Superhydrophobic Modification of Collagen Fiber: A Potential Substitute for Tanning

by

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Abstract

Tanning is considered to be the crosslinking reaction between collagen fibers and tanning agents, and a majority of tanning reactions result in suppressed water absorption and enhanced hydrophobicity of leather. However, extensive use of tanning agents may bring a burden to the environment. Herein, to facilitate a sustainable leather manufacturing industry, we propose a revolutionary strategy of "tanning" without tanning agents. Based on this strategy, superhydrophobic collagen fibers (FAS-CFs) were fabricated through dehydration, followed by superhydrophobic modification. Dehydration aimed to eliminate the "sticky" effect of water on collagen fiber to obtain a dispersed hierarchical structure. Superhydrophobic modification not only dispersed and stabilized the fiber structures, but also protected the fiber dispersity from water immersion. Compared with chrome-tanned collagen fibers (Cr-CFs) and glutaraldehyde-tanned collagen fibers (G-CFs), FAS-CFs showed higher hydrophobicity, lower water absorption, and superior mechanical properties. Meanwhile, FAS-CFs exhibited a high thermal denaturation temperature of 92.5°C and retained their original shape after being heated to 100°C. Therefore, our proposed strategy is expected to be a potential substitute for conventional tanning and might contribute to cleaner and sustainable leather manufacturing.

Introduction

For hundreds of years raw hides and skins have been converted into leather through physical and chemical processes[1]and tanning is an indispensable step in the conversion. Tanning agents demonstrate their tanning ability by forming intramolecular and intermolecular multi-point cross-links among the collagen fiber networks.[2-4] The effect of the cross-linking of most tanning agents on raw hides is manifested in the increase of hydrothermal stability, and the decrease of swelling capacity and water absorption.[5,6] Specifically, different types of tanning agents, such as glutaraldehyde and chromium salts, accurately capture amino groups and carboxyl groups on rawhide, respectively, to form new cross-linked bonds, and block the original hydrophilic sites of collagen, thereby reducing the water take-up and swelling capacity of leather. Contrary to this general trend, vegetable tanning enhances both the hydrophilicity and water absorption of leather due to the richness of hydrophilic phenolic hydroxyls of vegetable tannins. Vegetable tannins can generate cross-links among collagen fibers through multi-point hydrogen bond to increase the thermal stability of leather. Compared with chrome-tanned leather, the leather tanned by vegetable tannins has lower shrinkage temperature (75-85°C) with tighter character. This may relate to the fact that chrome tanning reduces the water absorption of leather and therefore remarkably improves the dispersity of collagen fibers.[7]

Water plays a crucial role in the geometrical and thermal properties of collagen fibers, since it is abundantly presented among the collagen fibers of the rawhide by forming stable hydrogen bonds with hydrophilic groups involving carboxyl, amino, and hydroxyl groups.[5,8] During the drying process of raw hides, the evaporation of water with high surface tension brings about fiber entanglement, cohesion, and compaction, severely ruining the dispersed structure of the collagen fiber. Other than fiber dispersity, the thermal stability of collagen is also closely related to water. The thermal stability temperature of anhydrous untanned collagen is high up to 200°C, whereas the fully water-filled collagen is only thermally stable at temperatures lower than 60°C[6]. Olle et al. developed a dehydration process for bovine/ovine hide with acetone to relieve the interference of water, and the dehydrated hides showed a porous fiber network and satisfactory organoleptic properties, similar to tanned leather.[9,10] Although the dehydrated hides are leather-like, in essence, they are not leathers because they are not waterproof.[6] Collagen fibers of the dehydrated hide will swell and recover to an adhesive state after water-absorbing, and the leather-like effect vanishes.

The most tanning methods, such as chrome tanning and aldehyde tanning, can weaken the hydration of collagen fibers and improve the thermal stability and mechanical properties of the leather. But the relation between these tanning methods and the surface wettability of leathers has seldom been investigated. We found that chrome-tanned leather with significant hydrophobicity presented superior thermal stability and mechanical properties compared with those of aldehyde-tanned leather and vegetable-tanned leather, leaving us contemplating the contribution of surficial wettability in leather properties. He et al.[11] reported that the hydrophobicity of chrome-tanned leather increased with the increase in chrome dosage, which may be attributed to the displacement of bound water by Cr (III) ions.[12] Zhu et al.[13] reported that the water contact angle (WCA)

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of leather tanned with 2% chrome tanning agent was 108.1°. The outstanding comprehensive properties of chrome-tanned leather may stem from the excellent ability of Cr (III) to weaken hydration and improve hydrophobicity. To date, chrome tanning still occupies the predominant position in tanning technology due to the superior comprehensive properties of chrome-tanned leather.[14,15] However, potential chrome pollution restricts the sustainable development of the leather industry.[16] Hence, it is of significance and urgency to propose a novel and sustainable process for leather tanning.

Based on the aforementioned analyses, we proposed a novel strategy for leather manufacturing without the use of conventional tanning agents. From the perspective of water removal and hydrophobicity construction, the 'tanning agent-free strategy' was designed to manufacture leather by eliminating hydration and stabilizing fiber dispersity. Focusing on the two characteristics, "tanning" is supposed to be replaced by dehydration followed by superhydrophobic modification of a pelt. In this study, collagen fibers were used as the model of pelt to explore the feasibility of this strategy so as to prevent the influence of penetration of hydrophobic material in pelt hide on this theoretical exploration. Ethanol was used to remove the water among collagen fibers to gain hierarchical structures. Superhydrophobic modification further strengthened the dispersibility and stability of the fiber and protected the porous and dispersed hierarchical structure from water interference. The hydrophobic properties, fiber dispersity, thermal stability, and mechanical properties of the superhydrophobic collagen fiber were evaluated, and conventional tanned collagen fibers were used for comparison.

Experimental

Materials

Pickled pelt of cow hide was provided by a local tannery in China. 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (FAS, 96 wt%) was purchased from Aladdin Co., Ltd. (Shanghai, China). Ethanol (95 wt%), isopropanol (99.7 wt%), glutaraldehyde (50 wt%), $Cr_2(SO_4)_3{\cdot}6H_2O$, $NaHCO_3$, HCOOH, and all of the other chemicals were purchased from Kelong Co., Ltd. (Chengdu, China).

Fabrication of collagen fibers (CFs)

The pickled cow hide pelt was deacidified and fully washed. Then, a piece of pelt was soaked into 150 wt% ethanol and stirred for 120 min. This operation was repeated for sixfold to remove water. The dehydrated pelt was dried at 35°C and crushed and sieved with a super centrifugal grinder (Retsch, zm200) to obtain collagen fibers (CFs) of 40 mesh.

Fabrication of superhydrophobic collagen fibers (FAS-CFs)

FAS-CFs were prepared by immersing 5 g of CFs into 50 mL of FAS/isopropanol solution (1:100, 3:100, 5:100, 7:100, w/v) for 24 h, followed by filtering, heating at 105°C for 4 h, ethanol washing, and drying at 105°C for 2 h.

Fabrication of Cr (III) cross-linked collagen fibers (Cr-CFs)

Five grams of CFs were immersed in 50 mL deionized water for 12 h. Subsequently, 50 mL of chromium sulfate solution (containing 0.5 g of Cr_2O_3) was added, and the pH was adjusted to 3.0 with 10 wt% formic acid. The solution was stirred at 25°C for 4 h. Then, the crosslinking system was stirred for 14 h at 40°C and stopped for 4 h at 25°C after basification to pH 4.0 with 10 wt% $NaHCO_3$ solution. The cross-linked CFs were washed with deionized water for three times, and dried at 50°C for 12 h to obtain Cr-CFs.

Fabrication of glutaraldehyde cross-linked collagen fibers (G-CFs)

Five grams of CFs were soaked into 0.4 wt% glutaraldehyde solution. The crosslinking reaction was first carried out at 25°C for 4 h and heated to 35°C for 4 h after the pH was adjusted to 7.0 with 10 wt% $NaHCO_3$ solution. The products were washed with deionized water for three times, and dried at 50°C for 12 h to obtain G-CFs.

Characterization of CFs and FAS-CFs

The surface structures of CFs and FAS-CFs were detected by using a field-emission scanning electron microscope (FESEM, Nova Nano SEM 450, FEI, USA) with an acceleration voltage of 15 kV. The element composition of FAS-CFs was obtained with a coupled energy dispersive X-ray spectrometer (EDS, Ultim Max, Oxford Instruments, U.K.). Fourier transform infrared spectrometer (FT-IR, NICOLET iS10, Thermo Fisher Scientific, USA) was used to confirm the functional groups of CFs and FAS-CFs. X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Escalab250Xi, USA) was used to further identify the chemical composition of CFs and FAS-CFs.

Measurements of surface wettability of CFs, G-CFs, Cr-CFs, and FAS-CFs

Surface wettability of CFs, G-CFs, Cr-CFs, and FAS-CFs was measured by a contact angle goniometer (Krüss, DSA30, Germany) with a deionized water droplet of 5μL under ambient condition. The fiber samples (0.1 g) were glued on the glass slide with a double-sided adhesive, and then the fiber samples were compacted by a weight of 100 g to ensure that the fibers were evenly distributed on the surface of the glass slide to facilitate the observation of WCA. The WCA result was the average of data from five different points on each sample surface. Besides, the distribution of water droplets on the surface of FAS-CFs was also observed under the Super Depth of Field 3D Microscope System (VHX-5000, KEYENCE, Japan).

Measurements of hydrophobic durability of FAS-CFs

One group of FAS-CFs were immersed in water for 24 h and then dried at 50°C. One group of FAS-CFs were immersed in water for 24 h without drying. One group of FAS-CFs were irradiated by UV light for 6, 12, 24 and 48 h. One group of FAS-CFs were immersed in the water with different pH values (2, 4, 6, 8, 10, 12) for 12 h and then dried at 50°C. The other two groups were immersed in ethanol and isopropanol for 1, 6, 12 and 24 h, respectively. Then WCA measurements were carried out as described above.

Measurements of water absorption of CFs, G-CFs, Cr-CFs, and FAS-CFs

Two grams of CFs, G-CFs, Cr-CFs, and FAS-CFs were immersed in 20 mL of deionized water for 24 h, separately. The water absorption rate of the samples was calculated by determining the mass change before and after the water immersion. Measurements were conducted in triplicate. In addition, the samples after water immersion were dried at 50°C for 5 h, and their microstructures were observed by FESEM under 15 kV accelerating voltage.

Measurements of the thermal stability

CFs, G-CFs, Cr-CFs, and FAS-CFs were first kept under 65% RH for 48 h at 30°C. Then, the thermal stability of which was determined using a differential scanning calorimetry (DSC, PerkinElmer, DSC8000, USA) from 30°C to 200°C with a heating rate of 5°C/min under nitrogen atmosphere. In addition, shrinkage behaviors of CFs, G-CFs, Cr-CFs, and FAS-CFs were measured. A single fiber bundle with a length of 2.5–3.5 mm was placed in the recess of a single-concave slide, covered with a cover glass, and heated from 20°C to 200°C with a heating rate of 1°C/min on a benchtop temperature controller (Shanghai Weitu Instrument Technology Development Co., Ltd.). The changes in fiber morphology and length were monitored and recorded by a stereomicroscope (Leica, M205 C, Germany) with a frequency of 10°C interval.

Measurements of the mechanical properties

The length and diameter of single fiber bundles (CFs, G-CFs, Cr-CFs, and FAS-CFs) were recorded with a stereomicroscope to calculate the mechanical properties. Then, two ends of the single fiber bundle were attached to a piece of paper by epoxy resin. The tensile strength of the single fiber bundle was determined with an electronic single fiber strength tester (Model LLY-06B, Laizhou Electronic Instrument Co., Ltd., Laizhou, China, 0.02% of sensitivity) in accordance with the standard method (GB/T 14337). The test was carried out at 25°C and 65% RH with 21 replicate measurements for each sample. The clamping gap was set to 30 mm, and the stretching speed was 5 mm/min.

Results and Discussion

"Tanning agent-free strategy" for leather manufacturing

Collagen fibers are hydrophilic in nature, and water can bind with functional groups on the polypeptide chains through hydrogen bonds and even form hydrogen-bond networks (Figure 1, left panel). However, the swelling behavior of CFs disappeared after ethanol dehydration, and they presented the porous and dispersed structures (Figure 1, middle panel) after drying, laying the foundation for superhydrophobic modification. Superhydrophobic modification aimed at manufacturing leather without tanning agents through eliminating water absorption, stabilizing, and protecting the hierarchical structure of collagen fibers. FAS with low surface energy was supposed to be hydrolyzed by the remaining moisture of CFs to form free silanol groups (–SiOH)[17]and covalently bonds with hydroxyl groups on CFs under heating,[18,19] depleting the remained water and blocking the hydrophilic sites. The low surface energy fluorine-containing long chain at the other end could endow FAS-CFs with superhydrophobicity to resist water infiltration (Figure 1, right panel).

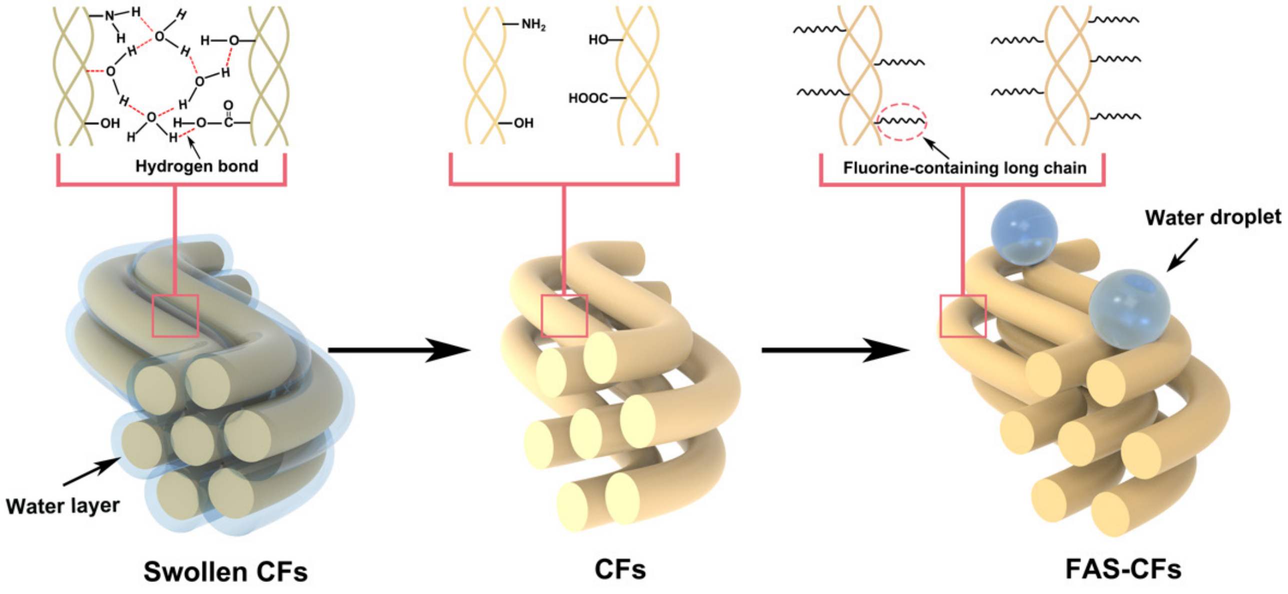

Figure 1. Schematic illustration of the fabrication of FAS-CFs

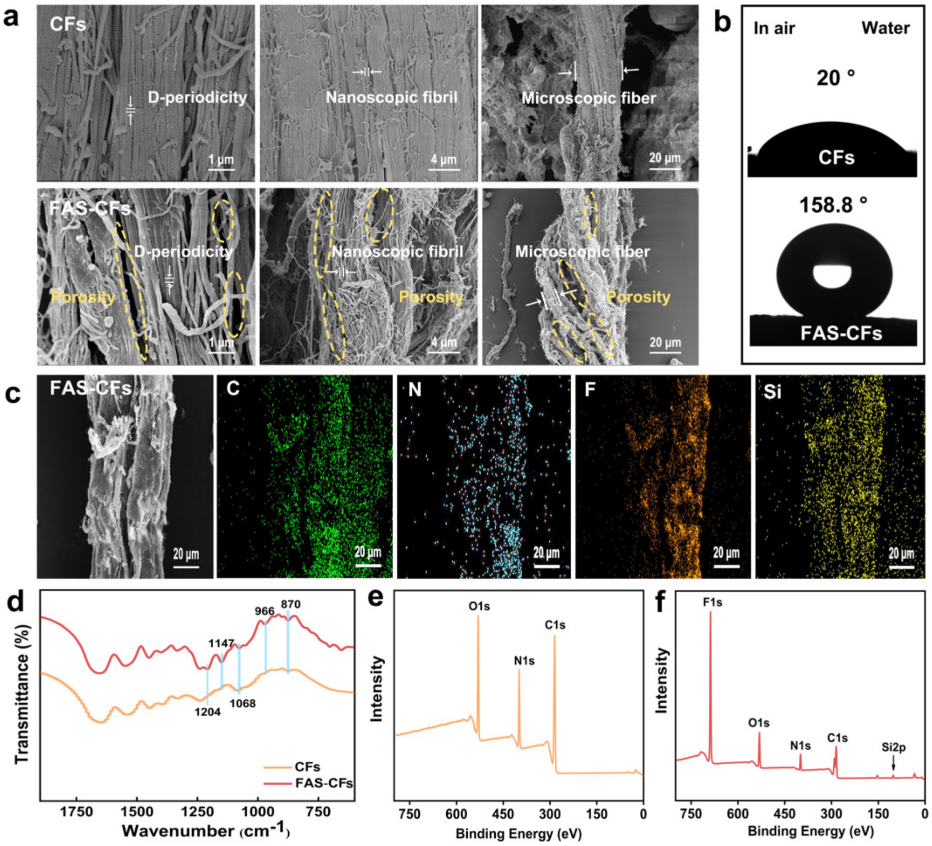

Figure 2. SEM images of CFs and FAS-CFs **(a)**, WCA of CFs and FAS-CFs in the air **(b)**, EDS mapping of FAS-CFs **(c)**, FT-IR spectra of CFs and FAS-CFs **(d)**, and XPS survey of CFs **(e)** and FAS-CFs **(f)**.

Characterization of CFs and FAS-CFs

After ethanol dehydration for six times, CFs with a water content of 3.86% maintained a hierarchical fibrous structure from nanofiber to microfiber and intertwined fiber bundles[20] (Figure 2a). The nanofibrils that are composed of parallel and staggered type I collagen molecules showed a distinct axial D-periodicity of approximate 67 nm.[21] The hierarchically self-assembled micro/nanostructure of CFs contributes to supplying natural and essential roughness for superhydrophobic modification.[22] After treatment by FAS, the hierarchical fibrous structures (Figure 2a) of FAS-CFs remained intact, including D-periodicity, nanofiber, microfiber, and fiber bundles. Significantly different from the CFs, more prominent porosity with different sizes appeared among nanofibers, microfibers, and fiber bundles, indicating that superhydrophobic modification facilitates fiber dispersity. From the water contact angle measurement result (Figure 2b), the instantaneous WCA of CFs surface was approximate 20°, indicating hydrophilicity of CFs. FAS-CFs was functionalized as superhydrophobic material because its WCA reached up to 158.8°.[23,24] To prove that CFs were successfully modified by FAS, EDS and FT-IR analyses of FAS-CFs were then performed to give evidence. As shown in Figure 2c, F and Si are evenly distributed on the fiber surfaces of FAS-CFs and display the same trend as those of C and N, proving the successful loading of FAS. Compared with the XPS spectrum of CFs (Figure 2e), F and Si peaks appear in the full spectrum of FAS-CFs,[24,25] and the F peak is significantly higher than the C, N, and O peaks (Figure 2f), indicating that FAS has formed a dense low-surficial-energy film on the surface of fibers, which could resist the water association with collagen fibers. The FT-IR spectra of FAS-CFs and CFs were illustrated in Figure 2d. As compared to CFs, FAS-CFs exhibits new peaks at 870, 966, and 1068 cm^{-1}, which could be assigned to the stretching vibrations of Si–C, Si–O–Si, and Si–O–C,[26,27] respectively. This result suggested that the silanol groups have reacted with the hydroxyl groups on CFs and converted into Si–O–C covalent bonds. The peaks at 1204 and 1147 $cm^{-1}$are ascribed to the stretching vibration of C–F,[24,28] which belongs to FAS. The above-mentioned results indicated that CFs are successfully chemically modified by FAS, and the superhydrophobic modification contributes to excellent fiber dispersity.

Effect of fluorine content on hydrophobicity of FAS-CFs

Figure 3a shows that the WCAs of FAS-CFs increased from 142.4° to 154.7° with the increase of FAS content from 1% to 7%, indicating enhanced hydrophobicity. The water absorption of FAS-CFs sharply decreased from 219% to 75.7% (Figure 3b), suggesting that increasing hydrophobicity resulted in significant reduction in water absorption. To further explore the hydrophobicity of FAS-CFs, the distribution of water droplets on the surface of FAS-CFs was also observed. The water droplets distributed on the fiber surface changed from a flat shape to a more pronounced spherical shape as the FAS content

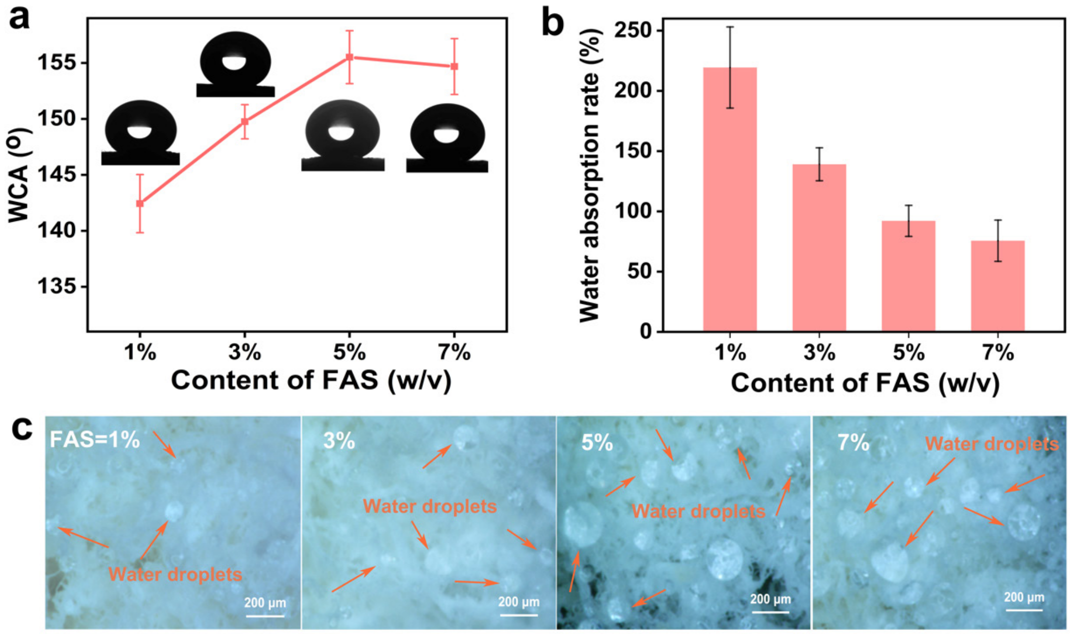

Figure 3. The influence of FAS content on WCA **(a)** and water absorption rate **(b)** of FAS-CFs

increased (Figure 3c). All the results above demonstrated that the increase in FAS content led to the enhancement of hydrophobicity. However, when FAS content was higher than 5%, the hydrophobicity of FAS-CFs was no longer enhanced greatly. In general, FAS-CFs fabricated by 5% of FAS exhibited outstanding superhydrophobicity (WCA >150°) and low water absorption.

Hydrophobic durability of FAS-CFs

Based on the results above, FAS-CFs fabricated with 5% FAS were selected for further investigation. The hydrophobic durability of FAS-CFs after treatment in different environments was investigated. WCAs of FAS-CFs showed a slight decrease to 150.1° under UV irradiation for 48 h (Figure 4a). As shown in Figure 4b, FAS-CFs still maintained outstanding superhydrophobic properties after immersion in the water with a wide pH range from 4 to 12 (Figure 4b). When FAS-CFs were soaked into ethanol and isopropanol for 24 h, the value of WCA decreased but still remained higher than 145° (Figure 4c and 4d). The above-mentioned results suggested that the hydrophobicity was stable enough to protect FAS-CFs against harsh environments.

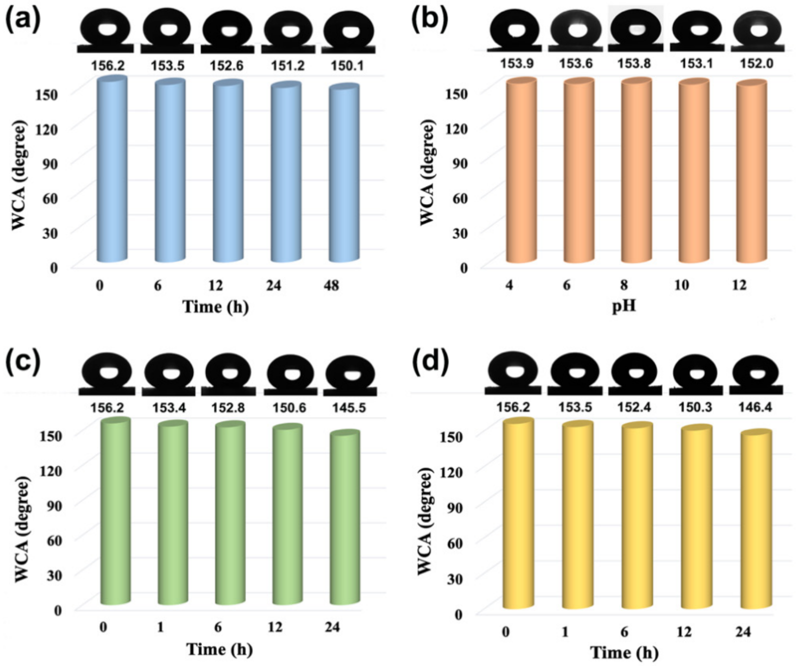

Figure 4. WCAs of FAS-CFs after treatment in different environments: **(a)** after irradiation by UV light, **(b)** after immersion in water with different pH values for 12 h, **(c)** after immersion in ethanol, **(d)** after immersion in isopropanol.

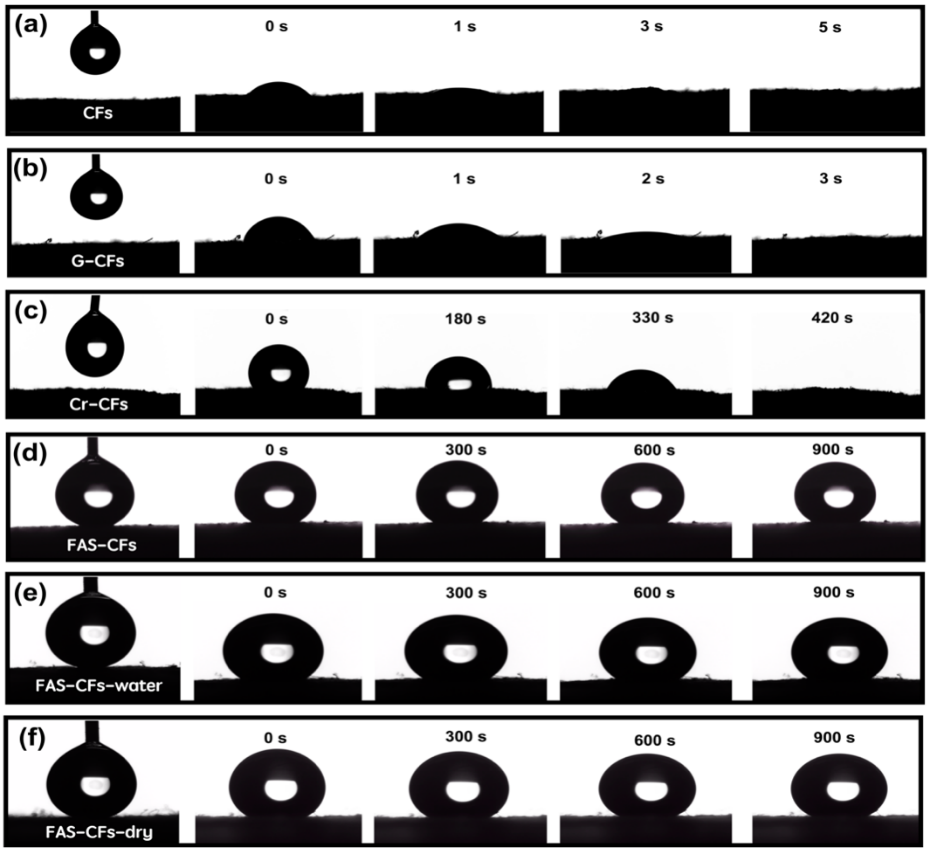

Figure 5. Shapes of a water droplet (5μL) on CFs **(a)**, G-CFs **(b)**, Cr-CFs **(c)**, FAS-CFs **(d)**, FAS-CFs after water immersion for 24 h **(e)**, and FAS-CFs after water immersion for 24 h and then dryingat 50°C for 5 h **(f)** at different testing moments.

Hydrophobicity of CFs, G-CFs, Cr-CFs, and FAS-CFs

The surface wettability of water on CFs, G-CFs, Cr-CFs, and FAS-CFs was evaluated by recording WCAs at different testing moments. As shown in Figure 5a–b, the water droplet rapidly spread out on the surface of CFs and G-CFs within 5 s and 3 s, respectively, revealing their hydrophilicity and poor water resistance. CFs exhibited poor hydrophobicity due to the fact that it contains a lot of hydrophilic groups. For G-CFs, glutaraldehyde only reacted with amino groups of CFs, and a lot of hydroxyl and carboxyl groups still remained. Therefore, G-CFs maintained hydrophilicity to some extent. Compared with CFs and G-CFs, Cr-CFs showed better hydrophobicity. It took 420 s for water droplets to penetrate into Cr-CFs (Figure 5c), which was consistent with the results stated in the previous report.[13] The hydrophobicity of chrome-tanned leather should be attributed to the strong coordination reaction of Cr (III) with carboxyl groups while having reactivity with amino and hydroxyl groups, which effectively reduced the number of hydrophilic functional groups. Unsurprisingly, WCA on the surface of FAS-CFs could be stabilized at around 155° for at least 900 s (Figure 5d). After immersion in water for 24 h, FAS-CFs still showed satisfactory hydrophobicity with the WCA of 149° within 900 s (Figure 5e). The WCA restored to 154° (Figure 5f) after the water immersed FAS-CFs were dried again. In addition, the water absorption rates of FAS-CFs and Cr-CFs were lower than that of CFs and G-CFs. Among them, the superhydrophobic FAS-CFs exhibited the lowest water absorption rate (92%) (Figure 6). These results suggested higher superhydrophobicity of FAS-CFs compared to CFs, G-CFs and Cr-CFs.

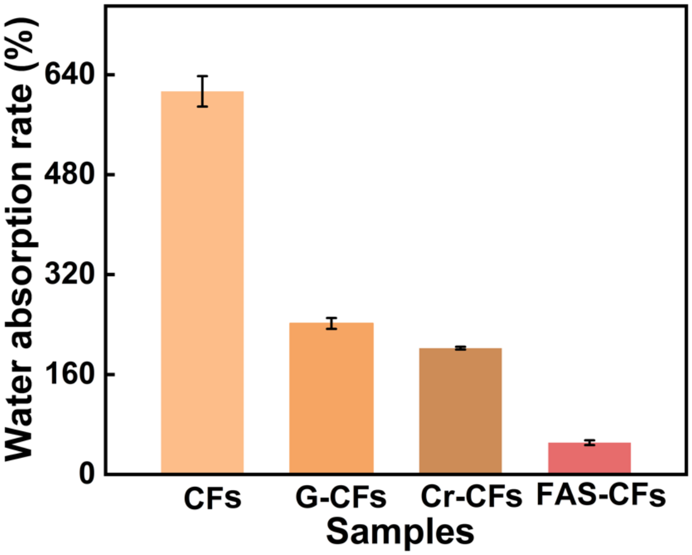

Figure 6. Water absorption rate of CFs, G-CFs, Cr-CFs, and FAS-CFs

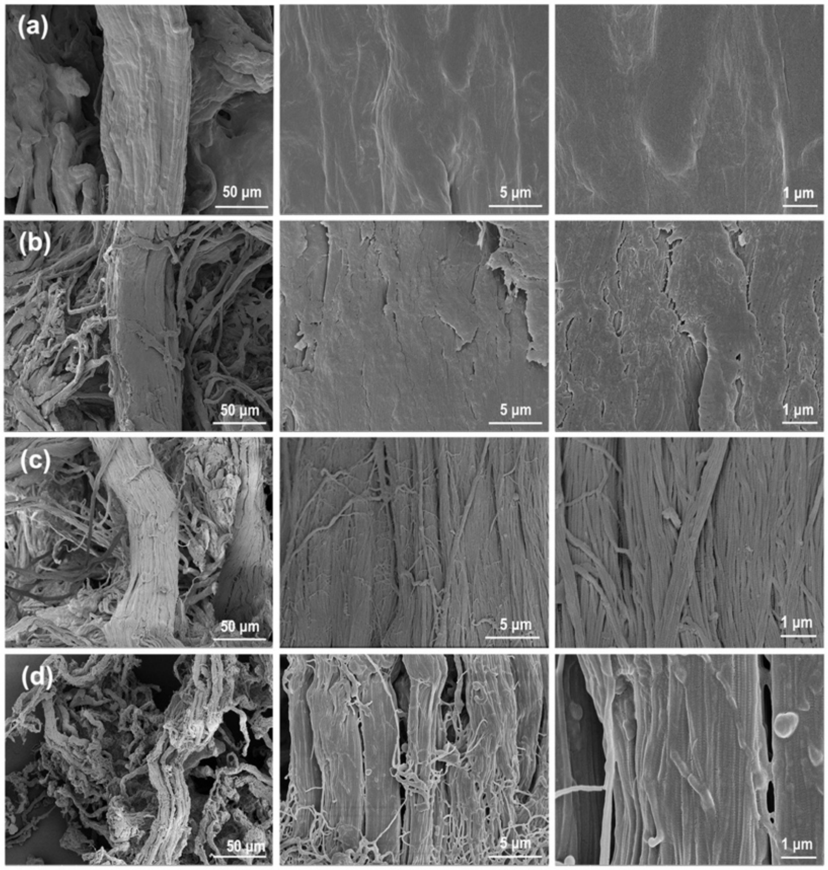

Figure 7. The SEM images of CFs (**a**), G-CFs (**b**), Cr-CFs (**c**), and FAS-CFs (**d**) after soaking in water for 24 h and then drying.

Afterward, the morphology of CFs, G-CFs, Cr-CFs, and FAS-CFs following water immersion and drying was analyzed to evaluate the durability of fiber dispersion. After soaking in water for 24 h and then drying, the initially dispersed multilayer structures of CFs and G-CFs were completely eliminated. During the drying process, the evaporation of water with high surface tension brought about the cohesion of collagen fibers, resulting in fiber entanglement and a smooth surface without hierarchical structures. Specifically, the D-period on the fibrils vanished, and nanofibers and microfibers cohered into a flat and smooth plane (Figure 7a and b). The destruction of the dispersed structures of CFs and G-CFs after water immersion may be attributed to their poor hydrophobicity. On the contrary, the porous and dispersed hierarchical structure of FAS-CFs was fully retained after water immersion and drying (Figure 7d), which is similar to Cr-CFs (Figure 7c). These phenomena confirmed that superhydrophobic modification can effectively stabilize and protect the fiber dispersibility of FAS-CFs. The significant difference in the morphology of FAS-CFs was closely related to its low surface energy. The covalent bonding of FAS with collagen fibers reduced the interfacial energy of FAS-CFs, resulting in a decreased surface affinity with water, so that the hierarchical fibrous structure of FAS-CFs remained intact. In a word, superhydrophobic modification of collagen fibers brings about nearly the same effect as conventional tanning in terms of weakening the hydration of collagen fibers and improving fiber dispersity. The performance of superhydrophobic modification is superior to glutaraldehyde tanning and comparable to chrome tanning.

Thermal stability and mechanical properties of CFs, G-CFs, Cr-CFs, and FAS-CFs

The thermal stability and mechanical properties of FAS-CFs were investigated in comparison with conventional tanned collagen fibers (G-CFs, Cr-CFs). As shown in DSC plots (Figure 8a), the onset and peak denaturation temperatures of FAS-CFs were remarkably higher than those of CFs and G-CFs and only slightly lower than Cr-CFs. Compared with CFs and G-CFs, the endothermic peak area of FAS-CFs was enlarged, suggesting that the enthalpy change of FAS-CFs denaturation increased. To further evaluate the heat resistance of FAS-CFs, their shrinkage behaviors were investigated. Specifically, a stereomicroscope was used to capture the changes in the length of fiber with increasing temperature (Figure 8b). The length of FAS-CFs remained unchanged at 100°C, while CFs, G-CFs, and Cr-CFs showed a slight shrinkage to 98.3%–99.1%. In Figure 8c–f, a significant plateau was found in the initial stage of the shrinkage curve of FAS-CFs, which was much broader than those of CFs, G-CFs, and Cr-CFs, indicating the outstanding thermal stability

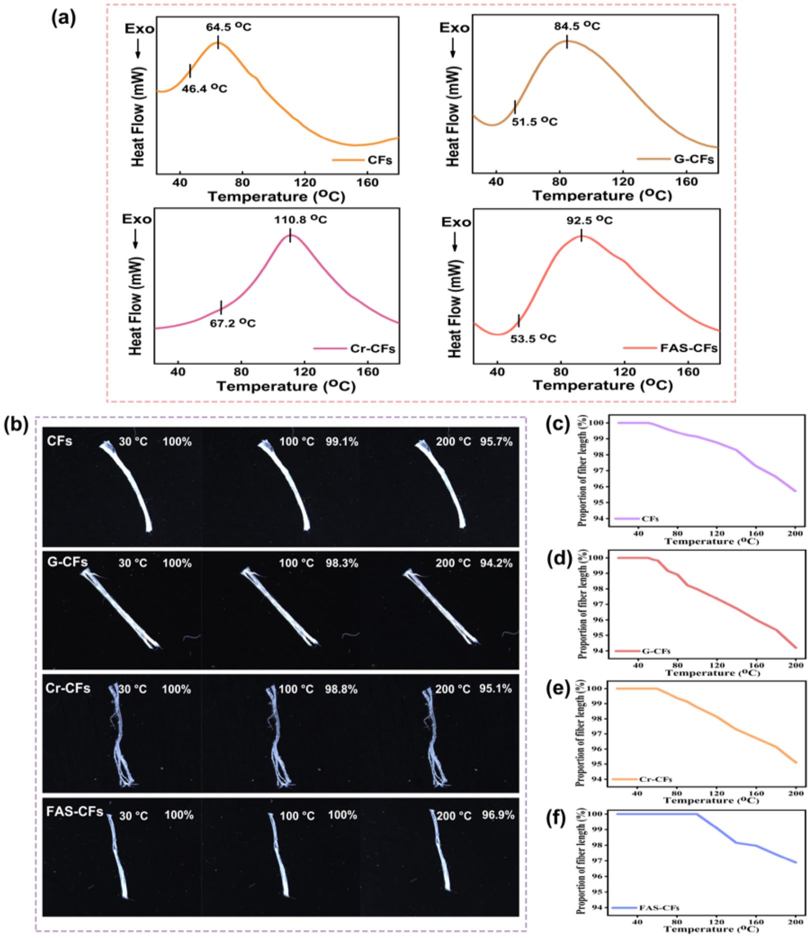

Figure 8. DSC curves of CFs, G-CFs, Cr-CFs, and FAS-CFs (**a**), stereomicrographs showing the shrinkage of CFs, G-CFs, Cr-CFs, and FAS-CFs (**b**) with rising temperature, shrinkage curve of CFs (**c**), G-CFs (**d**), Cr-CFs (**e**), and FAS-CFs (**f**) with rising temperature.

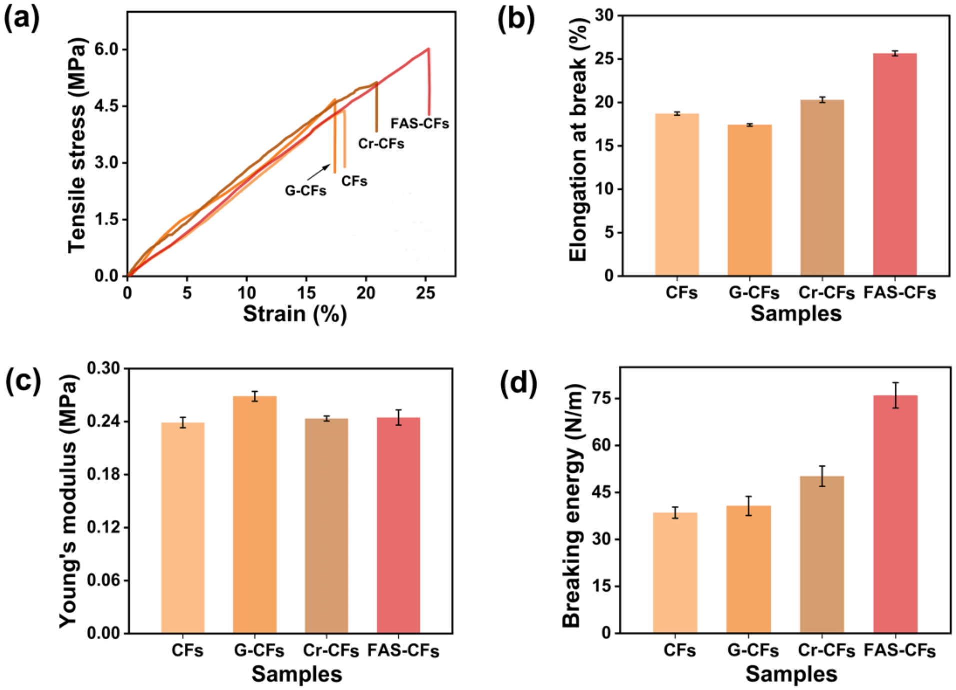

Figure 9. Stress-strain curves (**a**), elongation at break (**b**), Young's modulus (**c**), and breaking energy (**d**) of different collagen fibers.

of FAS-CFs. FAS was covalently bonded with the hydroxyl groups on the surface of CFs. The introduction of Si–O bonds with high cracking energy and C–F bonds with stable bond energy effectively protected the structural stability of FAS-CFs, thereby improving the thermal stability of FAS-CFs. In comparison, FAS-CFs possessed better heat resistance than conventional tanned collagen fibers, such as G-CFs and Cr-CFs.

Among four tested samples, CFs demonstrated the poorest flexibility because of their low tensile strength (Figure 9a) and breaking energy (Figure 9d). After conventional tanning, the tensile strength and breaking energy of G-CFs and Cr-CFs were improved. However, the higher Young's modulus (Figure 9c) and lower elongation at break (Figure 9b) of G-CFs showed that G-CFs were more fragile than Cr-CFs. In comparison, the tensile strength (Figure 9a), elongation at break (Figure 9b), and breaking energy (Figure 9d) of FAS-CFs were significantly higher than those of CFs, G-CFs, and Cr-CFs. Besides, Young's modulus of FAS-CFs was almost equivalent to that of Cr-CFs and CFs (Figure 9c). The above results indicated that FAS-CFs exhibited better strength flexibility than conventional tanned collagen fibers. The satisfactory mechanical properties of FAS-CFs may be attributed to the reduced hydration of collagen fibers and improved fiber dispersity brought by the superhydrophobic modification.[29, 30] In addition, the increased strength was likely due to the lubricating effect of the long hydrophobic chain of FAS, so that FAS-CFs can slide and reorient to adapt to the strain.[31] In short, FAS-CFs performed better mechanical properties than G-CFs and Cr-CFs, suggesting the feasibility of the established strategy based on dehydration followed by superhydrophobic modification without tanning.

Conclusions

We developed a "tanning agent-free" strategy for leather manufacturing. The core of this novel strategy aimed to manufacture leather by eliminating hydration and stabilizing fiber dispersity via dehydration and superhydrophobic modification. Superhydrophobic modification inhibited water infiltration and absorption and promoted porous and dispersed fibrous structures. The modified collagen fibers, FAS-CFs, showed durable water resistance against harsh environments, such as UV irradiation, immersion in water with a wide pH range, and soaking in organic solvents. FAS-CFs exhibited a high thermal denaturation temperature and a lower shrinkage change within 200°C compared to Cr-CFs. Besides, the mechanical properties of FAS-CFs far exceeded those of G-CFs and Cr-CFs. This "tanning agent-free" strategy is expected to be an alternative to conventional tanning and open up a new theory for greener and sustainable leather manufacturing.

In this research, perfluorodecyltriethoxysilane was chosen as hydrophobic agent for CFs modification since it can conveniently endow CFs with excellent hydrophobicity. But perfluorinated compounds may be toxic. Therefore, in consideration of practical application, we should screen environmentally friendly materials, such as organosilicon compounds, as hydrophobic modifier. This work is undertaking in our laboratory.

Acknowledgement

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