to S-O-S stretching. It shows that the sulfonic acid group has been introduced into the calix[4]arene.

By treatment with sulfuric acid, sulfonated calix[4]arene in ^{1}HNMR spectrum (Fig 2) shows

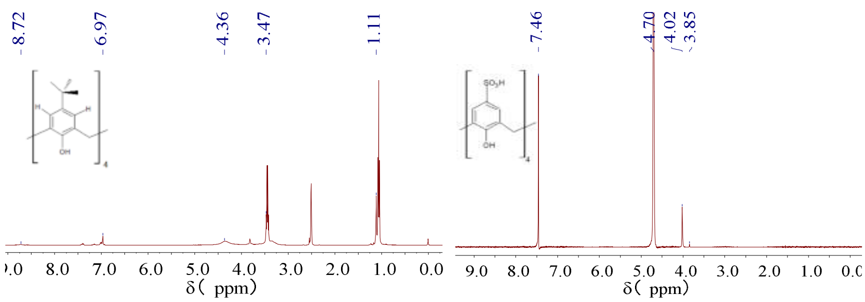

Figure 2. ^{1}H NMR spectra of calix[4]arene and sulfonated calix[4]arene(DMSO-d6 and D_2O, 400 MHZ).

resonance signals (δ=7.46ppm, s, 8H, -ArH; 4.02ppm, s, 8H, $-CH_2-$). Compared with the ^{1}HNMR spectra of calix[4]arene, the signal of 1.06ppm disappeared, which proved that the sulfonic acid was substituted for tert-butyl.

As shown in Figure 3, the Ts of leather tanned with sulfonated calix[4]arene was 65.1°C, which is lower than that of a conventional chrome tannnage. The major bond of conjugation was probably in the hydrogen bonding between the hydroxyl of sulfonated calix[4]arene and the amine of the collagen fibre, so the Ts of leather tanned sulfonated calix[4]arene was less than for conventional chrome tanning.

The tensile strength and tear strength of leather tanned with sulfonated calix[4]arene were respectively 34.2N/mm^2 and 90.65N/mm, which are better than those of conventional chrome tanning. The thickening ratio is also better than for conventional chrome tanning. The explanation for this is that sulfonated calix[4]arene enters into the collagen fibres, reacts with collagen amino by hydrogen bonding. At the same time, calixarene is a three-dimensional rigid structure and can play a supporting role in the fibres. The angle of weave of the collagen fibres was greaten, thus the leather showed higher physical and mechanical properties with the tensile strength and tear strength of the tanned leather increased.[12] The fullness of the crust improved.

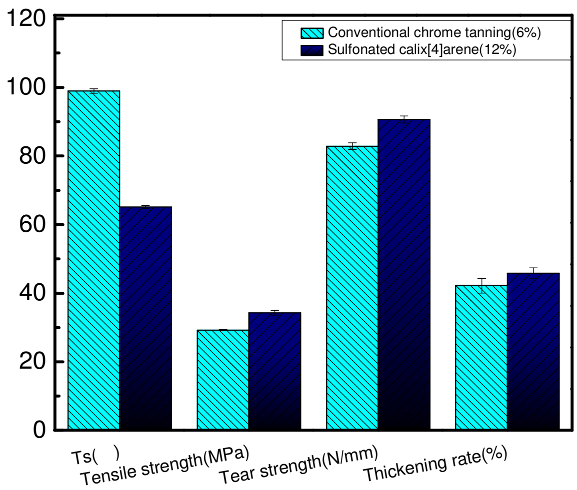

Figure 3. The properties of tanned leather.

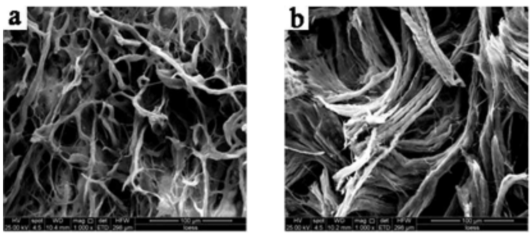

Figure 4. SEM photos of leather
a: sulfonated calix[4]arene; **b**: conventional chrome tanning).

The scanning electron photomicrographs of leather are shown in Figure 4. The figure shows that the fibre bundles of the samples tanned with sulfonated calix[4]arene seemed to be well dispersed compared with those of conventional chrome tanning, indicating that the sulfonated calix[4]arene can penetrate into the collagen fibres and form hydrogen bonds, which was beneficial to improving the collagen fibre bundle's dispersion and thus improving the leatherís fullness.

Figure 5 shows the roughness of the leather grain. Lighter areas corresponded to higher topography and darker areas correspond to lower topography. Additionally, according to the calculation results, the roughness of sample (a) and sample (b) was 44.03nm and 16.58nm. The leather tanned with sulfonated calix[4]arene showed a rougher texture than the conventional chrome-tanned leather sample. The explanation for this was that, sulfonated calix[4]arene has a three-dimensional rigid structure and when it entered the leather, it made the grain of the crust leather rough.

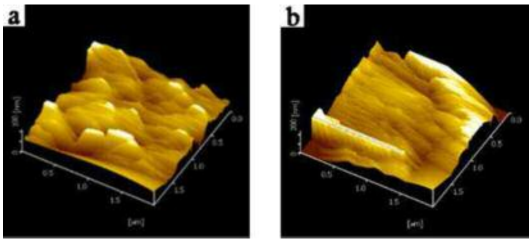

Figure 5. AFM photos of crust leather
a: sulfonated calix[4]arene; **b**: conventional chrome tanning.

CONCLUSIONS

In summary, sulfonated calix[4]arene was successfully synthesised and characterised by FTIR and ^{1}HNMR. The sulfonated calix[4]arene may improve the shrinkage temperature, physical and mechanical properties of leather. It has a potential for a chrome-free tannage, a new type of environmentally-friendly leather making process. As the tannage is free from aldehydes and chromium we consider it to be eco-friendly.

ACKNOWLEDGEMENTS

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